Inorganica Chimica Acta 522 (2021) 120360

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Synthesis, characterization and catalytic activity of *N*-heterocyclic carbene ligated Schiff base palladacycles

İlknur Babahan [a], Rukiye Fırıncı [a], Namık Özdemir [b], M. Emin Günay [a,*]

[a] Department of Chemistry, Aydın Adnan Menderes University, 09010 Aydın, Turkey
[b] Department of Mathematics and Science Education, Ondokuz Mayıs University, 55139 Samsun, Turkey

ARTICLE INFO

Keywords:
Imine-palladacycle
N-heterocyclic carbene
Schiff base
Imidazol-2-ylidene
Catalysis
Suzuki–Miyaura cross-coupling reaction

ABSTRACT

A series of *N*-heterocyclic carbene (NHC) ligated Schiff base palladacycles were synthesized by the reaction of μ-acetato-bridged Schiff base palladacycles (**PdL$_{1\text{-}2}$**) with imidazolium salts (**a-c**). The new NHC ligated palladacycles were fully characterized using ^{1}H NMR, ^{13}C NMR, infrared spectroscopy, MS analysis, and single-crystal X-ray diffraction for one complex (**PdL$_1$**). Further exploration of the catalytic application of the palladacycles for Suzuki-Miyaura cross-coupling reactions of aryl bromides with phenylboronic acid was carried out. It was determined that the new dimeric imine-palladacycle (**PdL$_2$**) exhibits the highest catalytic activity among the coupling compounds in this study.

1. Introduction

In recent years, Pd-catalyzed processes that assist the formation of C—C bonds have seen great progress [1] and reaction such as Suzuki-Miyaura cross-coupling is employed extensively in synthetic routes for a large number of natural products, new materials, and pharmaceuticals [2]. The use of cyclopalladated complexes, sometimes called palladacycles featuring bidentate ligands with a general structure C-X (X = N, P, S, etc.), as precatalysts have led to significant advances [3]. In this regard, phospha-containing palladacycles and Pd(II)-*N*-heterocyclic carbene (NHC) complexes were successfully used as catalysts for C—C coupling reactions. Since the first phosphapalladacyles were emphasized by Herrmann *et al.* [4], many new palladacyclic complexes have arisen. In addition to these complexes, "pincer" palladacycles containing functional groups bound by N, P, or S have also shown their efficiency in the Suzuki-Miyaura cross-coupling reaction [5].

Many groups have focused their research on the modification of palladacycles in order to tune and improve their catalytic properties. The electronic and steric properties of palladacycles are influenced by various factors, such as the size of the metallocyclic ring, the type of the donor atoms, and the nature of the ancillary ligand [6]. The activities of the palladacycles can often be modulated by ancillary ligands; the role is frequently performed by tertiary phosphines. However, the latter at present a certain disadvantage such as that they are the difficulties in removing the ligands and their degradation. An interesting approach could be combining Schiff base palladacycles with *N*-heterocyclic carbenes (NHCs) which are better σ-donor ligands. However, in spite of the widespread use of Pd(II)-NHCs as catalysts, the number of cyclopalladated derivatives with these ligands is rather limited [7–11], particularly those in which the metallated moiety is a Schiff base and an NHC ligand [12,13]. Some of these have shown to be active pre-catalysts in the Suzuki-Miyaura, Heck-Mizoroki, Buchwald-Hartwig reactions [14–16].

Schiff bases are well known as multidentate ligands in catalytic reactions among varied *N*-based ligands. According to the literature, there have been numerous studies regarding Schiff base ligands employment in palladium-catalyzed Suzuki-Miyaura cross-coupling reactions [17]. The utilization of nitrogen-containing ligands particularly Schiff base ligands in the Suzuki-Miyaura reaction instead of phosphine ligands is getting popular. Since nitrogen-based ligands are cheap, air-stable, having an easy handle and synthesis, they are preferred by researchers for the Suzuki-Miyaura reaction. It is favorable for the researchers that Schiff bases are obtained by a simple synthetic route with the commercial compounds. It is also worth mentioning that they also display high performance under a wide range of redox reactions and having readily varied electronic and steric properties [18–21]. With regard to imine-based palladacycles, Weissman and Milstein first reported the use of a dinuclear phosphine-free complex in the Suzuki coupling of nonactivated aryl bromides [22]. Bedford and co-workers then reported that the phosphine adducts of imine-based palladacycles exhibited

* Corresponding author.
E-mail address: megunay@adu.edu.tr (M. Emin Günay).

https://doi.org/10.1016/j.ica.2021.120360
Received 27 November 2020; Received in revised form 16 March 2021; Accepted 22 March 2021
Available online 26 March 2021

higher catalytic activities than dinuclear phosphine-free palladacycles in Suzuki coupling and elegantly highlighted the role played by the phosphine and the anionic X ligand in terms of both catalyst activity and lifetime [23]. The imine palladacycles have known as highly stabile catalysts for many cross-coupling reactions. Additionally, the imine palladacycles have the potential to be transformed into a diverse range of functionalized product. Therefore, this ability makes them easily recoverable and recyclable catalysts. These imine palladacycles are synthesized by the complexation of Pd precursors with imine which is synthesized via a condensation reaction between amines and aldehydes or ketones [24].

In this study, we aimed to obtain new coupling reagents that can work more efficiently with Pd-catalysts at very low metal loads in the Suzuki-Miyaura reaction under milder reaction conditions. For this purpose, two new acetato-bridge imine-palladacyclic dimers (**PdL$_{1\text{-}2}$**) from Schiff base ligands (**L$_{1\text{-}2}$**) were first synthesized. Subsequently, these two acetato-bridge imine-palladacyclic complexes synthesized were reacted with NHC precursors (**a-c**) to obtain NHC ligated Schiff base palladacycles (**PdL$_{1a\text{-}c}$** and **PdL$_{2a\text{-}c}$**). Finally, catalytic activities of all synthesized complexes in the Suzuki-Miyaura cross-coupling reaction were investigated. The Suzuki-Miyaura reaction has proved on the utilization of these complexes (**PdL$_{1\text{-}2}$**, **PdL$_{1a\text{-}c}$**, and **PdL$_{2a\text{-}c}$**) as an effective precatalyst for the cross-coupling of aryl bromides with phenylboronic acid at 82 °C temperature. It can be said that both imine-palladacycles (**PdL$_{1\text{-}2}$**) and *N*-heterocyclic carbene ligated Schiff base palladacycles (**PdL$_{1a\text{-}c}$** and **PdL$_{2a\text{-}c}$**) displayed a very important role in this situation. This study has been also included preliminary results on the very efficient performance of Schiff base palladacycle (**PdL$_{1\text{-}2}$**) as precatalysts in arylation reactions of aryl bromides.

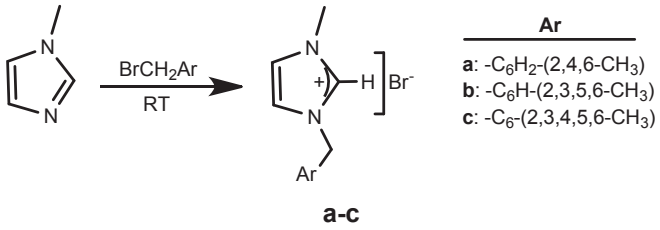
2. Experimental

2.1. Material and general methods

All reagents used were purchased from Merck. All reactions carried out under Argon in flame-dried glassware using a standard Schlenk type flask. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. Benzyl bromide derivatives were synthesized according to the literature [25]. ^{1}H and ^{13}C NMR spectrum of compounds was collected on Varian AS 400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts were measured in ppm relative to tetramethylsilane for ^{1}H and ^{13}C NMR spectra. All catalytic reactions were monitored with an Agilent 6890 N GC system using GC flame ionization detection with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness. Melting points were measured in open capillary tubes with a Stuart SMP 30 melting point apparatus. Single-crystal X-ray diffraction data of **PdL$_1$** was recorded with an STOE IPDS II diffractometer.

2.2. General method of synthesis of imidazolium salts (a-c)

The imidazolium salts were synthesized prepared according to previous reports [10]. The benzyl bromide (2,4,6-trimethylbenzyl-, 2,3,5,6-tetramethylbenzyl- and 2,3,4,5,6-pentamethylbenzyl bromides) derivatives (20 mmol) and 1-methylimidazole (1.6 mL, 20 mmol) were stirred in toluene (15 mL) for 3 h at room temperature as shown in Scheme 1. The volume of the solution was reduced to 5 mL, diethyl ether was added to the remaining solution, which was vigorously shaken and then decantated. The solid residue was washed with diethyl ether (3x20 mL) to obtain a white solid, which was recrystallized from ethanol/diethyl ether (3 mL/15 mL).



Scheme 1. Synthesis of imidazolium salts (**a-c**).

Compound a

Yield: 5.37 g, 91%, m.p.: 117–118 °C. Color: White. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 6H, $C_6H_2(CH_3)_3$), 2.38 (s, 3H, $C_6H_2(CH_3)_3$), 4.10 (s, 3H, NCH_3), 5.53 (s, 2H, $NCH_2C_6H_2(CH_3)_3$), 6.87 (d, 1H, J = 1.6 Hz, $NCHCHNCH_3$), 6.90 (s, 2H, $C_6H_2(CH_3)_3$), 7.46 (d, 1H, J = 1.6 Hz, $NCHCHNCH_3$), 10.16 (s, 1H, NCHN). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 ($C_6H_2(CH_3)_3$), 21.2 ($C_6H_2(CH_3)_3$), 37.2 (NCH_3), 48.1 ($NCH_2C_6H_2(CH_3)_3$), 120.9 ($NCHCHNCH_3$), 124.0 ($NCHCHNCH_3$), 125.5, 130.1, 137.0, 138.3 ($C_6H_2(CH_3)_3$), 140.1 (NCHN). Elemental analyses (%) calc. for $C_{14}H_{19}BrN_2$ (M_w : 295.2181): C, 56.96; H, 6.49; N, 9.49; found: C, 56.89; H, 6.27; N, 9.55.

Compound b

Yield: 5.13 g, 83%, m.p.: 123–125 °C. Color: White. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 6H, $C_6H(CH_3)_4$), 2.21 (s, 6H, $C_6H(CH_3)_4$), 4.09 (s, 3H, NCH_3), 5.59 (s, 2H, $NCH_2C_6H(CH_3)_4$), 6.90 (d, 1H, J = 1.6 Hz, $NCHCHNCH_3$), 7.01 (s, 1H, $C_6H(CH_3)_4$), 7.51 (d, 1H, J = 1.6 Hz, $NCHCHNCH_3$), 10.02 (s, 1H, NCHN). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1 ($C_6H(CH_3)_4$), 20.6 ($C_6H(CH_3)_4$), 37.3 (NCH_3), 48.8 ($NCH_2C_6H(CH_3)_4$), 121.1 ($NCHCHNCH_3$), 123.8 ($NCHCHNCH_3$), 128.1, 133.8, 134.3, 135.2 ($C_6H(CH_3)_4$), 137.2 (NCHN). Elemental analyses (%) calc. for $C_{15}H_{21}BrN_2$ (M_w : 309.2447): C, 58.26; H, 6.84; N, 9.06; found: C, 58.35; H, 6.57; N, 9.23.

Compound c

Yield: 6.08 g, 94%, m.p.: 192–194 °C. Color: White. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 6H, $C_6(CH_3)_5$), 2.18 (s, 6H, $C_6(CH_3)_5$), 2.21 (s, 3H, $C_6(CH_3)_5$), 4.08 (s, 3H, NCH_3), 5.57 (s, 2H, $NCH_2C_6(CH_3)_5$), 6.91 (d, 1H, J = 1.6 Hz, $NCHCHNCH_3$), 7.54 (d, 1H, J = 1.6 Hz, $NCHCHNCH_3$), 9.94 (s, 1H, NCHN). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.0 ($C_6(CH_3)_5$), 17.1 ($C_6(CH_3)_5$), 17.4 ($C_6(CH_3)_5$), 37.2 (NCH_3), 49.3 ($NCH_2C_6(CH_3)_5$), 121.1 ($NCHCHNCH_3$), 123.9 ($NCHCHNCH_3$), 125.4, 133.8, 133.9, 136.9 ($C_6(CH_3)_5$), 137.5 (NCHN).). Elemental analyses (%) calc. for $C_{16}H_{23}BrN_2$ (M_w : 323.2713): C, 59.45; H, 7.17; N, 8.67; found: C, 59.38; H, 7.07; N, 8.74.

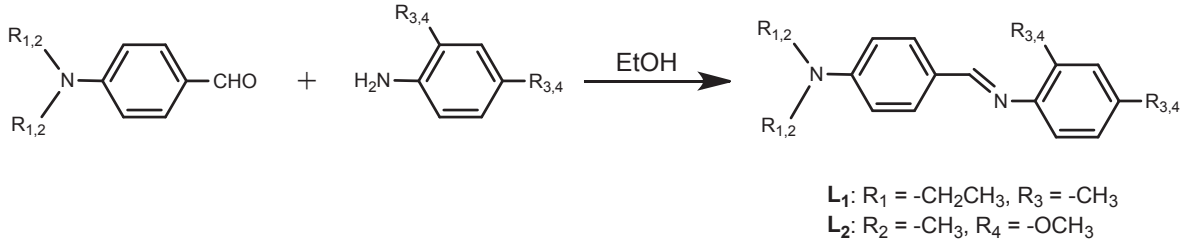
2.3. Synthesis of the Schiff base ligands (L_1 and L_2)

The Schiff base ligands were synthesized according to previous reports as shown in Scheme 2 [26]. 4-(diethylamino)benzaldehyde/4-(dimethylamino)benzaldehyde ethanolic solution was refluxed with 2,4-dimethylaniline/2,4-dimethoxylaniline (1:1 mmol ratio) with a few drops of an acetic acid catalyst, respectively. The resulting yellow precipitates of the Schiff base ligands were filtered, and then the yellow products were washed with the cold ethanol–water mixture and recrystallized from ethanol.

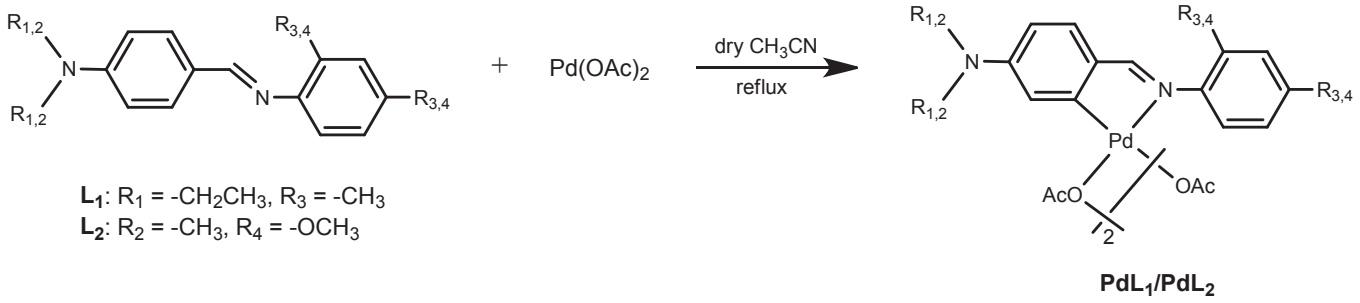
2.4. Synthesis of the PdL_1 and PdL_2 complexes

A solution of Schiff base ligands (1 mmol **L$_1$** or **L$_2$**), which had been synthesized according to the previous studies, [26] were reacted with palladium(II) acetate (1 mmol) dissolved in 10 mL of dry acetonitrile as shown in Scheme 3. Subsequently, the reaction was refluxed under Ar atmosphere. Finally, yellow precipitates were formed after 2 h. The crystals of the final product were collected by recrystallization from dichloromethane and diethylether as seen in Fig. 1 and, characterized by using FT-IR, ^{1}H and ^{13}C NMR, and single-crystal X-ray diffraction.

PdL$_1$: Yield: 75%, m.p.: 230–231 °C. Color: Red. FT-IR (KBr cm^{-1}):



Scheme 2. Synthesis of the Schiff base ligands ($\mathbf{L_1}$ and $\mathbf{L_2}$).



Scheme 3. Synthesis of the imine-palladacycles ($\mathbf{PdL_1}$ and $\mathbf{PdL_2}$ complexes).

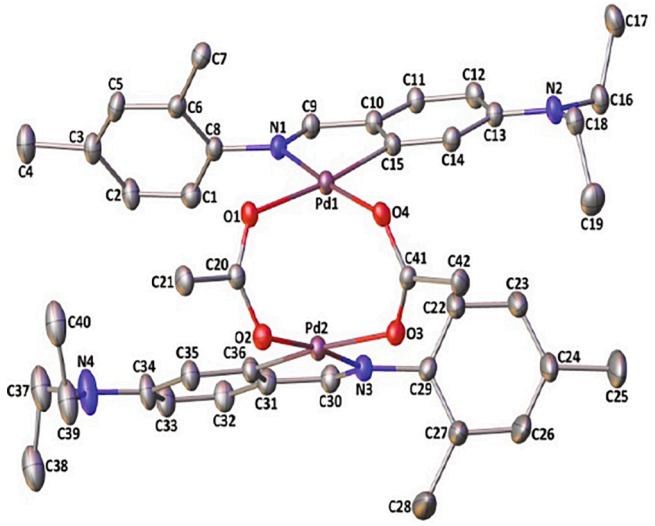


Fig. 1. Molecular structure of $\mathbf{PdL_1}$ showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogens have been omitted for clarity and only the major part of disordered fragment is drawn.

1565 (C═N), 1515 (C═C), 1203 (C—O). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, 6H, (CH_3CH_2)$_2$NC$_6$H$_3$), 1.77 (s, 3H, C$_6$H$_3$(CH$_3$)$_2$-*p*-CH_3), 2.21 (s, 3H, C$_6$H$_3$(CH$_3$)$_2$-*o*-CH_3), 2.78 (s 6H, –COO-CH_3), 3.23–3.36 (t, 4H, (CH_3CH_2)$_2$NC$_6$H$_3$), 5.88, 6.83 (s, 2H, Ar-*H*), 6.34, 6.98 (d, 2H, J = 8 Hz, Ar-*H*), 6.43, 6.58 (d, 2H, J = 7.4 Hz, Ar-*H*), 7.38 (s, 1H, –C*H* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6 (C$_6$H$_3$(CH$_3$)$_2$-*p*-CH_3), 18.3 (C$_6$H$_3$(CH$_3$)$_2$-*o*-CH_3), 21.0 (CH_3CH_2)$_2$NC$_6$H$_3$), 23.9 (–CO-CH_3), 44.3 (CH_3CH_2)$_2$NC$_6$H$_3$), 106.0, 114.9, 126.1, 128.2, 128.8, 129.0, 130.0, 133.2, 134.7, 145.7, 148.4, 157.1 (Ar–*C*), 171.5 (-*C*═N), 179.4 (–*C*O-). HRMS (ESI): *m/z* calcd for [$C_{42}H_{52}N_4O_4Pd_2$]: 889.7267 ($M^{\pm}$), found 889.3178.

$\mathbf{PdL_2}$: Yield: 72%, m.p. 250–251 °C. Color: Brown. FT-IR (KBr cm^{-1}): 1566 (C═N), 1528 (C═C), 1202 (C—O). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.82 (s, 3H, C$_6$H$_3$(OCH$_3$)$_2$-*p*-OCH_3), 3.75 (s, 3H, C$_6$H$_3$(OCH$_3$)$_2$-*o*-OCH_3), 2.87 (s, 6H, –COO-CH_3), 3.75 [s, 6H, (CH_3)$_2$NC$_6$H$_3$)], 5.91, 6.30 (s, 2H, Ar-*H*), 6.28, 7.07 (d, 2H, J = 8 Hz, Ar-*H*), 5.97, 6.22 (d, 2H, J = 7.4 Hz, Ar-*H*), 7.48 (s, 1H, –C*H* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (C$_6$H$_3$(OCH$_3$)$_2$-*p*-OCH_3), 55.9 (C$_6$H$_3$(CH$_3$)$_2$-*o*-CH_3), 40.0 (CH_3)$_2$NC$_6$H$_3$), 24.2 (–CO-CH_3), 98.2, 102.9, 106.5, 115.2, 125.4, 128.4, 131.6, 134.4, 149.9, 153.6, 157.1, 158.3 (Ar–*C*), 173.2 (-*C*═N), 179.3 (–*C*O-). HRMS (ESI): *m/z* calcd for [$C_{38}H_{44}N_4O_8Pd_2$]: 897.6180 ($M^{\pm}$), found: 897.8201.

2.5. Crystal structure determination of PdL_1

X-ray diffraction data of PdL_1 were recorded with an STOE IPDS II diffractometer at room temperature using graphite-monochromated Mo Kα radiation by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA [27] while data reduction was applied using X-RED32 [27a]. The structures were solved by direct methods with SIR2019 [27b] and refined by means of the full-matrix full-matrix least-squares calculations on F^2 using SHELXL-2018 [27c]. All H atoms were located in difference electron-density map and then treated as riding atoms in geometrically idealized positions, fixing the bond lengths at 0.93, 0.97, and 0.96 Å for CH, CH_2, and CH_3 atoms, respectively. The displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for methyl) of their parent atoms. In the complex, one of the two diethylamide moieties was disordered over two positions, and the refined site-occupancy factors of the disordered part are 0.635(19) and 0.365(19)% for N4/C37-C40. The disordered atoms were refined using the SIMU, DELU, and SAME restraints of SHELXL-2018, which resulted in the best parameters. The crystallographic data and refinement parameters are summarized in Table 1. The molecular graphic was created by using OLEX2 [27d].

2.6. General methods of synthesis of the $PdL_{1a\text{-}c}$ and $PdL_{2a\text{-}c}$

A sample of $\mathbf{PdL_1}$ or $\mathbf{PdL_2}$ (0.20 mmol) was refluxed with one of the compounds of **a-c** (0.40 mmol) in toluene (10 mL) at 110 °C for 2 h. The solvent was removed in vacuo, the remaining precipitate was then dissolved in dichloromethane (2 mL) and recrystallization from dichloromethane/toluene afforded the complexes of $\mathbf{PdL_{1a\text{-}c}}$ and $\mathbf{PdL_{2a\text{-}c}}$. The crystals of these complexes were characterized by using FT-IR, ^{1}H and

Table 1
Crystal data and structure refinement parameters for **PdL_1**.

CCDC depository	1,947,705
Color/shape	Red/prism
Chemical formula	$[Pd_2(C_{19}H_{23}N_2)_2(C_2H_3O_2)_2]$
Formula weight	889.67
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell parameters	
a, b, c (Å)	11.4991(11), 12.7569(12), 14.5849(14)
α, β, γ (°)	75.288(7), 80.481(7), 86.757(8)
Volume (Å^3)	2040.6(3)
Z	2
$D_{calc.}$ (g/cm^3)	1.448
μ (mm^{-1})	0.926
Absorption correction	Integration
$T_{min.}$, $T_{max.}$	0.7200, 0.8911
F_{000}	912
Crystal size (mm^3)	0.41 × 0.28 × 0.14
Diffractometer	STOE IPDS II
Measurement method	ω scan
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-17 \le l \le 17$
θ range for data collection (°)	$2.131 \le \theta \le 25.049$
Reflections collected	28,592
Independent/observed reflections	7220/4086
$R_{int.}$	0.1510
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7220/83/527
Goodness-of-fit on F^2	0.951
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0652$, w$R_2 = 0.1352$
R indices (all data)	$R_1 = 0.1197$, w$R_2 = 0.1558$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ (e/Å^3)	1.13, −0.51

Table 2
Selected geometric parameters for **PdL_1**.

Bond lengths (Å)			
Pd1—C15	1.977(7)	Pd2—C36	1.956(7)
Pd1—N1	2.027(6)	Pd2—N3	2.027(6)
Pd1—O4	2.035(5)	Pd2—O2	2.070(5)
Pd1—O1	2.137(5)	Pd2—O3	2.137(5)
Bond angles (°)			
C15—Pd1—N1	81.0(3)	C36—Pd2—N3	80.7(3)
C15—Pd1—O4	92.8(3)	C36—Pd2—O2	92.3(3)
N1—Pd1—O4	173.7(2)	N3—Pd2—O2	172.3(2)
C15—Pd1—O1	174.3(3)	C36—Pd2—O3	174.5(3)
N1—Pd1—O1	95.0(2)	N3—Pd2—O3	95.0(2)
O4—Pd1—O1	91.30(19)	O2—Pd2—O3	91.7(2)

^{13}C NMR as shown in Scheme 4.

Compound PdL_{1a}

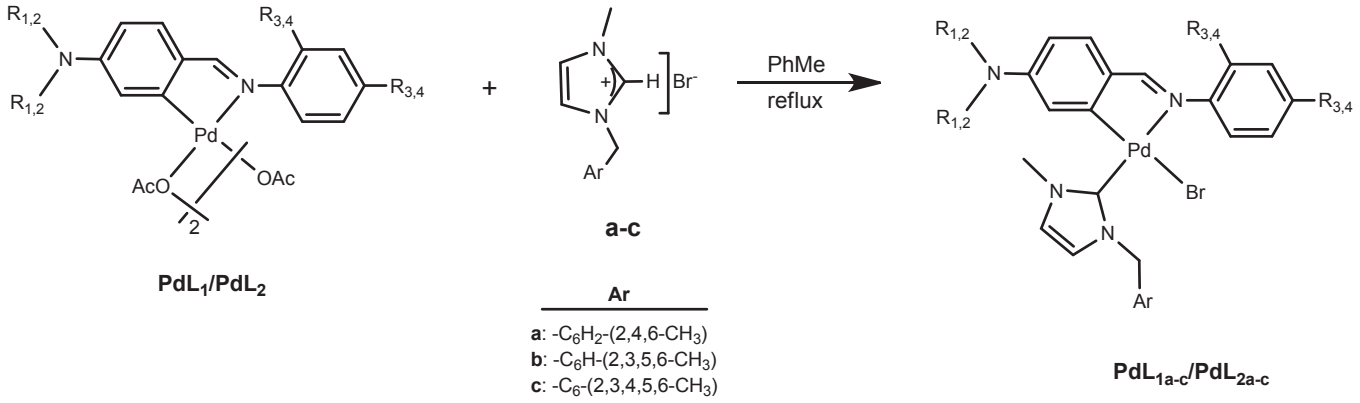
Yield: 68%, m.p.:190–191 °C. Color: Brown. FT-IR (KBr cm^{-1}): 1568 (C═N), 1521 (C═C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3H, $C_6H_3(CH_3)_2$-*p*-C*H*$_3$), 1.08, 2.31 (t, 6H, (C*H*$_3$CH$_2$)$_2$NC$_6$H$_3$), 2.27 (s, 3H, $C_6H_2(CH_3)_3$-*p*-C*H*$_3$), 2.51 (s, 3H, $C_6H_3(CH_3)_2$-*o*-C*H*$_3$), 3.98 (s, 3H, $C_6H_2(CH_3)_3$-*o*-C*H*$_3$), 3.23 (q, 4H, (CH$_3$C*H*$_2$)$_2$NC$_6$H$_3$), 4.12 (s, 3H, –NC*H*$_3$), 5.34, 5.80 (d, 2H, J = 6.6 Hz, –NC*H*$_2$-Ar), 5.84, 6.32 (d, 2H, J = 14.0 Hz, –NC*H*C*H*NCH$_3$), 5.74, 6.84, 6.90 (s, 3H, Ar-*H*), 6.34, 6.90 (d, 2H, J = 8.0 Hz, Ar-*H*), 5.44, 6.39 (d, 2H, J = 7.4 Hz, Ar-*H*), 7.89 (s, 1H, –C*H* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 ($C_6H_3(CH_3)_2$-*p*-*C*H$_3$), 21.0 ($C_6H_2(CH_3)_3$-*p*-*C*H$_3$), 19.5 ($C_6H_3(CH_3)_2$-*o*-*C*H$_3$), 20.2 ($C_6H_2(CH_3)_3$-*o*-*C*H$_3$), 20.8 (*C*H$_3$CH$_2$)$_2$NC$_6$H$_3$), 38.7 (–N*C*H$_3$), 44.4 (CH$_3$*C*H$_2$)$_2$NC$_6$H$_3$), 49.5 (-N-*C*H$_2$-Ar), 121.1, 122.5 (–N*C*H*C*HNCH$_3$), 106.3, 117.7, 119.2, 126.6, 128.0, 129.2, 130.1, 130.9, 131.9, 134.7, 135.3, 138.4, 138.6, 147.4, 149.3, 161.2 (Ar–*C*), 173.9 (-*C*═N),186.5 (Pd–$C_{carbene}$). HRMS (ESI): *m/z* calcd. for $[C_{33}H_{41}BrN_4Pd]^{\pm}$: 680.0294 (M$^{\pm}$), 601.2370 (M$^{\pm}$-Br), found; 601.1334 (M$^{\pm}$-Br).

Compound PdL_{1b}

Yield: 65%, m.p.: 227–228 °C. Color: Brown. FT-IR (KBr cm^{-1}): 1570 (C═N), 1520 (C═C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3H, $C_6H_3(CH_3)_2$-*p*-C*H*$_3$), 1.08, 2.18 (t, 6H, (C*H*$_3$CH$_2$)$_2$NC$_6$H$_3$), 1.57 (s, 6H, $C_6H(CH_3)_4$-*m*-C*H*$_3$), 2.50 (s, 3H, $C_6H_3(CH_3)_2$-*o*-C*H*$_3$), 3.99 (s, 6H, $C_6H(CH_3)_4$-*o*-C*H*$_3$), 3.24 (q, 4H, (CH$_3$C*H*$_2$)$_2$NC$_6$H$_3$), 4.13 (s, 3H, –NC*H*$_3$), 5.43, 5.90 (d, 2H, J = 6.6 Hz, –NC*H*$_2$-Ar), 5.82, 6.32 (d, 2H, J = 12.0 Hz, –NC*H*C*H*NCH$_3$), 5.87, 6.83, 7.02 (s, 3H, Ar-*H*), 6.34, 6.96 (d, 2H, J = 8.0 Hz, Ar-*H*), 5.45, 6.39 (d, 2H, J = 7.4 Hz, Ar-*H*), 7.90 (s, 1H, –C*H* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 ($C_6H_3(CH_3)_2$-*p*-*C*H$_3$), 16.2 ($C_6H(CH_3)_4$-*m*-*C*H$_3$), 19.5 ($NC_6H_3(CH_3)_2$-*o*-*C*H$_3$), 20.4 ($C_6H(CH_3)_4$-*o*-*C*H$_3$), 21.0 (*C*H$_3$CH$_2$)$_2$NC$_6$H$_3$), 38.6 (–N*C*H$_3$), 44.4 (CH$_3$*C*H$_2$)$_2$NC$_6$H$_3$, 50.2 (-N-*C*H$_2$-Ar), 120.9, 122.5 (N*C*H*C*HNCH$_3$), 106.3, 117.7, 119.5, 126.6, 130.1, 130.8, 130.9, 131.9, 132.2, 134.2, 134.6, 134.7, 135.3, 147.4, 149.3, 161.2 (Ar–*C*), 173.8 (-*C*═N), 186.4 (Pd–$C_{carbene}$). HRMS (ESI): *m/z* calcd. for $[C_{34}H_{43}BrN_4Pd]^{\pm}$: 694.0560 (M$^{\pm}$), 615.2527 (M$^{\pm}$-Br), found; 615.8601 (M$^{\pm}$-Br).

Compound PdL_{1c}

Yield: 62%, m.p. 266–267 °C. Color: Brown. FT-IR (KBr cm^{-1}): 1567 (C═N), 1518 (C═C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3H, $C_6H_3(CH_3)_2$-*p*-C*H*$_3$), 1.08, 2.32 (t, 6H, (C*H*$_3$CH$_2$)$_2$NC$_6$H$_3$), 1.60 (s, 6H, $C_6(CH_3)_5$-*m*-C*H*$_3$), 2.27 (s, 6H, $C_6(CH_3)_5$-*p*-C*H*$_3$), 2.49 (s, 3H, $C_6H_3(CH_3)_2$-*o*-C*H*$_3$), 3.98 (s, 6H, $C_6(CH_3)_5$-*o*-C*H*$_3$), 3.23 (q, 4H, (CH$_3$C*H*$_2$)$_2$NC$_6$H$_3$), 4.12 (s, 3H, (–NC*H*$_3$), 5.45, 5.86 (d, 2H, J = 6.6 Hz, (–NC*H*$_2$-Ar), 5.84, 6.33 (d, 2H, J = 12.0 Hz, (–NC*H*C*H*NCH$_3$), 5.88, 6.82 (s, 2H, Ar-*H*), 6.33, 6.96 (d, 2H, J = 8.0 Hz, Ar-*H*), 5.48, 6.71 (d, 2H, J = 7.4 Hz, Ar-*H*), 7.90 (s, 1H, –C*H* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ =



Scheme 4. Synthesis of the imine-palladacycles (**PdL_{1a-c}** and **PdL_{2a-c}**).

12.6 ($C_6H_3(CH_3)_2$-*p*-CH_3), 12.8 ($C_6(CH_3)_5$-*p*-CH_3), 17.1 ($C_6(CH_3)_5$-*m*-CH_3), 19.4 ($C_6H_3(CH_3)_2$-*o*-CH_3), 20.2 ($C_6(CH_3)_5$-*o*-CH_3), 21.0 ($CH_3CH_2)_2NC_6H_3$), 38.5 (–NCH_3), 44.3 ($CH_3CH_2)_2NC_6H_4$), 50.2 (-N-CH_2-Ar), 122.3, 121.2 (–NCHCHNCH$_3$), 106.0, 126.6, 128.7, 130.0, 130.9, 133.0, 133.2, 134.2, 134.3, 134.7, 135.3, 135.8, 147.4, 148.4, 149.3, 161.3 (Ar–*C*), 173.5 (-*C*═N), 186.1 (Pd–$C_{carbene}$). HRMS (ESI): *m/z* calcd for $[C_{35}H_{45}BrN_4Pd]^{\pm}$: 708.0826 ($M^{\pm}$), 628.1786 ($M^{\pm}$-Br), found; 628.3020 ($M^{\pm}$-Br).

Compound PdL$_{2a}$

Yield: 58%, m.p.: 150–151 °C. Color: Brown. FT-IR (KBr cm^{-1}): 1568 (C═N), 1528 (C═C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H, $C_6H_3(OCH_3)_2$-*p*-OCH_3), 2.36 (s, 6H, ($CH_3)_2NC_6H_3$), 2.18 (s, 6H, $C_6H_2(CH_3)_3$-*p*-CH_3), 2.83 (s, 3H, $C_6H_3(OCH_3)_2$-*o*-OCH_3), 3.87 (s, 6H, $C_6H_2(CH_3)_3$-*o*-CH_3), 4.02 (s, 3H, –NCH_3), 5.49, 5.81 (d, 2H, *J* = 6.6 Hz, –NCH_2-Ar), 5.84, 6.30 (d, 2H, *J* = 12.0 Hz, –NCHCHNCH$_3$), 5.81, 6.93, 7.38 (s, 3H, Ar-*H*), 6.52, 6.92 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 5.58, 6.69 (d, 2H, *J* = 7.4 Hz, Ar-*H*), 8.04 (s, 1H, –*CH* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4 ($C_6H_2(CH_3)_3$-*p*-CH_3), 21.2 ($C_6H_2(CH_3)_2$-*o*-CH_3), 40.3 (($CH_3)_2NC_6H_3$), 55.6 ($C_6H_3(OCH_3)_2$-*p*-OCH_3), 56.3 (s, 3H, $C_6H_3(OCH_3)_2$-*o*-OCH_3), 39.0 (–NCH_3), 49.8 (-N-CH_2-Ar), 121.8, 121.4 (–NCHCHNCH$_3$), 100.0, 103.8, 107.1, 111.2, 118.4, 119.4, 126.4, 128.5, 129.6, 130.3, 138.9, 138.9, 153.3, 158.7, 161.2, 169.5 (Ar–*C*), 174.5 (-*C*═N), 186.1 (Pd–$C_{carbene}$). HRMS (ESI): *m/z* calcd. for $[C_{31}H_{37}BrN_4O_2Pd_2]^+$: 683.9751 ($M^+$), 603.1951, found; 603.1932 ($M^{\pm}$-Br).

Compound PdL$_{2b}$

Yield: 64%, m.p.: > 300 °C. Color: Brown. FT-IR (KBr cm^{-1}): 1564 (C═N), 1528 (C═C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H, $C_6H_3(OCH_3)_2$-*p*-OCH_3), 2.27 (s, 6H, ($CH_3)_2NC_6H_3$), 1.71 (s, 6H, $C_6H(CH_3)_4$-*m*-CH_3), 2.20 (s, 3H, $C_6H_3(OCH_3)_2$-*p*-OCH_3), 2.85 (s, 3H, $C_6H_3(OCH_3)_2$-*o*-OCH_3), 3.85 (s, 6H, $C_6H(CH_3)_4$-*o*-CH_3), 3.99 (s, 3H, –NCH_3), 5.49, 5.88 (d, 2H, *J* = 6.6 Hz, –NCH_2-Ar), 5.84, 6.34 (d, 2H, *J* = 12.0 Hz, –NCHCHNCH$_3$), 5.52, 6.82, 7.00 (s, 3H, Ar-*H*), 6.52, 6.82 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 5.63, 6.72 (d, 2H, *J* = 7.4 Hz, Ar-*H*), 8.05 (s, 1H, (–*CH* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4 ($C_6H(CH_3)_4$-*o*-CH_3), 15.1 ($C_6H(CH_3)_4$-*m*-CH_3), 55.6 ($C_6H_3(OCH_3)_2$-*p*-OCH_3), 56.2 ($C_6H_3(OCH_3)_2$-*o*-OCH_3), 40.3 (($CH_3)_2NC_6H_3$), 38.9 (–NCH_3), 49.1 (-N-CH_2-Ar), 121.0, 121.9 (–NCHCHNCH$_3$), 102.6, 114.5, 118.5, 120.9, 130.2, 130.7, 131.3, 133.6, 134.7, 138.6, 138.2, 143.8, 147.6, 149.5, 161.3, 166.8 (Ar–*C*), 174.2 (-*C*═N), 186.2 (Pd–$C_{carbene}$). HRMS (ESI): *m/z* calcd. for $[C_{32}H_{39}BrN_4O_2Pd]^{\pm}$: 698.0017 ($M^{\pm}$), 617.2108 ($M^{\pm}$-Br), found; 617.2090 ($M^{\pm}$-Br).

Compound PdL$_{2c}$

Yield: 60%, m.p.: 253–254 °C. Color: Brown. FT-IR (KBr cm^{-1}): 1571 (C═N), 1529 (C═C). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 2.20 (s, 3H, ($C_6H_3(OCH_3)_2$-*p*-OCH_3), 2.36 (s, 6H, ($CH_3)_2NC_6H_3$), 1.82 (s, 6H, $C_6(CH_3)_5$-*m*-CH_3), 2.20 (s, 3H, $C_6(CH_3)_5$-*p*-CH_3), 2.84 (s, 3H, $C_6H_3(OCH_3)_2$-*o*-OCH_3), 3.88 (s, 3H, $C_6(CH_3)_5$-*o*-CH_3), 4.00 (s, 3H, NCH_3), 5.51, 5.91 (d, 2H, *J* = 6.6 Hz, –NCH_2-Ar), 5.84, 6.32 (d, 2H, *J* = 12.0 Hz, –NCHCHNCH$_3$), 5.87, 6.82, 7.38 (s, 3H, Ar-*H*), 6.54, 6.82 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 5.52, 6.41 (d, 2H, *J* = 7.4 Hz, Ar-*H*), 8.04 (s, 1H, –*CH* = N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.0 ($C_6(CH_3)_5$-*p*-CH_3), 17.3 ($C_6(CH_3)_5$-*o*-CH_3), 20.0 ($C_6(CH_3)_5$-*m*-CH_3), 55.6 ($C_6H_3(OCH_3)_2$-*p*-OCH_3), 56.3 ($C_6H_3(OCH_3)_2$-*o*-OCH_3), 40.2 (($CH_3)_2NC_6H_3$), 38.9 (–NCH_3), 50.9 (-N-CH_2-Ar), 121.1, 121.2 (–NCHCHNCH$_3$), 100.1, 103.9, 107.0, 115.9, 118.8, 119.9, 126.7, 128.5, 129.2, 130.3, 133.2, 134.4, 135.9, 138.3, 142.3, 158.7 (Ar–*C*), 174.4 (-*C*═N), 186.6 (Pd–$C_{carbene}$). HRMS (ESI): *m/z* calcd. for $[C_{33}H_{41}BrN_4O_2Pd]^{\pm}$: 712.0282 ($M^{\pm}$), 631.2264 ($M^{\pm}$-Br), found; 631.2244 ($M^{\pm}$-Br).

2.7. General procedure for Suzuki-Miyaura cross-coupling reaction

Under Argon atmosphere, a two-necked 25 mL flask was charged with palladium(II) complexes (**PdL$_1$**, **PdL$_2$**, **PdL$_{1a-c}$**, and **Pd$_{2a-c}$**, 0.5 mol %), Cs_2CO_3 (1.5 mmol), phenylboronic acid (0.75 mmol), aryl bromide (0.5 mmol), diethylene glycol di-*n*-butyl ether as an internal standard (0.3 mmol) in ^{i}PrOH (IPA, 3.0 mL). The flask was placed in a pre-heated oil bath at 82 °C. The reaction was followed by GC at a selected period of times (0.5 h, 1 h, 2 h, 4 h). After the sample was taken from the flask, ^{i}PrOH (2.0 mL) was added to the mixture, centrifuged and the solution was transferred to vials. The yields of the product obtained (based on the aryl bromides) were estimated by the area of GC chromatogram peaks.

3. Results and discussion

In this study, initially, the synthesized Schiff base ligands (**L$_{1-2}$**), derived from 4-(diethylamino)benzaldehyde/4-(dimethylamino)benzaldehyde and 2,4-dimethylaniline/2,4-dimethoxylaniline, were reacted with palladium(II) acetate to give two novel palladacycle dimers (**PdL$_1$** and **PdL$_2$**, Fig. 1), which are stable in the air. The structure of **PdL$_1$** has been also determined by single-crystal X-ray diffraction as shown in Fig. 1. Palladacycle dimers having acetato-bridged can be readily divided by using *N*-heterocyclic carbenes (NHCs) to form novel monomeric complexes. Therefore, *N*-heterocyclic carbenes (NHCs (**a-c**), Scheme 1) were easily reacted with the dinuclear palladium(II) acetate (**PdL$_1$** and **PdL$_2$**) complexes. The popular approach is to combine palladacycles as convenient Pd sources and special ligands in the catalytic system, e.g. NHC ligands, and to use a preformed 1:1 complex. These complexes are air-stable, and thus are more convenient in handling than toxic phosphines derivatives. The general route to the target palladacyclic complexes bearing NHC ligand is shown in Scheme 4 and the structures of the new catalysts are given in Scheme 5.

Mononuclear *N*-heterocyclic carbene-based imine palladacycles (**PdL$_{1a-c}$** and **PdL$_{2a-c}$**) were prepared from the imidazolium salts (**a-c**) by in situ deprotonation with palladium dimer [10]. Both the bridge-splitting reaction and replacement of acetato with bromide reaction occurred together to form new mononuclear NHC ligated *C,N*-palladacycle complexes (**PdL$_{1a-c}$** and **PdL$_{2a-c}$**). GC was used to evaluate the activity of the novel Pd(II) complexes in the Suzuki–Miyaura reaction for the coupling of phenylboronic acid with aryl bromides as seen in Table 3.

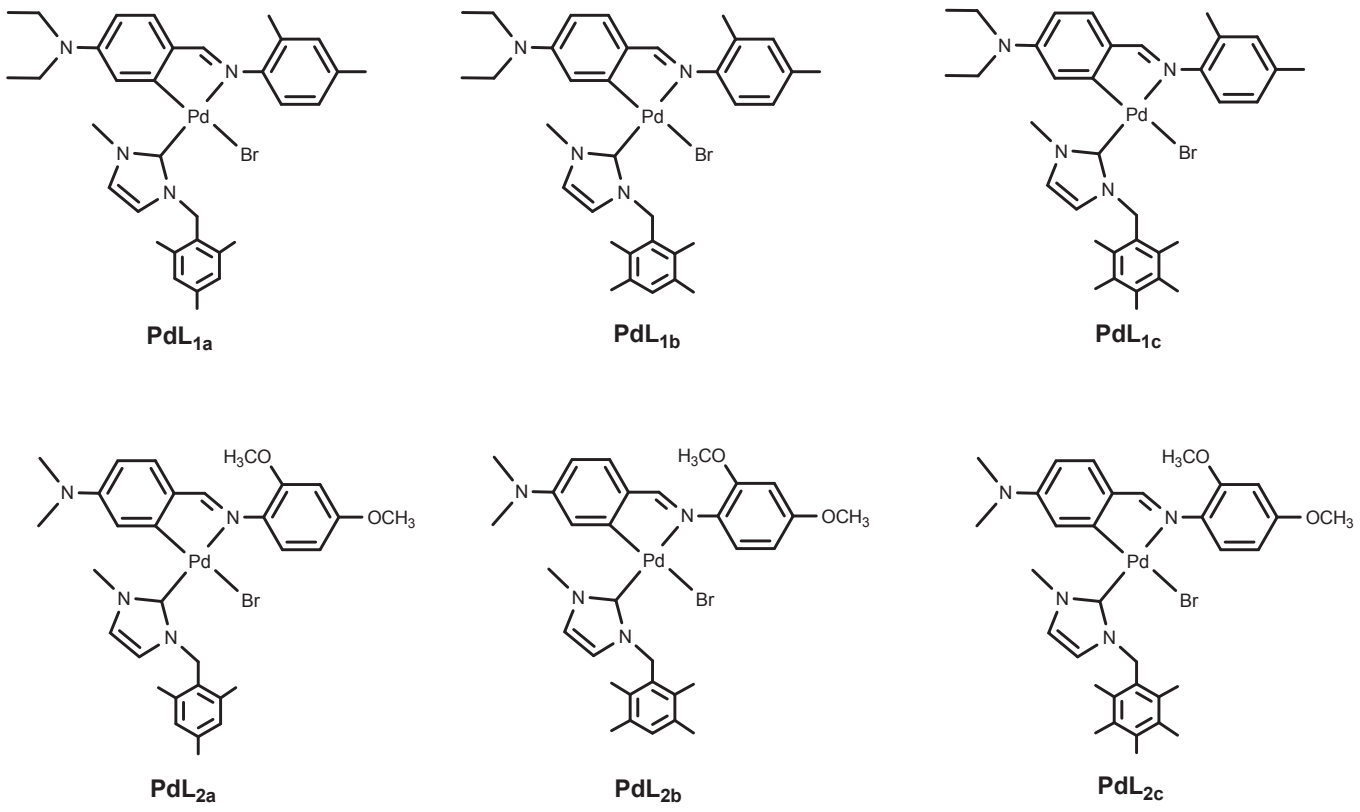
3.1. Preparation of the imidazolium salts (a-c)

The general pathway to the target NHC ligand precursors and palladacyclic complexes are shown in Scheme 1. Unsymmetrical imidazolium salts (**a–c**) were synthesized by the reaction of 1-methylimidazole with 2,4,6-trimethylbenzyl, 2,3,5,6-tetramethylbenzyl or 2,3,4,5,6-pentamethylbenzyl bromides, respectively (Scheme 1). The imidazolium protons display at 10.16, 10.02, and 9.94 ppm in the ^{1}H NMR spectra of (**a–c**), respectively. The ^{13}C NMR shift of the NCN sp^2 carbon atoms in (**a–c**) appears between 140.1 and 137.5 ppm, respectively. As expected, signals at 48.1–49.3 ppm correspond to the benzylic methylene carbon are observed for (**a–c**). The NMR spectroscopic data of (**a–c**) confirms the proposed structures and also the ^{1}H and ^{13}C NMR chemical shift data are consistent with those reported in the literature [28].

3.2. Synthesis of and characterization of PdL$_{1-2}$, PdL$_{1a-c}$ and PdL$_{2a-c}$

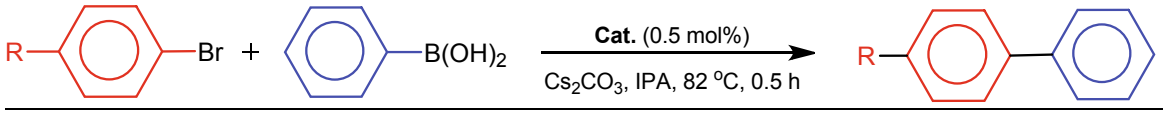
3.2.1. FT-IR spectra

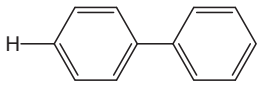
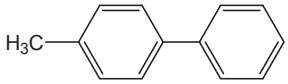
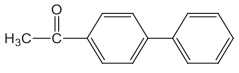
It is well known that the Schiff base based ligands and their metal complexes are seen that the coordination of the azomethine nitrogen to the palladium metal produces the shift of imine stretching frequencies to the lower value in the FT-IR spectra. On complexation, this band was shifted to lower frequency values in all the complexes [29]. Therefore, it was observed that the Schiff base ligand (**L$_{1-2}$**) showed $\nu_{(C=N)}$ azomethine band at 1618 cm^{-1} for **L$_1$** and 1606 cm^{-1} for **L$_2$** and, palladium metal complexes displayed $\nu_{(C=N)}$ azomethine bands at 1565 cm^{-1} for **PdL$_1$** and 1566 cm^{-1} for **PdL$_2$**. These results comply with the previous



Scheme 5. The structure of the new catalysts (**$PdL_{1a\text{-}c}$/$PdL_{2a\text{-}c}$**).

Table 3
Suzuki-Miyaura Cross-Coupling Reactions with Aryl Bromides[a]



Entry	Product	Cat.	GC Yield (%)[b,c]	TOF (h^{-1})
1		PdL_{1a}	90	180
2		PdL_{1b}	98	196
3		PdL_{1c}	98	196
4		PdL_{1}	98	196
5		PdL_{2a}	48	96
6		PdL_{2b}	73	146
7		PdL_{2c}	78	156
8		PdL_{2}	98	196
9		PdL_{1a}	42	84
10		PdL_{1b}	36	72
11		PdL_{1c}	16	33
12		PdL_{1}	45	90
13		PdL_{2a}	10	20
14		PdL_{2b}	21	42
15		PdL_{2c}	21	42
16		PdL_{2}	99	198
17		PdL_{1a}	40	80
18		PdL_{1b}	67	134
19		PdL_{1c}	71	142
20		PdL_{1}	75	150
21		PdL_{2a}	76	152
22		PdL_{2b}	80	160
23		PdL_{2c}	80	160
24		PdL_{2}	99	198

[a] *Reagents*: an aryl bromide (0.50 mmol), $PhB(OH)_2$ (0.75 mmol), Cs_2CO_3 (1.50 mmol), diethyleneglicol di-*n*-butyl ether (0.3 mmol, internal standard), catalyst (0.5 mol %), and IPA (3.0 mL).
[b] Yields based on the aryl halide and average of two runs.
[c] All reactions were followed by GC.

studies. In the previous studies, it has been displayed that the characteristic ν(C═N) band in the Pd complexes was shifted to a lower wave number, compared to that of the free ligand, due to π-back donation of electron density from metal ion to the π* orbital of imine group [29a-g]. The $\nu_{(C\overline{\ }C)}$ and $\nu_{(C-O)}$ vibrational frequencies could be seen in the range of 1515 and 1203 cm^{-1} for **PdL$_1$** and 1528 and 1202 cm^{-1} for **PdL$_2$**. The $\nu_{(C\overline{\ }C)}$ bands are exhibited in the range of 1521–1518 for **PdL$_{1a-c}$** and 1529–1528 for **PdL$_{2a-c}$**. It can be said that the absence of ν(COO) bands in the IR spectrum for **PdL$_1$** and **PdL$_2$** supported substitution of the expected acetate moiety, MeCO-O, by a bromide ligand and comply with the previous studies [11].

3.2.2. ^1H and ^{13}C NMR spectra

The ^{1}H and ^{13}C NMR data of the new complexes, **PdL$_{1-2}$**, **PdL$_{1a-c}$,** and **PdL$_{2a-c}$**, are given in the experimental section. The studies of the ^{1}H NMR data of **PdL$_1$** displayed that the methyl groups were existence in the form of a single peak at 1.77 ppm for ($C_6H_3(CH_3)_2$-*p*-CH_3), 2.21 ppm for ($C_6H_3(CH_3)_2$-*o*-CH_3) and a triplet peak at 1.17 ppm for ($CH_3CH_2)_2NC_6H_3$). While the methyl groups of **PdL$_2$** have been observed at 2.94 ppm for (($CH_3)_2NC_6H_3$-), the methoxy groups of **PdL$_2$** have been shown at 1.82 ppm for ($C_6H_3(OCH_3)_2$-*p*-OCH_3) and at 3.75 ppm for ($C_6H_3(OCH_3)_2$-*o*-OCH_3).

The chemical shifts for the methyl groups atom were observed at 1.06 ppm for ($C_6H_3(CH_3)_2$-*p*-CH_3), in the range 2.49–2.51 ppm for ($C_6H_3(CH_3)_2$-*o*-CH_3) and in the range 1.06–1.08 and 2.18–2.32 ppm as two different triplets for (($CH_3CH_2)_2NC_6H_3$) for **PdL$_{1a-c}$** and in the range of 2.27–2.36 ppm as singlets for (($CH_3)_2NC_6H_3$) for **PdL$_{2a-c}$**. The methoxy groups of **PdL$_{2a-c}$** displayed as singlets in the range of 2.18–2.43 ppm for ($C_6H_3(OCH_3)_2$-*p*-OCH_3) and 2.83–2.85 ppm for ($C_6H_3(OCH_3)_2$-*o*-OCH_3).

As it was expected that the aromatic hydrogen atoms could be seen in the range of 5.88–6.98 and 5.91–7.07 ppm and the imine hydrogen atoms (*H*C = N) were observed at 7.38 ppm and 7.48 ppm for **PdL$_1$** and **PdL$_2$**, respectively. The aromatic hydrogen atoms and the imine hydrogen atoms (*H*C = N) for their NHC imidazolium salts (**PdL$_{1a-c}$** and **PdL$_{2a-c}$**) exhibited similarly in the range of 5.44–7.02 ppm, 7.89–7.90 ppm for **PdL$_{1a-c}$**, 5.58–7.38 ppm, and 8.04–8.05 ppm for **PdL$_{2a-c}$** [30].

The chemical shifts for the carbene carbon atoms were exhibited in the range 186.5–186.1 ppm and 186.6–186.1 ppm for **PdL$_{1a-c}$** and **PdL$_{2a-c}$** and, azomethine carbons (C═N) 173.9–173.5 ppm for **PdL$_{1a-c}$** and 174.4–174.2 ppm for **PdL$_{2a-c}$**. It is also observed that the carbene C_2 resonance was shifted to the lower field, ca. 46 ppm when compared to the carbene resonance in unreacted imidazolium salts [31].

In studying in ^{1}H NMR, the proof that the C═N resonances of the metallated ring in of **PdL$_{1-2}$** were not affected by reaction with the imidazolium salts could be seen with the similarity of the peak which is attributed to C═N of **PdL$_{1a-c}$** and **PdL$_{2a-c}$**. Though C═N resonances of metallated ring usually shift to the higher field, as compared to the spectrum of the imidazolium salt, it does not display any difference as for the shift of the azomethine in **PdL$_1$** and **PdL$_2$** [32].

Absences of acetate bands in **PdL$_{1a-c}$** and **PdL$_{2a-c}$** complexes in IR, ^{1}H and ^{13}C NMR spectra displayed of replacing acetate moiety in **PdL$_{1-2}$** complexes with bromide. The substation reaction type of replacing acetate by bromide reaction in Pd(II) dimeric complexes is known to be labile and inclined to be replaced by bromide under mild conditions and short reaction times [31].

3.2.3. Description of the crystal structure

The molecular diagram of **PdL$_1$** with the adopted atom-labeling scheme is shown in Fig. 1, while important geometric parameters are listed in Table 2. The dinuclear complex **PdL$_1$** adopts a U-shaped or closed-book conformation where the two five-membered chelate rings of the Schiff base ligands stack on top of each other. The tilting of the complex along the bridging acetate groups is indicated by the interplanar angle of 35.6(3)° between the coordination planes of the two palladium ions. Each palladium atom is surrounded by one *ortho* carbon atom of the phenyl ring and one imine nitrogen atom of the Schiff base ligand and one oxygen atom from each of the two bridging acetate ligands and therefore has a slightly distorted square-planar geometry. The most noticeable deviation from the ideal square-planar arrangement is mainly observed in the C—Pd—N bite angles of 81.0(3)° and 80.7(3)°. The distance of the Pd atoms from the plane through the four coordinating atoms is small [0.0395(6) Å for Pd1 and 0.0638(6) Å for Pd2]. The four-coordinate geometry index for the complex, τ_4 [33], is 0.01 for atom Pd1 and 0.04 for atom Pd2 (where 0 would be perfectly square-planar, and 1 is perfectly tetrahedral). These values also indicate that the coordination polyhedron of the palladium atoms is a distorted square planar.

The Pd···Pd distance of 2.9970(10) Å is at the upper limit accepted for a palladium-palladium single bond length, which is between 2.5 and 3.0 Å [33b]. The sum of angles around the palladium atoms is approximately 360°. The Pd—C bond lengths vary from 1.956(7) to 1.977(7) Å, as both the Pd—N distances are equal to 2.027(6) Å. The Pd—O bond distances *trans* to the aryl carbon donor are slightly longer (*ca*. 0.09 Å) than those *trans* to the nitrogen donor due to the *trans* lengthening influence of carbon σ-donors [33c]. The bond lengths of C9—N1 and C30—N3 [1.288(9) Å] are characteristic for C═N double bonds. All bond lengths and angles are normal and in agreement with values previously reported for similar complexes [33d-h].

3.3. Catalytic studies of Pd complexes (PdL$_{1-2}$, PdL$_{1a-c}$ and PdL$_{2a-c}$)

Awareness of the coupling of organoboron reagents with organic halides in the Suzuki-Miyaura reaction has been growing since 1979. Pd-catalysts, the most powerful catalysts in these reactions, are used for the installation of biaryls compounds obtained by the formation of new C^{sp^2}-C^{sp^3} and C^{sp^2}-C^{sp^2} bonds [34].

The activities of Pd(II) complexes were investigated in the Suzuki-Miyaura cross-coupling reactions of various aryl bromides with phenylboronic acid yielding the corresponding biphenyl products. The results are summarized in Table 3. The Suzuki–Miyaura reaction was employed by using three different substrates to compare. For this purpose, 4-bromotoluene as an electron-rich substrate, 4-bromoacetophenone as an electron-poor substrate, and 4-bromobenzene as an electron-neutral substrate have been used. It is well known that the optimum temperature range is 80–100 °C with for aryl halide for the catalytic tests. Therefore, the catalytic activity reactions were carried out in IPA, Cs_2CO_3 as base and temperature at 82 °C following reaction optimization for the synthesized complexes (**PdL$_1$, PdL$_2$, PdL$_{1a-c}$**, and **PdL$_{2a-c}$**). The reaction was carried out with 0.5 mol% catalysts to achieve a high yield. Aryl bromides with different functional groups adequately reacted with phenylboronic acid using Cs_2CO_3 and IPA (3.0 mL) at 82 °C temperature in the presence of the palladium(II) complexes as a catalyst.

Interestingly, the most facile reaction is between 4-bromobenzene, which is electron-neutral, and phenylboronic acid with yields of 48–98% (Table 3, entries 1–8). As expected, the aryl bromide substituted by an electron-withdrawing group (MeCO-, entries 17–24) in the *para*-position was more reactive than those substituted by an electron-donating group (Me-, entries 9–15). The reaction between the electron-rich *p*-bromotoluene and phenylboronic acid proved to be more difficult and the formation of the coupling products in moderate yields (Table 3, entries 9–15).

When the catalytic activities of palladacyclic complexes were compared, the acetato-bridge palladium complexes (**PdL$_1$** and **PdL$_2$**) were found to be more than the active catalyst NHC-ligated Schiff base palladacycles (**PdL$_{1a-c}$** and **PdL$_{2a-c}$**) (Table 3, entries 4,8,12,16,20,24). Among them (**PdL$_1$** and **PdL$_2$**), it was concluded that **PdL$_2$** is the most active catalyst in Suzuki-Miyaura cross-coupling reactions (Table 3, entries 8,16,24).

There is a lot of data in the literature for Suzuki-coupling reactions catalyzed by palladacyclic complexes under a variety of different experimental conditions. With respect to the related Milstein,[22]

Bedford,[35] Yang,[7] Shaughnessy,[36] and Liu [37] in the Suzuki–Miyaura reaction,[22] our results show that Pd(II) complexes exhibit moderate to good catalytic activity.

The catalytic activities of the imine-palladacyclic complexes (**PdL$_{1\text{-}2}$**) are slightly higher than that of the NHC-bearing palladacyclic complexes (**PdL$_{1a\text{-}c}$**, **PdL$_{2a\text{-}c}$**). We know from the literature that the dimeric palladium complexes readily undergo bridge-cleavage reactions with a variety of compounds containing donor functionalities [38]. Also, during catalytic experiments, the dimeric palladium complex can easily break in the presence of Cs_2CO_3 as a base in the ^{i}PrOH. This is probably due to the fact that the palladacycles (**PdL$_{1\text{-}2}$**) bearing weakly coordinating acetato-groups give the coupled product biaryls in higher yields than those of Pd(II)–NHC complexes (**PdL$_{1a\text{-}c}$** and **PdL$_{2a\text{-}c}$**). On the other hand, from a steric and electronic perspective, it appears that the **PdL$_{1a\text{-}c}$** and **PdL$_{2a\text{-}c}$** catalysts are competitive, but the active species are not sufficiently electron-rich to facilitate the oxidative addition of aryl bromides [39]. It is possible that the carbene ligand is not actually present in the active species – these ligands have been shown to be reasonable labile on both Pd(0) and Pd(II) centers [40,41]. This would mean that the active catalyst would only contain imine ligands which tend to give poor performances.

4. Conclusion

In conclusion, we have synthesized and fully characterized novel air- and moisture-stable Schiff base- and NHC ligated *C,N*-palladacycle complexes. The structure of the dinuclear complex **PdL$_1$** was also determined by X-ray analysis. The coordination around the Pd^{II} ion is distorted square-planar, and the Pd^{II} ion is coordinated by one amine N atom and one aryl C atom from the bidentate ligand, one carbenic C atom from the monodentate ligand, and one Br atom. Also, the activities of all Pd(II) complexes were evaluated in the Suzuki-Miyaura cross-coupling for the coupling of phenylboronic acid with aryl bromides. We have developed two novel imine-palladacyclic dimer complexes **(PdL$_{1\text{-}2}$)** and six novel imine-Pd-NHC complexes **(PdL$_{1a\text{-}c}$** and **PdL$_{2a\text{-}c}$)** which showed moderate to high activity in the coupling of aryl bromides and phenylboronic acid. The use of ^{i}PrOH as the solvent and Cs_2CO_3 as the base at 82 °C proved to be an efficient and mild condition for the synthesis of biphenyls in good yields with 0.5 mol% catalysts loadings. As a result of the catalytic tests, it can be said that **PdL$_2$** which is an imine-palladacycle was found to be the most active catalyst when compared to the novel imine-Pd-NHC complexes **(PdL$_{1a\text{-}c}$** and **PdL$_{2a\text{-}c}$)** in this study. Palladacyclic dimer complexes (**PdL$_{1\text{-}2}$**) bearing weakly coordinating acetato-groups are quite effective catalysts in this reaction to give the corresponding coupled products in high yields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Funding of our research from the TUBITAK (Project No: 104T203) and Ondokuz Mayıs University (Project No: PYO.FEN.1906.19.001) are gratefully acknowledged.

Appendix A. Supplementary data

CCDC 1,947,705 contains the supplementary crystallographic data for the compound reported in this article. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/].

References

[1] (a) Á. Molnár, Palladium-Catalyzed Coupling Reactions: Pratical Aspects and Future Developments, ed., Wiley-VCH, Weinheim, 2013; (b) A. Kapdi, D. Maiti, Palladacycles: Catalysis and Beyond, ed., Elseiver, Amsterdam, 2019; (c) E.I. Negishi, Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley, New York, 2002; (d) J.J. Li, G.W. Gribble, Palladium in Heterocyclic Chemistry: A Guide for the Synthetic Chemist, Pergamon, New York, 2000.
[2] a) I.D. Kostas, Suzuki–Miyaura Cross-Coupling Reaction and Potential Applications, ed., MPDI, 2017; b) T. Colacot, New Trends in Cross-Coupling: Theory and Applications, ed., RSC, 2014.
[3] J. Dupont, M. Pfeffer, Palladacycles: Synthesis, Characterization and Applications, ed, Wiley-VCH, Weinheim, 2008.
[4] a) W.A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1844–1848; b) M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Brossmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1848–1849.
[5] M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750–3781.
[6] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527–2572.
[7] H. Wang, J. Yang, Appl. Organometal. Chem. 30 (2016) 262–267.
[8] J.L. Serrano, L. Garcia, J. Perez, E. Perez, J. Garcia, G. Sanchez, P. Sehnal, S. De Ornellas, T.J. Williams, I.S. Fairlamb, Organometallics 30 (2011) 5095–5109.
[9] E.A.B. Kantchev, J.Y. Ying, Organometallics 28 (2009) 289–299.
[10] a) M.E. Günay, R. Gümüşada, N. Özdemir, M. Dinçer, B. Çetinkaya, J. Organomet. Chem. 694 (2009) 2343–2349; b) R. Gümüşada, N. Özdemir, M.E. Günay, M. Dinçer, M.S. Soylu, B. Çetinkaya, Appl. Organometal. Chem. 28 (2014) 324–331; c) M.E. Günay, G.G. Çoğaşlıoğlu, R. Fırıncı, Turk. J. Chem. 39 (2015) 1310–1316; d) R. Kılınçarslan, M.E. Günay, R. Fırıncı, S. Denizaltı, B. Çetinkaya, Appl. Organometal. Chem. 30 (2016) 268–272.
[11] L. Naya, D. Vazquez-Garcia, A. Fernandez, M. Lopez-Torres, I. Marcos, O.A. Lenis, M.T. Pereira, J.M. Vila, J. Organomet. Chem. 772–773 (2014) 192–201.
[12] a) P. Das, W. Linert, Coord. Chem. Rev. 311 (2016) 1–23; b) O. Navarro, R.A. Kelly, S.P. Nolan, J. Am. Chem. Soc. 125 (2003) 16194–16195; c) R. Singh, M.S. Viciu, N. Kramareva, O. Navarro, S.P. Nolan, Org. Lett. 7 (2005) 1829–1832; d) N. Marion, O. Navarro, J. Mei, E.D. Stevens, N.M. Scott, S.P. Nolan, J. Am. Chem. Soc. 128 (2006) 4101–4111; e) B. Tao, D.W. Boykin, Tetrahedron Lett. 44 (2003) 7993–7996; f) P. Das, C. Sarmah, A. Tairai, U. Bora, Appl. Organomet. Chem. 25 (2011) 283–288; g) A. Tairai, C. Sarmah, P. Das, Ind. J. Chem. 51B (2012) 843–848; h) L. Botella, C. Najera, Angew. Chem. Int. Ed. 41 (2002) 179–181; i) G.K. Rao, A. Kumar, J. Ahmed, A.K. Singh, Chem. Commun. 46 (2010) 5954–5956; j) J.-Y. Li, A.-J. Yu, Y.-J. Wu, Y. Zhu, C.-X. Du, H.-W. Yang, Polyhedron 26 (2007) 2629–2637; k) G.-R. Peh, E.A.B. Kantchev, J.-C. Er, J.Y. Ying, Chem. Eur. J. 16 (2010) 4010–4017.
[13] W. Wang, T. Zhang, F. Wang, M. Shi, Tetrahedron 67 (2011) 1523–1529.
[14] O. Navarro, N. Marion, Y. Oonishi, R.A. Kelly III, S.P. Nolan, J. Org. Chem. 71 (2006) 685–692.
[15] G.D. Frey, J. Schütz, E. Herdtweck, W.A. Herrmann, Organometallics 24 (2005) 4416–4426.
[16] J. Li, M. Cui, A. Yu, Y. Wu, J. Organomet. Chem. 692 (2007) 3732–3742.
[17] a) G.K. Rao, A. Kumar, B. Kumar, D. Kumar, A.K. Singh, Dalton Trans. 41 (2012) 1931-1937; b) T. Kylmälä, N. Kuuloja, Y. Xu, K. Rissanen, R. Franzén, Eur. J. Org. Chem. (2008) 4019-4024; c) E. Tas, A. Kilic, M. Durgun, I. Yilmaz, I. Ozdemir, N. Gurbuz, J. Organomet. Chem. 694 (2009) 446-454; d) D. Srimani, A. Sarkar, Tetrahedron Lett. 49 (2008) 6304-6307; (e) J. Cui, M. Zhang, Y. Zhang, Inorg. Chem. Commun. 13 (2010) 81-85; f) Y.-C. Lai, H.-Y. Chen, W.-C. Hung, C.- C. Lin, F.-E. Hong, Tetrahedron 61 (2005) 9484-9489; g) E.G. Bowes, G.M. Lee, C.M. Vogels, A. Decken, S.A. Westcott, Inorg. Chim. Acta 377 (2011) 84-90.
[18] M.N. Sedighipoor, A.H. Kianfar, G. Mohammanezhad, H. Görls, W. Plass, Inorg. Chim. Acta 476 (2018) 20–26.
[19] N. Shahnaz, B. Banik, P. Das, Tetrahedron Lett. 54 (2013) 2886–2889.
[20] M. Wang, H. Zhu, K. Jin, D. Dai, L. Sun, J. Catal. 220 (2003) 392–398.
[21] F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, D. Leonesiand, A. Lorenzotti, Polyhedron 18 (1999) 3041–3050.
[22] H. Weissman, D. Milstein, Chem. Commun. (1999) 1901–1902.
[23] a) R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, P.N. Horton, M. B. Hursthouse, M.E. Light, Organometallics 22 (2003) 987–999; b) R.B. Bedford, M.E. Blake, C.P. Butts, D. Holder, Chem. Commun. (2003) 466–467; c) R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, M.B. Hursthouse, V.J. M. Scordia, Dalton Trans. (2003) 3350–3356.
[24] A. Kumbhar, J. Organomet. Chem. 881 (2019) 79–129.
[25] A.W. van der Made, R.H. van der Made, J. Org. Chem. 58 (1993) 1262–1263.
[26] a) M.E. Belowicha, J.F. Stoddart, Chem. Soc. Rev. 41 (2012) 2003-2024; b) J.N. Asegbeloyin, E.C. Okafor, N.N. Ukwueze, I. Babahan, I.C. Agbo, Asian J. Chem. 26 (9) (2014) 2753-2758; c) I. Babahan, E. Coban, A. Ozmen, H.H. Bıyık, B. Isman, African J. Microbiog. Res. 5(3) (2011) 271-283.

[27] a) Stoe & Cie, X-AREA Version 1.18 and X-RED32 Version 1.04, Stoe & Cie, Darmstadt, Germany, 2002. b) M.C. Burla, R. Caliandro, B. Carrozzini, G.L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, J. Appl. Crystallogr. 48 (2015) 306-309; c) G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3-8; d) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339-341.

[28] M. Niehues, G. Kehr, G. Erker, B. Wibbeling, R. Fröhlich, O. Blacque, H. Berke, J. Organomet. Chem. 663 (2002) 192-203; b) L. Canovese, F. Visentin, C. Levi, C. Santo, V. Bertolasi, J. Organomet. Chem. 732 (2013) 27-39.

[29] a) M. Sedighipoor, A.H. Kianfar, G. Mohammadnezhad, H. Gorls, W. Plass, Inorg. Chim. Acta 20 (2018) 476; b) Y. Kim, J. Lee, Y-H. Son, S-U. Choi, M. Alam, S. Park, J. Inorg. Biochem. 205 (2020) 111015; c) E.T.G. Cavalheiro, F.C.D. Lemos, J.Z. Schpector, E.R. Dockal, Thermochim. Acta 370 (2001) 129-133; d) A.A. Soliman, W. Linert, Thermochim. Acta 338 (1999) 67-75; e) E.C. Okafor, J.N. Asegbeloyin, I. C. Agbo, P.O. Ukoha, I. Babahan, Asian J. Chem., 26 (23), (2014) 8127-8133; f) J. N. Asegbelogin, O.T. Ujam, E.C. Okafor, I. Babahan, E. Poyrazoglu, A. Ozmen, H.H. Biyik, Bioinorg. Chem. Appl. (2014) ID:718175; g) R. Fırıncı, M.E. Günay, N. Ozdemir, M. Dincer, J. Mol. Struct., 1146 (2017) 267-272.

[30] a) L. Naya, D. Vazquez-García, M. Lopez-Torres, A. Fernandez, J.M. Vila, N. Gomez-Blanco, J.J. Fernandez, J. Organomet. Chem. 693 (2008) 685–700;
b) D. Vazquez-García, A. Fernandez, M. Lopez-Torres, A. Rodríguez, A. Varela, M. T. Pereira, J.M. Vila, J.J. Fernandez, Organometallics 30 (2011) 396–404;
d) I. Babahan, A. Ozmen, N. Orhan, D. Kazar, E.H. Degirmenci, Bioorganic Chemistry 53 (2014) 92–98;
e) R. Fırıncı, E. Fırıncı, G. Başbülbül, M.B. Dabanca, D.B. Celepci, M.E. Günay, Transit. Metal. Chem. 44 (2019) 391–397;
f) I. Babahan, A. Ozmen, K. Aslan, Appl. Organometal. Chem. 31 (2017), e3752.

[31] a) R. Fırıncı, M.E. Günay, A.G. Gökçe, Appl. Organometal. Chem. 32 (2018), e4109;
b) J. Granell, D. Sainz, J. Sales, X. Solans, M. Font-Altaba, J. Chem. Soc., Dalton Trans. (1986) 1785–1790.

[32] a) J.J. Fernandez, A. Fernandez, D. Vazquez-García, M. Lopez-Torres, A. Suarez, N. Gomez-Blanco, J.M. Vila, Eur. J. Inorg. Chem. (2007) 5408–5418;
b) J.M. Vila, M. Gayoso, M.T. Pereira, M. Lopez-Torres, J.J. Fernandez, A. Fernandez, J.M. Ortigueira, J. Organomet. Chem. 532 (1997) 171–180.

[33] a) L. Yang, D.R. Powell, R.P. Houser, Dalton Trans. (2007) 955–964;
b) T. Murahashi, H. Kurosawa, Coord. Chem. Rev. 231 (2002) 207–228;
c) F.S. Mancilha, L. Barloy, F.S. Rodembusch, J. Dupont, M. Pfeffer, Dalton Trans. 40 (2011) 10535–10544;
d) J. Albert, R. Bosque, L. D'Andrea, J. Granell, M. Font-Bardia, T. Calvet, Eur. J. Inorg. Chem. 24 (2011) 3617–3631;
e) J.M. Chitanda, S.-C. Wu, J.W. Quail, S.R. Foley, Inorg. Chim. Acta 379 (2011) 122–129;
f) K. Gopi, P. Saxena, M. Nethaji, N. Thirupathi, Polyhedron 52 (2013) 1041–1052;
g) D. Ning, Y. Cao, Y. Zhang, L. Xia, G. Zhao, Inorg. Chem. Commun. 58 (2015) 57–59;
h) P. Agarwal, N. Thirupathi, M. Nethaji, Organometallics 35 (2016) 3112–3123.

[34] a) M.S. Viciu, R.A. Kelly III, E.D. Stevens, F. Naud, M. Studer, S.P. Nolan, Org. Lett. 5(9) (2003) 1479-1482; b) N. Miyaura, K. Yamada, A. Suzuki, Tetrahedron Lett. 36 (1979) 3437-3440; c) A. Suzuki, J. Organomet. Chem. 576 (1999) 147-168; (b) N. Miyaura, Top. Curr. Chem. 219 (2002) 11-59; d) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633-9695; e) A. Suzuki, J. Organomet. Chem. 653 (2002) 83-90.

[35] R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, M.B. Hursthouse, V.J.M. Scordia, Dalton Trans. (2003) 3350–3356.

[36] R. Huang, K.H. Shaughneesy, Organometallics 25 (2006) 4105–4112.

[37] C.-L. Chen, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Organometallics 24 (2005) 1075–1081.

[38] F. Fuge, C.W. Lehman, J. Rust, F. Mohr, J. Organomet. Chem. 694 (2009) 2395–2401.

[39] R.B. Bedford, M. Betham, M.E. Blake, R.M. Frost, P.N. Horton, M.B. Hursthouse, R.-M. Lopez-Nicolas, Dalton Trans. (2005) 2774–2779.

[40] L.R. Titcomb, S. Caddick, F.G.N. Cloke, D.J. Wilson, D. McKerrecher, Chem. Commun. (2001) 1388–1389.

[41] A.K. de K. Lewis, S. Caddick, F.G.N. Cloke, N.C. Billingham, P.B. Hitchcock, J. Leonard, J. Am. Chem. Soc. 125 (2003) 10066-10073.