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FULL PAPER

N,N′-bridged binuclear NHC palladium complexes: A combined experimental catalytic and computational study for the Suzuki reaction

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This work examines how *N*-donor bridged spacer ligands affect *N*-heterocyclic carbene (NHC) palladium complexes catalytic activities for Suzuki coupling reaction. Different degrees of structural flexibility binuclear NHC palladium complexes were synthesized. The more flexible nitrogen-based alkyl chain ligand shows similar performance with cycloamine counterparts in the Suzuki coupling reaction. Suzuki coupling examples were used in air and ambient temperature to reach moderate to completion yields in short time. Density functional theory calculations showed that the chelate effect, associated with a single Pd complex mechanism, plays a fundamental role in the pre-catalysis stage, supporting a reasonable of the kinetic activity observed experimentally.

KEYWORDS

binuclear NHC–palladium complexes, density functional theory (DFT), *N*-donor, pre-catalysis, Suzuki–Miyaura reaction

1 | INTRODUCTION

In recent decades, *N*-heterocyclic carbene (NHC) ligands have emerged as very highly powerful theme in transition metal organometallic chemistry with properties including ease of preparation and modification, good stability, functionality tolerance, and good catalytic activities.[1] To date most applications have included the construction of not only carbon–carbon but also carbon–heteroatom bonds in a broad range of chemistry fields such as bioactive, conductive and fluorescent compounds, which are widely employed in pharmaceutical and materials sciences.[2] Initial cross-coupling reactions paid more attention to the rich variety of organometallic

nucleophiles that could be used for these reactions[3] and recent research interest has focused on the activation of more varied and challenging electrophiles such as aryl chlorides,[4] aryl ethers,[5] aryl esters,[6] and aldehydes,[7] or finding mild reaction conditions.[4a,c–f,8] Resulted from increasing numbers of studies gaining hands-on experiences of developing catalysts as well as raising more insight and clear information referred to mechanistic studies have been investigated.[2b,d,e,9]

In NHC ligands the carbene is located in an *N*-heterocyclic framework. Many different NHCs have been presented in the literature, and much has been learned about their properties and reactivity. Various studies have been carried out on NHCs and have led to a growing familiarity and understanding of them. Importantly, they have been found to enhance reactivity on the combinations different donors to cooperate metal centers. In coupling reactions, high-performance catalysts bearing both NHCs and different auxiliary ligands have been synthesized, such as *N*-donors,[4e,8a,10] *P*-donors[11] and other donors.[4c,12] Attention has turned to designing an effective catalyst from a stable Pd(II) complex go into the active Pd(0) species in the transition state during the catalytic cycle is the vital research topic. From our previous studies, the "throw-away" ligand(s) are the most crucial key due to the "throw-away" property like a switch to incorporate active metal center to produce active Pd(0) species during the catalytic process.[4e,f]

Hundreds of NHC palladium complexes exhibit excellent activities toward the Suzuki coupling reaction under mild conditions, such as oxygen-containing donor groups,[4d] as well as NHC palladacycle complexes supported by an *N*-donor using IPA (Isopropyl alcohol) as a solvent at room temperature.[13] In the literature, examples of the impact of mononuclear NHC Pd complexes bearing *N*-donor groups indicated highly cooperating abilities because of labile or hemi-labile properties of *N*-donor groups[1b] have been presented by Organ,[14] Navarro,[4e,10b,15] Lu,[16] and our group[4f,17] Mononuclear NHC Pd complexes have been studied and show excellent activity in coupling reactions. Less research has focused on binuclear NHC Pd systems, and fewer examples have been reported.[10n,18] Also, attribution in literature review, fine-tuning steric hindrance has led to major breakthroughs and improvements in catalysis.[19] Bulky ligands stabilize the active species and disfavor bimolecular decomposition and other deactivation events.[20] However, steric bulk hinders the approach of the substrate, which might diminish catalytic activity. Although electron richness and steric bulk are important, a delicate balance with the degree of ligand flexibility seems to be the key to successful enhancement of catalytic efficacy. Fine-tuning flexibility/steric bulk allows the ligand to adapt to the changing needs in the catalytic cycle.[21] Therefore, a less sterically demanding ligand is favorable for oxidative addition and transmetalation, and reductive elimination should benefit from more demanding conformations around the metal center.[22] To find out a good ligand to synthesize a good activity of complex, we chose flexible and labile tertiary alkyl diamines instead of cycloamines bridged two NHC Pd complexes, as depicted in Figure 1. Furthermore, depending on experimental and density functional theory (DFT) studies to discuss differences of catalytic systems in Suzuki coupling reaction.

2 | EXPERIMENTAL

2.1 | Reagents and methods

Unless otherwise noted, all experiments were performed in air. All solvents and reagents were used as received. The reagents were purchased from Sigma-Aldrich, Acros, Merck, TEDIA, and Alfa-Aesar of USA. The imidazolium salt IPr·HCl and NHC palladium complexes were prepared by following literature procedures and their identities and purities were confirmed by ^{1}H NMR spectroscopy.[23]

All aryl halides and boronic acids were used as received. Technical grade ethyl alcohol was used to carry out Suzuki–Miyaura cross-coupling reactions. All reactions were carried out in air at ambient temperature. Flash chromatography was performed on silica gel 60 (230–400 mesh) using mixtures of hexanes/ethyl acetate (10:1), unless otherwise noted.

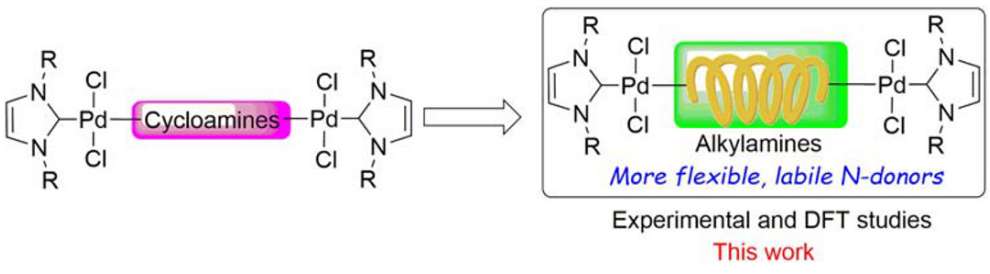


FIGURE 1 The idea for comparison catalytic studies

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker-AV-400 (400 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relatives to tetramethylsilane. Elemental analyses were performed by Elementarvario EL III. The melting points were determined using a FARGO MP-2D melting point apparatus.

The Suzuki–Miyaura cross-coupling reactions were analyzed by two methods.

Method 1: Gas chromatography barrier ionization discharge (GC-BID) on a Nexis GC-2030 gas chromatograph coupled with a Shimadzu BID detector (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA) equipped with a Bruker BR-5 ms column.

Method 2: Gas chromatography–mass spectrometry (GC–MS) on a Bruker SCION 436 SQ instrument equipped with a Bruker BR-5 ms column. The MS detector was configured with an electronic impact ionization source.

Synthesis of 1a: A vial was charged with [Pd(μ-Cl)Cl(IPr)]$_2$ (110 mg, 0.1 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (11.6 μl, 0.1 mmol), with DCM (dichloromethane, 2 ml) as solvent. The solution was stirred at room temperature for 1 hr. The solution was filtered through a pad of Celite, and the filtrate was removed from the solvent to afford a pale yellow solid, obtaining the desired compound in 88% yield (110 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (d, J = 6.8 Hz, CH(CH_3)$_2$, 24H), 1.35 (d, J = 6.8 Hz, CH(CH_3)$_2$, 24H), 1.89 (s, N(CH_3)$_2$, 12H), 2.56(s, NCH_2, 4H), 3.05 (sep, J = 6.8 Hz, CH(CH$_3$)$_2$, 8H), 7.00 (s, NCH, 4H), 7.25–7.28 (m, ArH, 8H), 7.41 (t, J = 7.6 Hz, ArH, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 23.0 (s, *i*Pr), 26.3 (s, *i*Pr), 28.6 (s, *C*HiPr), 50.2 (s, N(*C*H$_3$)$_2$), 58.5 (s, NCH_2), 123.9 (s, *C*H aromatic), 124.8 (s, *C*H aromatic), 130.0 (s, *C*H aromatic), 135.3 (s, *C* aromatic), 147.0 (s, *C* aromatic), 154.3 (s, $C_{carbene}$). Anal. calcd for $C_{60}H_{88}Cl_4N_6Pd_2$: C 57.74, H 7.11, N 6.73; found: C 58.19, H 7.07, N, 6.52. Melting point 247.9° C.

Synthesis of 1b: The procedure for the preparation of **1b** was similar to that used for **1a** but with [Pd(μ-Cl)Cl(IPr)]$_2$ (110 mg, 0.1 mmol) and *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (13.2 μl, 0.1 mmol) and DCM (2 ml). The pale yellow desired solid was obtained in 92% yield (110 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (d, J = 6.8 Hz, CH(CH_3)$_2$, 24H), 1.26 (m, CH_2(CH$_2$)$_2$, 2H), 1.40(d, J = 6.8 Hz, CH(CH_3)$_2$, 24H), 1.93 (s, N(CH_3)$_2$, 12H), 1.96–2.14 (m, overlap, NCH_2CH_2CH_2N + N(CH_3)$_2$, 18H), 3.10 (sep, J = 6.8 Hz, CH(CH$_3$)$_2$, 8H), 7.03 (s, NCH, 4H), 7.27 (d, J = 8 Hz, ArH, 8H) 7.41 (t, J = 7.6 Hz, ArH, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 23.2 (s, CH*C*H$_3$), 25.3 (s, *C*H$_2$(CH$_2$)$_2$), 26.3 (s, CH*C*H$_3$), 28.6 (s, *C*HCH$_3$), 49.7 (s, NCH_3), 59.3 (s, NCH_2), 123.8 (s, *C*H aromatic), 124.8 (s, *C*H aromatic), 130.1 (s, N–*C*H), 135.1 (s, *C* aromatic), 146.8 (s, *C* aromatic), 154.2 (s, $C_{carbene}$). Anal. calcd for $C_{61}H_{90}Cl_4N_6Pd_2$: C 58.05, H 7.19, N 6.66; found: C 58.15, H 7.09, N 6.26. Melting point 278.5° C.

Synthesis of 1c[18b]: The procedure for the preparation of **1c** was similar to that used for **1a** but used [Pd(μ-Cl)Cl(IPr)]$_2$ (110 mg, 0.1 mmol), 1,4-diazabicyclo[2.2.2]octane (11.2 mg, 0.1 mmol), and DCM (2 ml). The pale yellow desired solid was obtained in 72% yield (90 mg).

Synthesis of 1d[18b]: The procedure for the preparation of **1d** was similar to that used for **1a** but used [Pd(μ-Cl)Cl(IPr)]$_2$ (110 mg, 0.1 mmol), pyrazine (8 mg, 0.1 mmol), and DCM (2 ml). The pale yellow desired solid was obtained in 90% yield (110 mg).

2.2 | X-ray data collection and structure refinement

Crystals of complexes **1a–1c** were grown from concentrated dichloromethane/hexane solution and isolated by filtration. Suitable crystals were mounted on a glass fiber using perfluoropolyether oil (FomblinY) and cooled rapidly under a stream of cold nitrogen gas to collect diffraction data at 150 K using a Bruker APEX2 diffractometer. The intensity data were collected in 1350 frames with increasing ω (width of 0.5° per frame). Absorption correction was applied using SADABS.[24] The structure was solved by direct methods using a SHELXTL package.[25] All non-H atoms were located from successive Fourier maps and H atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic parameters were used for H atoms. Details of the data collection and refinement are given in Supporting Information Table S1 (Data 2 in Supporting Information).

CCDC 1939941 and 1,939,943–1,939,944 are given in the supplementary data for this paper. These detail crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif) and cif checked files can be obtained in Supporting Information (Data 1).

2.3 | Procedure for the Suzuki–Miyaura cross-coupling reaction

Complex (1 mol% Pd), base (1.8 equiv.), and phenylboronic acid (1.5 equiv.) were added in turn to a

vial equipped with a magnetic bar and sealed with a screw cap. Technical grade solvent (1 ml) was injected into the vial and the mixture stirred on a stirring plate at room temperature. Aryl chloride (0.5 mmol, if liquid) was then injected (or charged if solid). The reaction was monitored by GC-BID or GC–MS. When the reaction was finished, the solvent was evaporated under vacuum and the product isolated by flash chromatography. The amount of product shown is the average of two runs.

2.4 | DFT studies

All calculations were performed at density functional theory (DFT) level[26] available in Gaussian 09 suite software (version D01).[27] Geometry optimizations for the kinetic profile and its respective vibrational frequencies were performed with M06L functional[28] at gas phase; the 6-31G(d,p) basis set was applied for all main group elements and the valence/relativistic-pseudopotential SDD[29] for palladium (Pd) atom. Geometries for the thermodynamic analysis were optimized in condensed-phase (ethanol) described by the SMD (The Solvation Model based on Density)[29] continuum-dielectric solvation model. The intrinsic reaction coordinate method[30] was used to confirm the connection between the transition states and the corresponding intermediates. All the energy profiles were discussed as a function of Gibson-free energies relative to separated reactants and related energies and cartesian coordinates can be obtained in Supporting Information (Data 3 and 4).

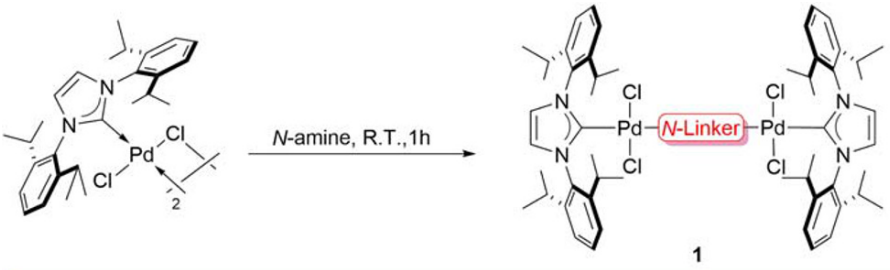
3 | RESULTS AND DISCUSSION

3.1 | Synthesis of binuclear NHC complexes

The practical and very efficient protocol for the preparation of binuclear NHC Pd complexes was carried out according to our previous studies.[4e,f,10b] Synthesis of complexes **1a**–**1d** was straightforward and they were obtained from the corresponding parent $[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ dimer combined with 1 equiv. of *N*-linker reagent in CH_2Cl_2 at room temperature for 1 hr. Synthetic details are shown in Scheme 1. In order to discuss comparison of the catalytic activities of complexes and complexes **1c**-**1d** were prepared and checked with the literature.[18b] The target complexes were isolated in satisfactory to good yields of 88% for **1a**, 92% for **1b**, 72% for **1c**, and 90% for **1d** as yellow solids by evaporating the solvent. Complexes **1a** and **1b** are new complexes that are moisture- and air-stable and can be stored and handled in air.

3.2 | Spectral and structural studies

Complexes **1a** and **1b** were fully characterized by elemental analysis as well as ^1H and ^{13}C NMR spectroscopy. An obvious and expected downfield shift in the $^{13}C\{^1H\}$ NMR of the carbene carbon signal for the σ-donating of the *N*-donor groups was observed for complexes **1a** and **1b**. The ^{13}C NMR spectra showed a diagnostic $Pd\text{–}C_{carbene}$ peak at 154.3 ppm for **1a** and 154.2 ppm for **1b**. These ^{13}C signals showed a similar trend as complexes **1c** and **1d** (**1c** 153.1 ppm; **1d** 152.4 ppm).[18b]



N-linker		Yield (%)
N,*N*,*N*′,*N*′-tetramethylethylanediamine	**1a**	88
N,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine	**1b**	92
1,4-Diazabicyclo[2.2.2]octane[a]	**1c**	72
Pyrazine[a]	**1d**	90

[a] Complexes **1c-d** were prepared and confirmed with reference.[18b]

SCHEME 1 Synthesis of *bis*(NHC) $PdCl_2$-*N*-linker complexes **1a**–**1d**

Solid-state structures were determined by single-crystal X-ray diffraction for complexes **1a**–**1c**. All crystal structures were grown from dichloromethane or a mixture of dichloromethane/hexane. Crystal structural images of complexes **1a**–**1c** are depicted in Figures 2–4. The summary of the crystallographic data is given in Supporting Information Table S1 (Data 2 in Supporting Information). As expected, the structures of **1a**–**1c** demonstrated a dinuclear scaffold with two palladiums centers bound together by a tertiary diamine ligand. Each palladium center adopted a lightly distorted square-planar geometry with two chloride ligands perpendicular to the plane of the NHC and a *N*-donor group *trans* to it. Structures **1a**–**1c** exhibited similar coordinative behaviors to those found in mononuclear NHC palladium complexes.

All molecular structures of **1a**–**1c** bearing the same NHC backbone are quite similar except for the substituent bridged *N*-donor ligands. The predominant molecular geometry for **1a** and **1c** is a zigzag chain structure of *N*-donor groups, N–C–C–N for **1a** and N-C-C-N for **1c**, in which the NHC groups are oriented in opposite directions as reported in the literature for bridged diphosphine palladium complexes.[18c] The two carbene ring planes adopt a parallel geometry in complex **1a**, but non-coplanar carbene ring plane orientation was found with vertical separation angles of 76.20° for complex **1b** and 49.70° for complex **1c**. The dihedral angles between the carbene ring plane and the Pd–C–N–Cl coordination plane were 74.78° for complex **1a**, 71.74° and 70.72° for complex **1b**, and 71.96° and 70.91° for complex **1c**, which are located typically in NHC palladium complexes to relieve steric congestion.

As shown in Figures 2–4, in complexes **1a**–**1c** each Pd center is a four-coordinated by an *N*-heterocyclic carbene ligand, an *N*-donor from the bridged diamine ligand, and two chloride ligands, with angles between adjacent ligands ranging from 85.29(8)° to 94.3(2)°. The details of structural structures analysis focused on the structural parameters around the palladium centers, like the bond angles and bond distances, are located in a similar range to those found in mononuclear NHC palladium complexes. Selected bond distances and angles are listed in Table 1.

3.3 | Catalytic studies for the Suzuki coupling reaction

Previous studies by our group have shown that mononuclear NHC palladium complexes bearing *N*,*N*′-dimethylbenzylamine are effective in the Suzuki coupling reaction when aryl chlorides or benzyl chlorides are used as the starting materials.[4f,17] Here, we carried out catalyst testing by screening the activities of complexes **1a**–**1d** in the Suzuki coupling reaction. In the initial studies, the model reaction conditions used 2-chloro-*m*-xylene and phenylboronic acid at room temperature. Four bases (K_3PO_4, K_2CO_3, KOH, KO^{t}Bu) and five solvents (toluene, THF, DME, EtOH, IPA) were used to combine in a crossing way to seek the best optimum condition. The results are collected in Table 2.

Based on this preliminary screening of conditions, complex **1a** achieved 60% and 64% yields for 12 hr at room temperature for KO^{t}Bu/EtOH and KOH/EtOH, respectively (Table 2, entry 9 vs. 11). When arylchloride

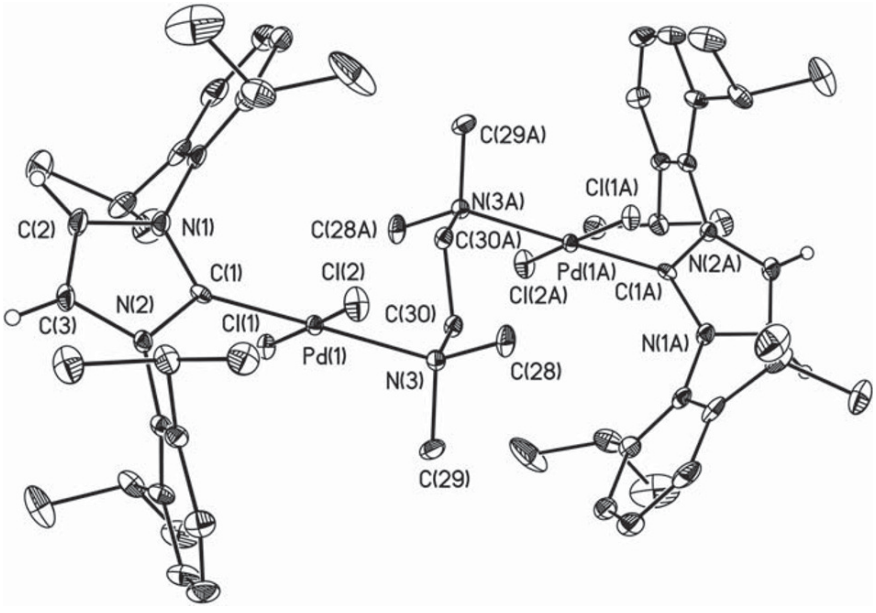


FIGURE 2 Crystal structure of **1a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

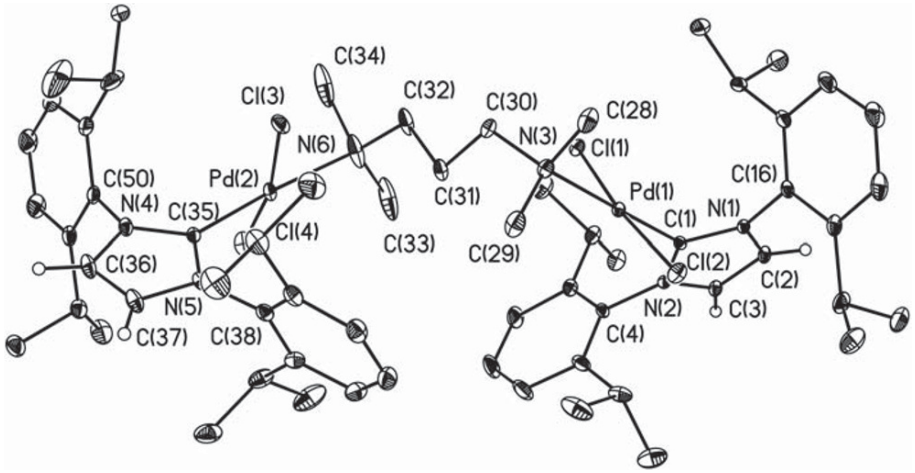


FIGURE 3 Crystal structure of **1b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

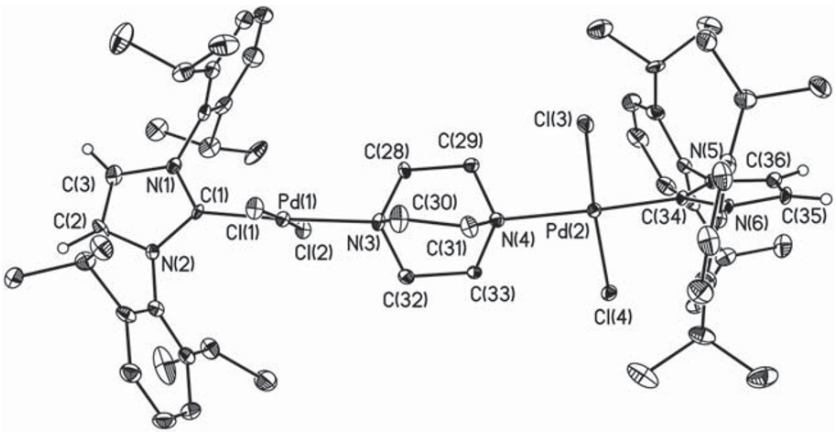


FIGURE 4 Crystal structure of **1c** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

TABLE 1 Selected bond distances (Å) and angles (°) around Pd in complexes **1a**–**1c**

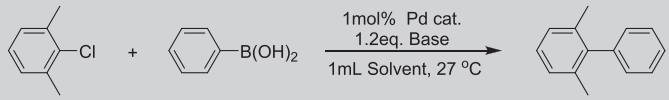
	1a	1b	1c
Pd(1)–Cl (1)	2.3139 (13)	2.2980 (7), 2.3024 (8)[a]	2.284 (3), 2.303 (3)[a]
Pd(1)–Cl (2)	2.2841 (15)	2.3138 (7), 2.3144 (9)[a]	2.313 (3), 2.305 (3)[a]
Pd(1)–C (1)	1.958 (5)	1.962 (3), 1.964 (3)[a]	1.972 (10), 1.958 (10)[a]
Pd(1)–N (3)	2.180 (4)	2.187 (2), 2.159 (3)	2.166 (9), 2.162 (9)
C(1)–Pd (1)–Cl (1)	88.06 (14)	85.29 (8), 86.40 (8)[a]	87.4 (3), 89.5 (3)[a]
C(1)–Pd (1)–N (3)	179.09 (18)	178.89 (10), 174.82 (13)[a]	176.5 (4), 177.3 (4)[a]
Cl(2)–Pd (1)–N (3)	92.84 (12)	91.10 (7), 91.95 (10)[a]	89.0 (2), 94.3 (2)[a]

[a]Reported structural data measured by the other Pd metal center.

was changed for 2-chloroanisole to compare their reactivity, the combination of KO^{t}Bu/EtOH showed better conversion (63%) than KOH/EtOH (42%) over 4 hr (Table 2, entry 12 vs. 13). In addition, to modify the optimum condition, we explored different equiv. values for phenylbornoic acid and KO^{t}Bu (1.2, 1.8, and 2.4 equiv.). With 1.8 equiv. loading of phenylbornoic acid/KO^{t}Bu gave completion yield for complexes **1c** and **1d** (Table 2, entries 15–17). Complex **1a** needed an extended reaction time of 6 hr to reach 97% conversion (Table 2, entry 14). We plotted conversion versus time to observe the catalytic activity, and found that complexes **1b** and **1d** afforded closed good activity than the others (Figure 5). To determine the best catalytic performance, the catalyst loading was reduced to half dosage as 0.5 mol% Pd. Only complex **1b** allowed the coupling to proceed in high yield in a shorter reaction time at room temperature than the other complexes including its parent complex, [Pd(μ-Cl)Cl(IPr)]$_2$ (Table 2, entries 18–21).

In the initial optimum conditions studies, KO^{t}Bu/EtOH showed the best performance, giving higher yield when using 2-chloro-*m*-xylene or

TABLE 2 Optimum conditions for the Suzuki–Miyaura coupling reaction[a]



Entry	Complex (mol%)	Solvent	Base	Time (hr)	Yield (%)[b]
1	**1a** (0.5)	Toluene	K_3PO_4	12	0
2	**1a** (0.5)	THF	K_3PO_4	12	0
3	**1a** (0.5)	DME	K_3PO_4	12	0
4	**1a** (0.5)	EtOH	K_3PO_4	12	38
5	**1a** (0.5)	IPA	K_3PO_4	12	0
6	**1a** (0.5)	Toluene	K_2CO_3	12	1
7	**1a** (0.5)	EtOH	K_2CO_3	12	48
8	**1a** (0.5)	Toluene	KOH	12	18
9	**1a** (0.5)	EtOH	KOH	12	60
10	**1a** (0.5)	DME	KO^{t}Bu	12	0
11	**1a** (0.5)	EtOH	KO^{t}Bu	12	64
12[c]	**1a** (0.5)	EtOH	KOH	4	42
13[c]	**1a** (0.5)	EtOH	KO^{t}Bu	4	63
14[d]	**1a** (0.5)	EtOH	KO^{t}Bu	6	97
15[d]	**1b** (0.5)	EtOH	KO^{t}Bu	1.33	99
16[d]	**1c** (0.5)	EtOH	KO^{t}Bu	1.33	97
17[d]	**1d** (0.5)	EtOH	KO^{t}Bu	1.33	99
18[d]	**1b** (0.25)	EtOH	KO^{t}Bu	1.66	88
19[d]	**1c** (0.25)	EtOH	KO^{t}Bu	1.66	62
20[d]	**1d** (0.25)	EtOH	KO^{t}Bu	1.66	65
21[d]	[Pd(μ-Cl)Cl(IPr)]$_2$ (0.25)	EtOH	KO^{t}Bu	1.66	74

[a]Reaction conditions: 2-chloro-*m*-xylene (0.5 mmol), phenylboronic acid (0.6 mmol), 1.2 equiv. base, 1 mol% Pd catalyst loading, and 1 ml solvent, 27°C.
[b]Determined by GC-BID, average of two runs.
[c]Using 2-chloroanisole instead of 2-cholor-*m*-xylene.
[d]Using 1.8 equiv. phenylboronic acid and 1.8 equiv. KO^{t}Bu.

2-chloroanisole combined with phenylboronic acid as the starting materials in the presence of complex **1b** (Table 2). The *mono*-, *di*-or *tri*-substituted coupling products between either of functionalized arylchlorides or phenylboronic acid were examined (Table 3). To reduce the cost, the amount of phenylboronic acid was reduced to 1.5 equiv. and yield for the coupling results did not decrease. Suzuki coupling reactions were carried out using a 1:1.5 stoichiometric ratio of aryl chlorides and phenylboronic acid, with 1.8 equiv. KO^{t}Bu and 1 mol% Pd loading of complex **1b** as precatalyst in nonpurified ethanol medium at room temperature. The reactions between aryl chlorides and phenylboronic acid were found to proceed smoothly and the corresponding coupled products were obtained in a short time (from minutes to 24h). Results are shown in Table 3.

All reactions were carried out at room temperature and in air. Under optimum conditions allowed the coupling of *mono*-substituted activated, neutral and unactivated aryl chlorides, all reaction time fall into 20 to 49 min to achieve 89–99% isolated yield (**4a**–**4c**, **4f**–**4i**). When using 2-chloroaniline as the starting material, a longer reaction time was required to obtain moderate yield (**4d**, 75%, 120 min). The catalyst poisoning starting material such as 2-chlorothiophene took 120 min to afford 76% yield, but on heating to 60 °C the completion yield was reached in 10 min (**4e**). Because the competitive coordination abilities of starting materials to

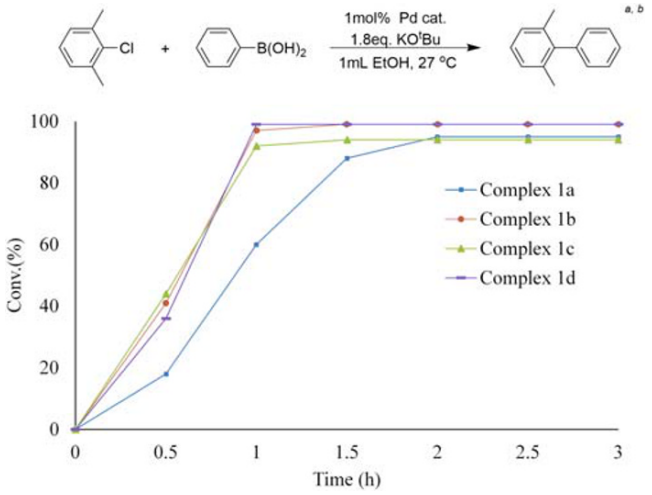


FIGURE 5 Plotted conversion vs. time. [a]Reaction conditions:2-chloro-*m*-xylene (0.5 mmol), 1.8 equiv. phenylboronic acid, 1.8 equiv. KO^{t}Bu, 0.5 mol% complexes **1a**–**1d** catalyst loading, and 1 ml EtOH, 27 °C. [b]Determined by GC-BID, average of two runs

palladium center led to more reaction time to reach good yield. *Di-* substituted products were afforded in coupling reaction: di-*ortho-* (**4j** and **4k**), one *ortho-* and one *meta-* (**4l** and **4m**), one *para-* and one *ortho-* (**4n–4p**), one *para-* and one *meta-* (**4q**–**4s**), both *para-*(**4t** and **4u**), and both *ortho*-substituted (**4v**), and reaction times of 30–120 min to afford 75–98% yield. Some *tri*-substituted products were obtained after a longer time of 1–24 hr or by heating at 60°C for 60 min to achieve 73–97% yield (**5a**–**5g**). After these substrates were analysed, complex **1b** showed expected active abilities for Suzuki cross-coupling reaction than cycloamine bridged ligands.[18b,c,e] There have been reports of multinuclear complexes displaying cooperative reactivity between multiple metal centers and are far more catalytically active potential to outperform existing mononuclear counterparts.[31] Unfortunately, our dinuclear palladium complex catalytic system did not have a good synergy effect but demonstrated a similar level of catalytic activity as Pd-PEPPSI catalyst (pyridine-enhanced precatalyst preparation stabilization and initiation) and exhibited higher activities in comparison with NHC palladium complexes generated *in situ.* In overall catalytic activities comparison jobs toward arylchlorides as staring materials for Suzuki reaction, mononuclear NHC palladium complexes bearing tertiary amines[4e,f] showed the best performance than Pd-PEPPSI,[14] similar referred to our dinuclear palladium complexes bearing tertiary amines spacer, then mononuclear NHC palladium complexes mixed with ligands, such as phosphines,[11d] or phosphites.[11b] This is because the soft acid of palladium(II) favors coordination with soft base ligands, like phosphines. This affords more stable complexes then led to diminish the catalytic activity or needed high activation energy to overcome in the reactions. In the other words, if we choose more flexible ligands such as tertiary amines (hard base) play an ancillary ligand role, this will help to shorten the preactivation step time in the catalytic cycle.

3.4 | Scale-up in the Suzuki reaction

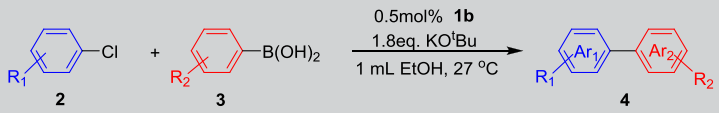
The high cost and lack of availability of palladium are important issues for any large-scale application. To examine the application of our synthesized Pd complexes, the gram scale experiment was carried out with 4-cholorobenzadehyde and phenylboronic acid as the starting materials under the described optimum conditions. After 2 min of reaction time, the completion yield was observed by GC–MS. After column chromatography purification, the cross-coupling biaryl product **4i** was obtained in 95% yield (1.73 g), as shown in Scheme 2.

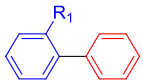
3.5 | DFT studies

From a review of reports in the literature, NHC Pd complexes bearing alkyl amine(s) were found to exhibit higher activities than cycloamines.[4e,f,15a,17] Hence, some computational studies were performed. And ry to understand why the addition of one methylene group in the central carbon chain resulted in **1a** and **1b** exhibiting different catalytic activities.

Entries 14–18 in Table 2 show that higher coupling yields were observed, increasing the base and boronic acid concentrations. Moreover, the yields also were higher in presence of an electron-rich aryl halide such as 2-chloroanisole (entries 12 and 13). These results lead us to carry out computational studies on the transmetalation and reductive elimination steps of the Suzuki–Miyaura reaction mechanism. To obtain the final biphenyl (Ar = Ph) product, the activation barrier for the transmetalation step was 4.2 kcal/mol for **1a_1** to overcome the transition state and produce **1a_2** (Table 4, entry 1). Since the activation barrier for **1b_1** to **1b_2** was calculated to be 5.2 kcal/mol (Table 4, entry 2), the barrier involving **1a** complex is 1.0 kcal/mol lower than for the transmetalation step catalyzed by **1b**. In the case of the reductive elimination step, the activation barrier was calculated to be 10.9 kcal/mol for **1a_2** to produce **1a_3** (Table 4, entry 3) and 8.5 kcal/mol for intermediate **1b_2** to achieve **1b_3** (Table 4, entry 4). However, this reactivity inverts if we calculate the same step for applying the *o*-xylenyl

TABLE 3 Suzuki–Miyaura coupling products[a,b]



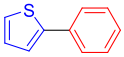


4a: R_1 = H, 28 min, 99%

4b: R_1 = CH_3, 49 min, 89%

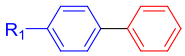
4c: R_1 = OCH_3, 35 min, 90%

4d: R_1 = NH_2, 120 min, 75%[c]



4e: 120 min, 76%[c]

60 °C, 10 min, 93%[c]

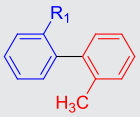


4f: R_1 = CH_3, 35 min, 96%

4 g: R_1 = OCH_3, 40 min, 98%

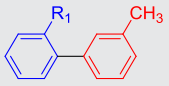
4 h: R_1 = CF_3, 35 min, 97%

4i: R_1 = C(O)H, 20 min, 98%



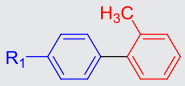
4j: R_1 = CH_3, 50 min, 90%

4 k: R_1 = OCH_3, 30 min, 98%



4 l: R_1 = CH_3, 45 min, 95%

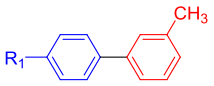
4 m: R_1 = OCH_3, 35 min, 85%



4n: R_1 = CH_3, 45 min, 90%

4o: R_1 = CF_3, 35 min, 88%

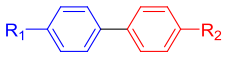
4p: R_1 = C(O)H, 30 min, 97%



4q: R_1 = CH_3, 40 min, 85%

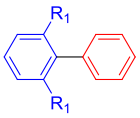
4r: R_1 = CF_3, 40 min, 92%

4 s: R_1 = C(O)H, 30 min, 96%

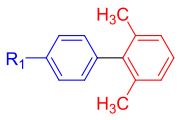


4 t: R_1 = OCH_3, R_2 = CO_2CH_3, 120 min, 75%

4u: R_1 = OCH_3, R_2 = CF_3, 140 min, 87%



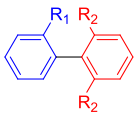
4v: R_1 = CH_3, 80 min, 98%



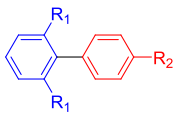
5a: R_1 = CH_3, 24 h, 73%

5b: R_1 = OCH_3, 24 h, 74%

60°C, 60 min, 97%[c]



5c: R_1 = OCH_3, R_2 = CH_3, 24 h, 78%[c]

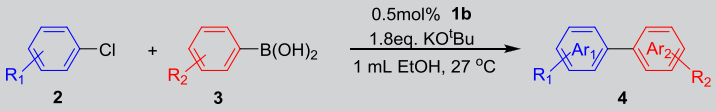


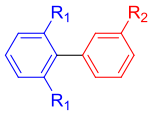
5d: R_2 = CF_3, 4 h, 85%

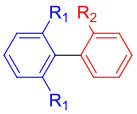
5e: R_2 = CO_2CH_3, 24 h, 75%[c]

(Continues)

TABLE 3 (Continued)

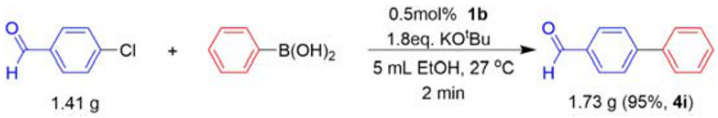






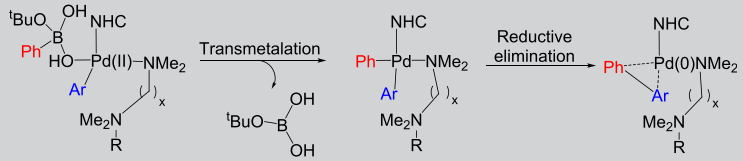
5f: $R_1 = R_2 = CH_3$, 1.33 h, 85% **5 g**: $R_1 = R_2 = CH_3$, 1 h, 91%

[a]Reaction conditions: 0.5 mmol arylchloride, 0.75 mmol arylboronic acid, 1.8 equiv. KO^{t}Bu, 0.5 mol% **1b**, $T = 27°C$, and 1 ml EtOH.
[b]Determined by GC-BID, average of two runs; values refer to isolated yield after column chromatography.
[c]Determined by GC–MS.



SCHEME 2 Scale-up in the Suzuki reaction

TABLE 4 Relative activation barrier for transmetalation and reductive elimination for starting catalysts **1a** and **1b** considering mono- and binuclear intermediates pathways



Entry	Reference intermediate	Starting catalyst	Method	ΔG
1[a]	**1a_1**	**1a**	M06L/6-31G(d,p)	4.2
2[a]	**1b_1**	**1b**	M06L/6-31G(d,p)	5.2
3[b]	**1a_2**	**1a**	M06L/6-31G(d,p)	10.9
4[b]	**1b_2**	**1b**	M06L/6-31G(d,p)	8.5
5[c]	**1a_2a**	**1a**	M06L/6-31G(d,p)	16.8
6[c]	**1b_2a**	**1b**	M06L/6-31G(d,p)	17.3
7[a]	**duo1a_1**	**1a**	oniom(m06l:pm6)/6-31G(d,p)	25.2
8[a]	**duo1b_1**	**1b**	oniom(m06l:pm6)/ 6-31G(d,p)	29.1
9[b]	**duo1a_2**	**1a**	oniom(m06l:pm6)/ 6-31G(d,p)	11.6
10[b]	**duo1b_2**	**1b**	oniom(m06l:pm6)/ 6-31G(d,p)	12.3

[a]Transmetalation step, Ar = Ph.
[b]Reductive elimination step, Ar = Ph.
[c]Reductive elimination step, Ar = *o*-xylenyl. Relative free energies presented in kcal/mol.

as aryl group (Table 4, entries 5 and 6). In these cases, the presence of *o*-xylenyl groups increases the steric hindrance, so the activation barrier for **1a_2a** (16.8 kcal/mol; Table 4, entry 5) is lower than for **1b_2a** at only 0.5 kcal/mol (17.3 kcal/mol; Table 4, entry 6).

We also considered a mechanism in which both palladium centers could participate in the cross-coupling reaction (Table 4, entries 7–10) because it was presumed that catalyst **1b** could be kinetically favorable compared to **1a** if both palladium centers are coordinated to two amine heads during the transmetalation and/or reductive elimination steps. At **1b** the two palladium centers are separated by a longer distance (Figure 6), what would contribute to reduce the steric hindrance, lowering the activation barriers, when compared to the **1a** complex. The activation barrier for the transmetalation step was lower for **duo1a_1** (25.2 kcal/mol, Table 4, entry 7) than for **duo1b_1** (29.2 kcal/mol, Table 4, entry 8). It is important to note that was calculated an increasing of about 20.0 kcal/mol to the activation barriers in presence of monopalladium complexes. These results suggest that mechanistic pathways through binuclear palladium intermediates are less favorable than those through mononuclear palladium complexes. For the reductive elimination (Ar = Ph), the increase in the total activation barrier was less than 3.0 kcal/mol, but the selectivity inverts been also lower for **duo1a_2** than for **duo_1b_2** (Table 4, entries 9 and 10). This indicates that **1a** should react faster than **1b**, i.e. the opposite of what is found by kinetic experiments (Figure 5).

A mononuclear mechanism was expected since two free active sites *cis* to each other at the palladium center are needed for the oxidative addition and the reductive step to occur. Hence, the starting binuclear precatalysts **1a** and **1b** must suffer a discoordination liberating two Pd(II) complexes at the bulk reaction at the precatalysis step where the Pd(0) species is formed so the main Suzuki–Miyaura mechanism reaction cycle can start.[32]

In the mechanistic studies of cross-coupling reactions, precatalysis commonly involves Pd(II) reduction to Pd(0), but this is rarely described in the literature due its high complexity, especially if no phosphine species as reductive agents are present in the chemical system.[33] However, for the Suzuki reaction there already some elucidations considering as part of the precatalysis a reductive elimination step starting from transmetalation aryl group from the arylboronic acid substrate.[14,34] Figure 7 shows two possible pathways based on the literature examples for arylboronic participation in precatalysis after the *cis* site be obtained from a chelate effect.

For the cheat effect and considering the higher degree of freedom for the open chain linker of **1a** and **1b** compared with **1c** and **1d**, we presumed that it could be possible that when the precatalyst splits into two monopalladium center complexes, the free amine head could substitute one of the chlorides ligands affording the chelate effect, especially in the case of the dimethylethyldiamine which presents the better bite angle[35] forming a five-membered ring (Figure 7, **1a_7**).

Thermodynamic analysis (Figure 8) of the precatalyst intermediates showed that both **1a** and **1b** form stable chelate complexes with total energy stabilization of −37.5 kcal/mol for **1a** and −28.7 kcal/mol for **1b**. In addition, **1a_7** reduces the system total energy in almost 10.0 kcal/mol compared to **1b_7** formation. This step is exergonic for **1a_7** while for **1b_7** it is endergonic. We suppose that **1b** linker although also presents chelate effect, the propyl chain would lead to lesser effect due to the six-membered ring providing worst bite angle.

The energetic profile also indicates the importance of the chemical base used, since the precatalysis pathway through chloride ligand dissociation to form **1a_4** (Figure 8, path a) is an endergonic process; if a base substitution with the chloride occurs through concerted

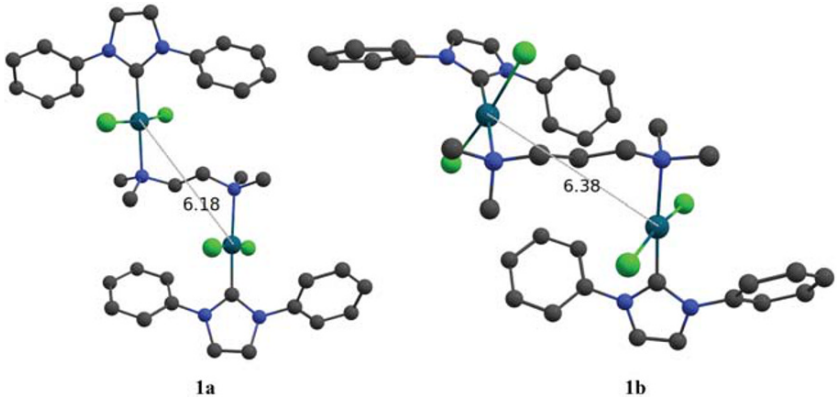


FIGURE 6 Optimized geometries for model structures for **1a** and **1b** at condensed phase (ethanol) with Pd–Pd distances shown in Angstroms (Å)

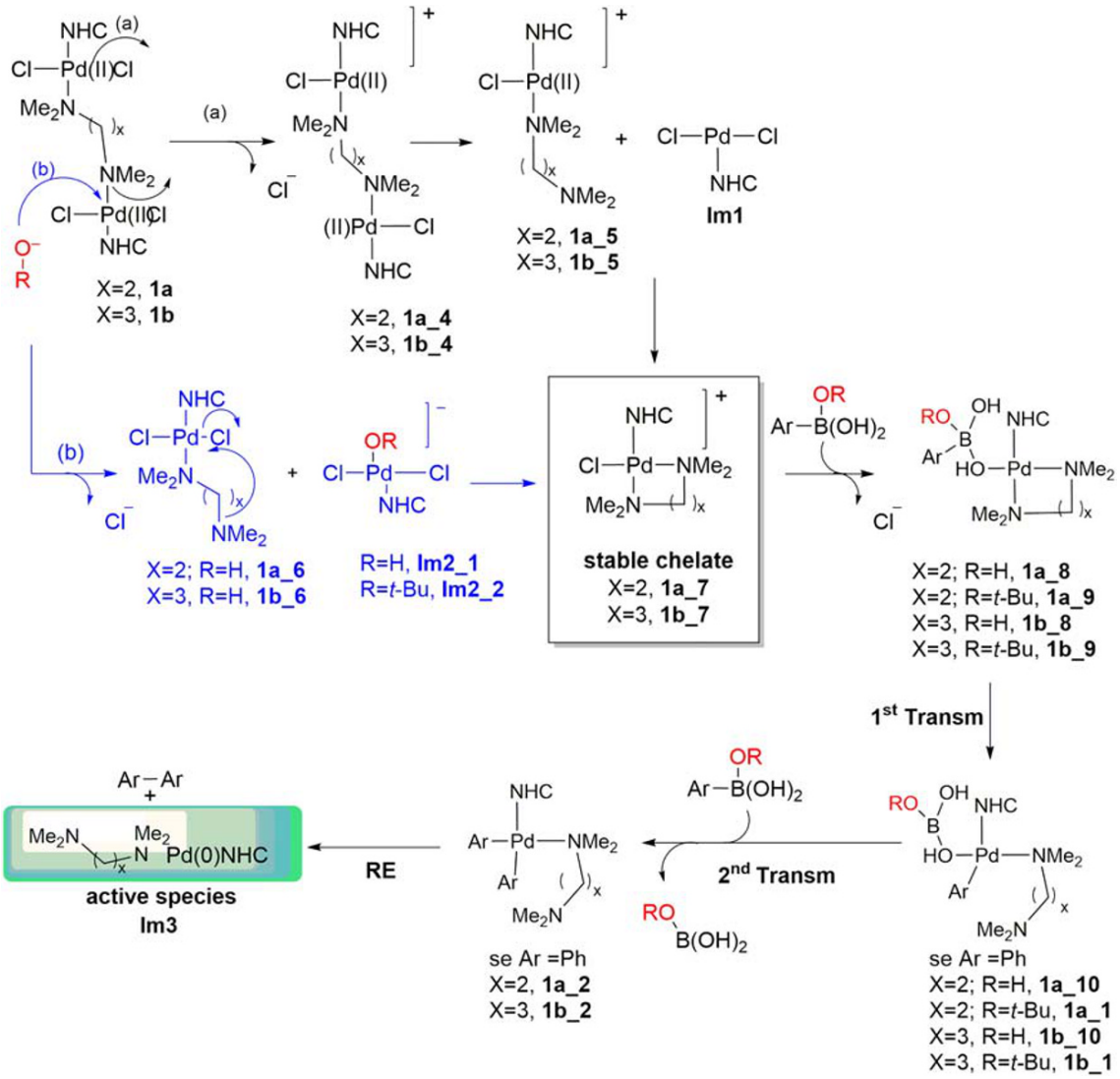


FIGURE 7 Proposed route to active Pd(0) species via a common stable chelate intermediate **1_7** without (path a) and with (path b) base assistance. Transm, transmetalation step; RE, reductive elimination step

mechanism (Figure 8, path b) to form **1a_6** and Pd(NHC)Cl_2, it becomes an exergonic process, reducing the total energy of the system by about −34 kcal/mol for both starting catalysts reflected by the entropy contribution and the oxophilic character of palladium center, suggesting one of the reasons of the total yield increasing when a stronger base is applied (Table 2, entries 12 and 13). The total energy is slightly higher (−34.0 kcal/mol for **1a_8** and −25.5 kcal/mol for **1b_8**) when the remaining chloride is replaced by base-activated arylboronic acid, indicating the higher steric hindrance of the group overcome the electronic advantage of the new RO–Pd bond formation in this second chloride substitution.

Mononuclear advantage over binuclear precatalysis was also observed by recent literature.[32,36] However, Hazari and co-workers suggested that catalyst reduction to Pd(0) via arylboronic acid is less favorable than precatalysis pathways through (a) the oxidation of the alcoholic solvent to a ketone or (b) a β-hydride elimination involving a ligand olefin followed by base-assisted deprotonation of the formed palladium hydride.[36] In our case, solvent oxidation should occur, but since there is no ligand or olefin-like substrate, hydride elimination occurs via oxidation of the alkylamine linker from both the **1_5** and **1_11** intermediates. These intermediate structures also are stabilized by an agostic bond between the alpha-amine metilene hydrogen and the palladium center.

The activation barrier for **1a_11** conversion to **1a_12** was +10.9 kcal/mol (Figure S1, Data 1 in Supporting Information) in an endergonic reversible step (reverse barrier of only +0,4 kcal/mol from **1a_12**). The same trend was observed for **1b_11**, forming **1b_12**. Despite a

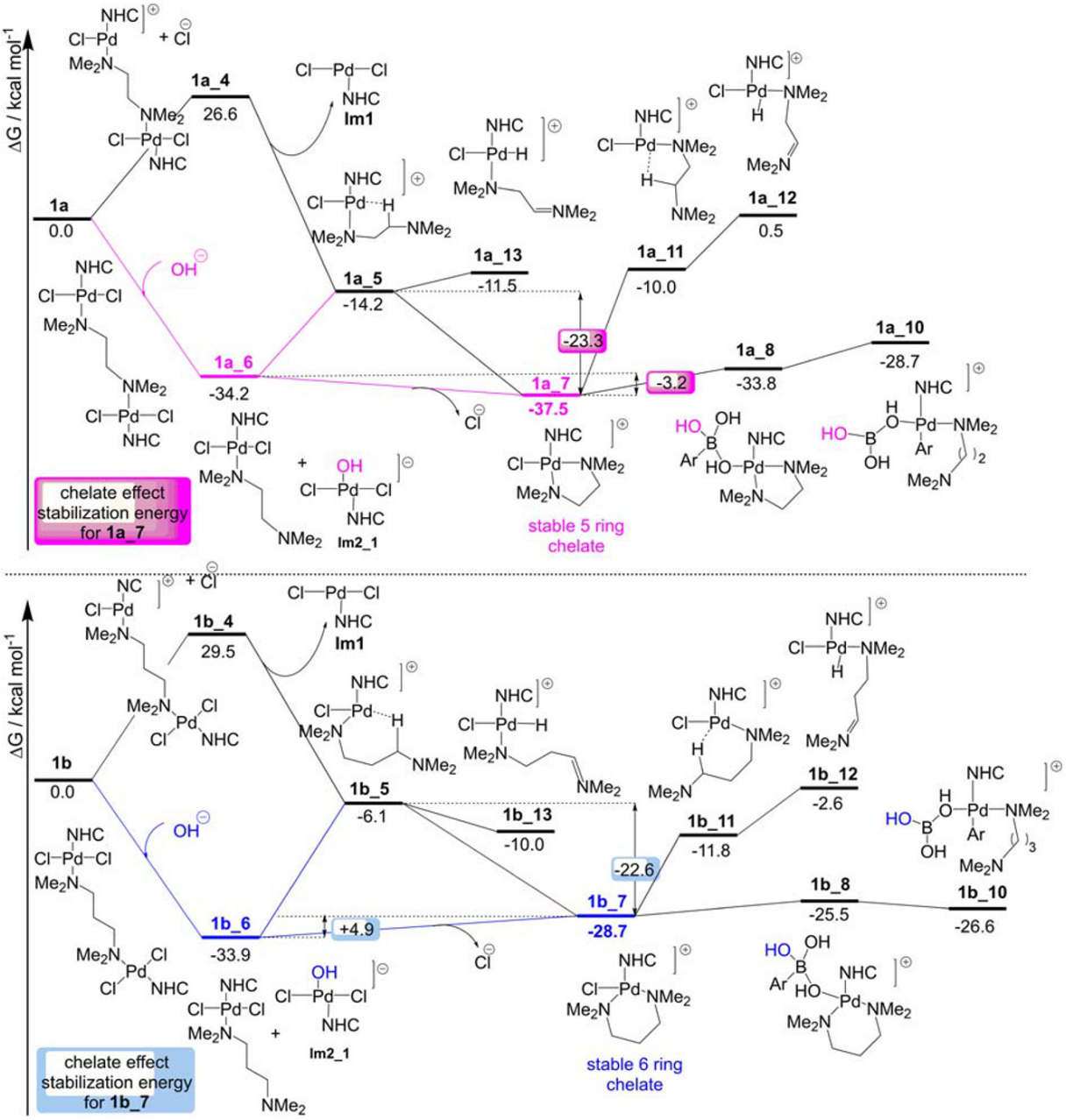


FIGURE 8 Thermodynamic profile in the condensed-phase (SMD-M06L/6-31G(d,p)) corresponding to palladium discoordination to form **Im1** starting from **1a** and **1b**, and the chelate effect associated with **1a_7**and **1b_7**. Relative free energies presented in kcal/mol

slightly higher activation barrier (12.6 kcal/mol, see Supporting Information Figure S1), the step produces a less instable product, with a reverse barrier of +3,4 kcal/mol from **1b_12** to **1b_11**. **1b_13** is formed from **1b_5** in an exergonic step, reducing the total energy of the system to −10.0 kcal/mol (Figure 8). Although the hydride elimination from **1_5** and **1_11** seems to be a more straightforward pathway to achieve the starting active Pd(0) catalyst, it is important to observe that this reaction mechanism leads to a more energetically demanding reaction pathway compared to the pathway via arylboronic acid.

4 | CONCLUSIONS

In summary, binuclear NHC palladium complexes bearing nitrogen-based alkyl chain ligands were synthesized and showed high activities in the Suzuki coupling reaction under milder and easier conditions such as in air at room temperature and user friendly operations-all reagent are used directly without purification than required for cycloamine ligands. Scope on hindered, activated, neutral or unactivated aryl chlorides coupled with sterically hindered, electron-withdrawing,-donating or neutral phenylboronic acids led to *mono*-, *di*- and *tri*-

ortho-substituted biaryls in completion yields in very shorter reaction time at room temperature in air. The synthesized binuclear Pd complexes exhibited a similar catalytic level to Pd-PEPPSI complexes. With the claim of green chemistry, the environmental friendliness solvent-ethanol and no heating condition were applied in general case studies. Scale-up examination in gram experiment was successfully carried out to prove the application of our Pd catalytic system. DFT studies showed that the single Pd complex mechanism is more consisted with our experimental results and the precatalysis may be definitive to improve our understanding of the kinetic activity difference between **1a** and the other starting catalysts. The computational studies indicated that the Suzuki–Miyaura reaction occurs through monopalladium complexes and the base assistance for its generation through a highly exergonic step followed by chelate species formation is more stable for the **1a** starting catalyst than for **1b**. In terms of experimental and DFT studies, it is likely that the role of mononuclear NHC Pd complexes designed is more significant for Suzuki reaction.

ACKNOWLEDGEMENTS

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