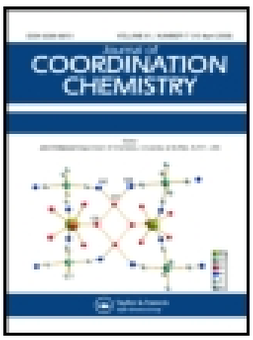

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Mono- and dinuclear N-heterocyclic carbene palladium complexes with diazine ligands and their catalytic activities toward the Mizoroki–Heck reaction

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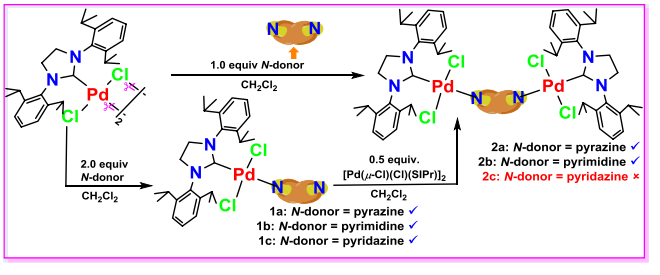
ABSTRACT

Mono- and dinuclear N-heterocyclic carbene palladium complexes with diazine ligands were synthesized and characterized through adjusting the stoichiometric ratio of the reactants. The catalytic properties of all complexes were further studied in the Mizoroki–Heck reaction. The results indicated that the dinuclear complexes induced some benefits in catalytic behavior.



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N-Heterocyclic carbene; palladium complexes; diazine ligands; Mizoroki–Heck reaction

1. Introduction

Since the discovery of N-heterocyclic carbenes (NHCs) [1], NHCs have emerged as efficient ligands and their transition metal complexes have been widely applied in organometallic catalysts [2–8]. In particular, NHC–Pd complexes have been extensively utilized in coupling reactions [2–4]. In many cases, NHC–Pd complexes are formed *in situ*, which sometimes gave different results compared to preformed compounds [9–12]. As a result, a series of well-defined NHC–Pd complexes were developed and their catalytic activities were fully evaluated in organic transformation [13–18]. A family of well-defined NHC–Pd complexes (NHC)$PdCl_2$(3-chloropyridine) was reported by Organ. In this system, 3-chloropyridine stabilizes the Pd center, while in the catalytic process the Pd center can lose the pyridine ligand, opening up a coordination site for substrate [19]. The coordination and dissociation of ancillary ligands considerably affect the catalytic activity of the complexes.

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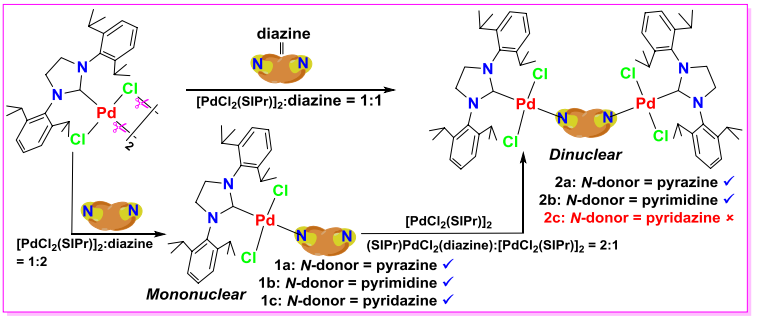


Scheme 1. Synthetic route of the mono- and dinuclear NHC–Pd complexes.

Despite excellent progress in mononuclear complexes, the properties of dinuclear NHC-Pd complexes are less studied. Suitable ligands join two or more NHC–Pd units to form multinuclear complexes and provide models to test catalytic activities of the multi-metallic catalysts [20–28]. Hor and Peris have reported that the catalytic performance of dinuclear NHC-Pd complexes could be improved by cooperative effect of two metals [21, 24]. This prompted our study of new dinuclear NHC–Pd complexes with bridging heterocycle linkers. Pyrazine-bridged dinuclear NHC–Pd complexes based on unsaturated imidazol-2-ylidenes have been employed as precatalysts for the Hiyama reaction [23]. However, its saturated analogs have not been described. Saturated imidazolidin-2-ylidenes were superior to their unsaturated analogs in some catalytic reactions [29–31]. To compare catalytic properties of the NHC–Pd complexes, herein the synthesis of mono- and dinuclear NHC–Pd complexes based on saturated imidazolidin-2-ylidene and diazines (pyrazine, pyrimidine, and pyridazine) was attempted and their catalytic potential toward the Mizoroki–Heck reaction was explored (Scheme 1).

2. Experimental

2.1. General considerations

All reactions were carried out under air. The chemicals were purchased from commercial suppliers and used without purification. [Pd(μ-Cl)(Cl)(SIPr)]$_2$ was prepared according to the literature method [32].

2.2. Preparation of the mononuclear NHC–Pd complexes (1a–1c)

A mixture of [Pd(μ-Cl)(Cl)(SIPr)]$_2$ (0.10 mmol, 113.6 mg) and diazine (0.20 mmol, 16.0 mg) was stirred in CH_2Cl_2 (5.0 mL) at ambient temperature for 6 h to give a yellow solution. The solvent was reduced and the resulting residue was washed with diethyl ether to give mononuclear NHC–Pd complexes.

2.2.1. [(SIPr)PdCl$_2$(pyrazine)] (1a)

The procedure yielded 110 mg (85%) of **1a**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.61 (br, 2H, pyrazine-*H*), 8.42 (br, 2H, pyrazine-*H*), 7.42–7.41 (m, 2H, Ar–*H*), 7.31–7.30 (m, 4H, Ar–*H*), 4.09 (s, 4H, NCH_2CH_2 N), 3.57 (br, 4H, C*H*(CH_3)$_2$), 1.59 (br, 12H, CH(CH_3)$_2$), 1.10 (br 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 184.2 ($C_{carbene}$), 147.4, 145.6, 145.2, 135.0, 129.5, 124.4,

53.8 (NCH_2CH_2 N), 28.7 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). HR-MS (ESI): calcd for $C_{31}H_{42}ClN_4Pd$ $[M - Cl^-]^+$ 611.2133; found 611.2141. IR (KBr, cm^{-1}): 3180, 2951, 2916, 1604, 1480, 1419, 1408, 1378, 1326, 1279, 1228, 1134, 1062, 928, 860, 740. Anal. Calcd for [(SIPr)$PdCl_2$(pyrazine)] ($C_{31}H_{42}Cl_2N_4Pd$): C, 57.46; H, 6.53; N, 8.65%. Found: C, 57.72; H, 6.75; N, 8.38%.

2.2.2. *[(SIPr)$PdCl_2$(pyrimidine)]* (1b)

The procedure yielded 115 mg (89%) of **1b**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 9.24 (s, 1H, pyrimidine-*H*), 8.76 (d, 1H, J = 4.0 Hz, pyrimidine-*H*), 8.54 (d, 1H, J = 2.4 Hz, pyrimidine-*H*), 7.44–7.40 (m, 2H, Ar–*H*), 7.32–7.26 (m, 4H, Ar–*H*), 7.13–7.10 (m, 1H, pyrimidine-*H*), 4.09 (s, 4H, NCH_2CH_2 N), 3.58 (sept, J = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.56 (d, J = 6.4 Hz, 12H, $CH(CH_3)2$), 1.28 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 184.6 ($C_{carbene}$), 159.9, 157.8, 157.6, 147.5, 135.1, 129.5, 124.4, 120.8, 53.8 (NCH_2CH_2 N), 28.7 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). HR-MS (ESI): calcd for $C_{31}H_{42}ClN_4Pd$ $[M - Cl^-]^+$ 611.2133; found 611.2144. IR (KBr, cm^{-1}): 3133, 2966, 2866, 1604, 1462, 1418, 1380, 1350, 1288, 1210, 1162, 1128, 1070, 946, 802, 763, 757. Anal. Calcd for [(SIPr)$PdCl_2$(pyrimidine)] ($C_{31}H_{42}Cl_2N_4Pd$): C, 57.46; H, 6.53; N, 8.65%. Found: C, 57.68; H, 6.80; N, 8.36%.

2.2.3. *[(SIPr)$PdCl_2$(pyridazine)]* (1c)

The procedure yielded 102 mg (79%) of **1c**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.87 (d, J = 5.2 Hz, 1H, pyridazine-*H*), 8.77 (d, J = 4.0 Hz, 1H, pyridazine-*H*), 7.42–7.38 (m, 2H, Ar–*H*), 7.32–7.30 (m, 4H, Ar–*H*), 7.24–7.21 (m, 1H, pyridazine-*H*), 7.19–7.16 (m, 1H, pyridazine-*H*), 4.06 (s, 4H, NCH_2CH_2 N), 3.58 (sept, J = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.58 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.27 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 185.9 ($C_{carbene}$), 153.9, 151.5, 147.5, 135.3, 129.3, 128.6, 127.7, 124.3, 53.8 (NCH_2CH_2 N), 28.7 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). HR-MS (ESI): calcd for $C_{31}H_{42}ClN_4Pd$ $[M - Cl^-]^+$ 611.2133; found 611.2132. IR (KBr, cm^{-1}): 3145, 3106, 3090, 2960, 1606, 1482, 1470, 1380, 1330, 1230, 1188, 1054, 849, 740. Anal. Calcd for [(SIPr)$PdCl_2$(pyridazine)] ($C_{31}H_{42}Cl_2N_4Pd$): C, 57.46; H, 6.53; N, 8.65%. Found: C, 57.28; H, 6.35; N, 8.83%.

2.3. *Preparation of dinuclear NHC–Pd compounds* (2a *and* 2b)

Procedure 1: [Pd(μ-Cl)(Cl)(SIPr)]$_2$ (0.10 mmol, 113.6 mg) and diazine (0.10 mmol, 8.0 mg) were stirred in CH_2Cl_2 (5.0 mL) at ambient temperature for 6 h to give a yellow solution. The solvent was reduced and the resulting residue was washed with diethyl ether to give the dinuclear NHC-Pd complexes.

Procedure 2: A mixture of **1a** or **1b** (0.10 mmol, 64.8 mg) and [Pd(μ-Cl)(Cl)(SIPr)]$_2$ (0.05 mmol, 56.8 mg) was stirred in CH_2Cl_2 (5.0 mL) at ambient temperature for 3 h. The solvent was reduced and the resulting residue was washed with ether to give dinuclear NHC–Pd complexes **2a** and **2b**.

2.3.1. *[(SIPr)$PdCl_2$]$_2$(μ-pyrazine)* (2a)

The procedure yielded 98 mg (81%) of **2a**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.52 (br, 4H, pyrazine-*H*), 7.29 (br, 4H, Ar–*H*), 7.27 (br, 8H, Ar–*H*), 4.07 (s, 8H, NCH_2CH_2 N), 3.50 (sept, J = 6.8 Hz, 8H, $CH(CH_3)_2$), 1.48 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.25 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 183.9 ($C_{carbene}$), 147.4, 145.9, 134.9, 129.5, 124.3, 53.8 (NCH_2CH_2 N), 28.6 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). HR-MS (ESI): calcd for

$C_{58}H_{81}Cl_4N_6Pd_2$ $[M + H^+]^+$ 1217.3321; found 1217.3324. IR (KBr, cm^{-1}): 3128, 3070, 2970, 1616, 1590, 1466, 1445, 1380, 1366, 1348, 1269, 1214, 1126, 1070, 1060, 946, 801, 757, 746. Anal. Calcd for $[(SIPr)PdCl_2]_2$(μ-pyrazine) ($C_{58}H_{80}Cl_4N_6Pd_2$): C, 57.29; H, 6.63; N, 6.91%. Found: C, 57.44; H, 6.87; N, 6.70%.

2.3.2. *[(SIPr)PdCl$_2$]$_2$(μ-pyrimidine)* (2b)

The procedure yielded 102 mg (84%) of **2b**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 9.20 (s, 1H, pyrimidine-*H*), 8.72 (d, 2H, *J* = 5.6 Hz, pyrimidine-*H*), 7.41–7.37 (m, 4H, Ar–*H*), 7.28–7.26 (m, 8H, Ar–*H*), 6.90 (t, *J* = 5.6 Hz, 1H, pyrimidine-*H*), 4.06 (s, 8H, NCH_2CH_2 N), 3.53 (sept, *J* = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.51 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 184.6 ($C_{carbene}$), 159.9, 157.8, 157.6, 147.5, 135.1, 129.5, 124.4, 120.8, 53.8 (NCH_2CH_2 N), 28.7 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). HR-MS (ESI): calcd for $C_{58}H_{81}Cl_4N_6Pd_2$ $[M + H^+]^+$ 1217.3321; found 1217.3341. IR (KBr, cm^{-1}): 3130, 3089, 2969, 1608, 1600, 1580, 1460, 1440, 1378, 1365, 1344, 1280, 1210, 1136, 1080, 1059, 940, 810, 740. Anal. Calcd for $[(SIPr)PdCl_2]_2$(μ-pyrimidine) ($C_{58}H_{80}Cl_4N_6Pd_2$): C, 57.29; H, 6.63; N, 6.91%. Found: C, 57.11; H, 6.41; N, 6.69%.

2.4. General procedure for the Mizoroki–Heck reaction

In a reaction vessel, aryl bromide (0.50 mmol), styrene (0.60 mmol, 62.4 mg), Cs_2CO_3 (0.75 mmol, 245 mg), and NHC–Pd complex (0.25 or 0.5 mol%, about 3.0 mg) were mixed in DMF (2.0 mL). The mixture was stirred at 140 °C for 3 h. After cooling to room temperature, the filtrate was concentrated and the residue was subjected to purification via flash column chromatography to give the pure product.

2.5. Crystallography

Data collection was performed on a Bruker-AXS SMART CMOS area detector diffractometer at 296 K using ω rotation scans with a scan width of 0.5° and Mo-Kα radiation (λ = 0.71073 Å). Multi-scan corrections were applied using SADABS [33]. Structure solutions and refinements were performed with the SHELX-97 package [34]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. Hydrogens on carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of carbon.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

To assess the coordination of diazines (pyrazine, pyrimidine, and pyridazine) toward NHC–Pd complexes, reactions of $[Pd(\mu\text{-}Cl)(Cl)(SIPr)]_2$ with diazines in various stoichiometric ratios were done. When $[Pd(\mu\text{-}Cl)(Cl)(SIPr)]_2$ reacted with diazines (pyrazine, pyrimidine, and pyridazine) in the stoichiometric ratio of 1:2, mononuclear complexes **1a**–**1c** were achieved, while reactions of $[Pd(\mu\text{-}Cl)(Cl)(SIPr)]_2$ with diazines (pyrazine and pyrimidine) in the stoichiometric ratio of 1:1 afforded dinuclear complexes **2a** and **2b**. The dinuclear complexes **2a** and **2b** could be also obtained through reaction of **1a** and **1b** with $[Pd(\mu\text{-}Cl)(Cl)(SIPr)]_2$. The only exception is the dinuclear complexes with pyridazine. Due to the steric congestion, the bidentate pyridazine could not bridge two SIPr–Pd units to form the dinuclear compound.

The formation of the mono- and dinuclear complexes is evident from the distinctive stoichiometric proton signal resonances of SIPr with diazines in ^{1}H NMR spectra. The single resonances at 4.06–4.09 ppm for methylene protons of NCH_2CH_2N are in agreement with the related SIPr-Pd complexes. The number of signals observed in ^{13}C NMR spectra of the complexes was as expected and the carbene carbons were observed at 183.9–185.9 ppm, similar with SIPr-Pd complexes. FT-IR spectra of the NHC-Pd complexes were in agreement with the results of the ^{1}H NMR analysis. IR spectra of the free diazine ligands show medium absorptions for C=N stretches at 1618–1605 cm^{-1}, while the complexes show strong C=N stretches at 1580 and 1598 cm^{-1}. The red shift and reduced intensity indicate that the diazine ligands are coordinated to Pd(II) in the latter cases [35–38]. Formation is confirmed by their $[M - Cl^-]^+$ or $[M + H]^+$ fragments observed in high-resolution mass spectra.

3.2. Structural analyses

In agreement with the spectral data, the crystal structures of **1a**–**1c** show mononuclear complexes with each palladium coordinated by a SIPr, a nitrogen donor from diazines and two chlorides in an essentially square planar geometry (Figure 1). As expected, the SIPr and the

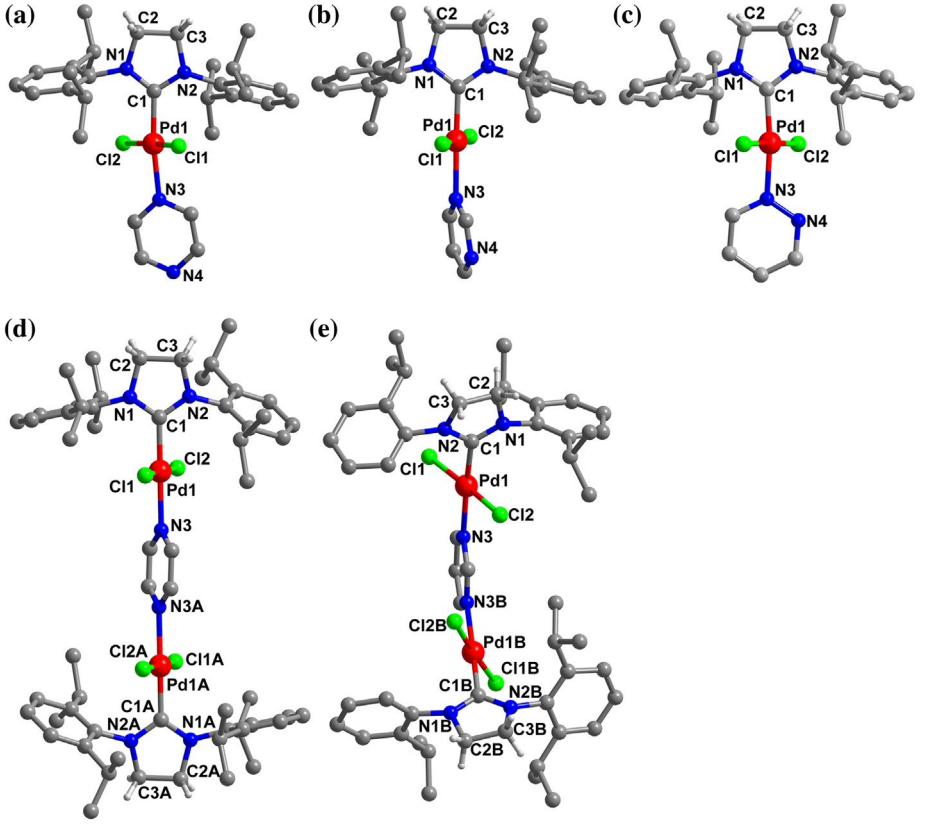


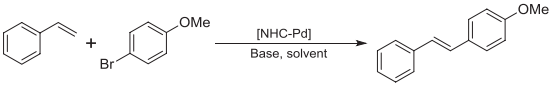
Figure 1. Molecular structures of **1a–1c** and **2a–2b**. Some hydrogens and solvent molecules (CH_2Cl_2 and n-C_6H_{14}) have been omitted for clarity.
Notes: Symmetry codes: ^{A}–x, 2 – y, –z; ^{B}1 – x, –y, z.

diazines are *trans* to each other. The dihedral angles between the carbene ring planes and the $PdCNCl_2$ planes are 60.91 to 74.71°, which are typical for complexes to reduce steric congestion. Although **1a**, **1b,** and **1c** are isostructural, there are some differences. For example, the dihedral angles between the $PdCNCl_2$ planes and the diazines in **1a** and **1b** (13.06–45.90°) are shorter than that found in **1c** (62.72°); the diazines which are tilted by 16.54–88.30° relative to the carbene ring planes in **1a** and **1b** are larger than that in **1c** (6.08°). The Pd–C bonds in **1a**–**1c** from 1.956(3) to 1.978(3) Å are somewhat shorter than that found in (SIPr)$PdCl_2$(3-chloropyridine) [1.990(3) Å]. The Pd–N bonds in **1a** and **1b** [2.103(3)–2.152(3) Å] are comparable to (SIPr)$PdCl_2$(3-chloropyridine) [2.108(3) Å], but are slightly longer than that found in **1c** [2.043(3) Å]. For **2a** and **2b**, the diazines link two SIPr–Pd units to form dinuclear frameworks with Pd···Pd separations from 6.70 to 11.13 Å. The Pd–C [1.964(3) and 1.969(4) Å] and Pd–N bond distances [2.127(2) and 2.159(3) Å] are slightly longer than their unsaturated analog, $[(IPr)PdCl_2]_2$(μ-pyrazine) [23]. The carbene ring planes are twisted out of the $PdCNCl_2$ planes with dihedral angles of 72.61 to 74.63° in order to avoid intra-ligand repulsion. The diazines are tilted by 25.07–35.25° relative to the $PdCNCl_2$ planes, while carbene ring planes are approximately perpendicular to the diazines with dihedral angles of 73.97 and 81.39°.

3.3. Catalytic reactions

The palladium-catalyzed Mizoroki–Heck reaction is a powerful method for preparation of biaryl derivatives [39]. Much effort has been done to develop efficient NHC–Pd systems for the reaction [40–44]. With the synthesis of this series of mono- and dinuclear NHC–Pd complexes, we were able to test and compare their catalytic activities. Since the bases and solvents as well as Pd-precatalysts have been employed, herein, the model reaction between 4-bromoanisole and styrene was directly performed in common polar solvents (Table 1).

Table 1. Optimization of the reaction conditions for the Mizoroki–Heck reaction[a].



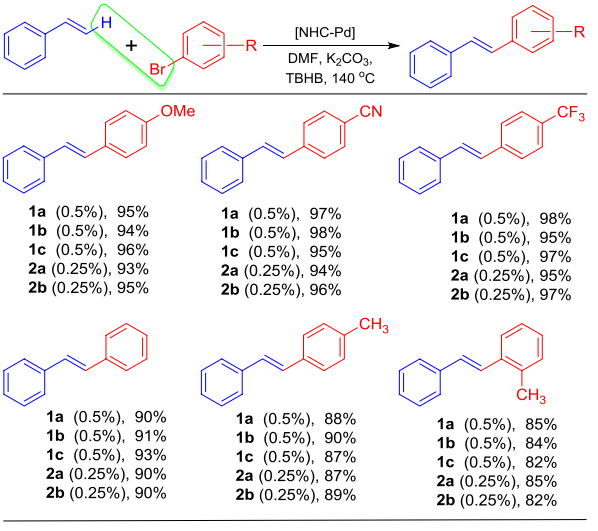
Entry	[Pd]	Solvent	Base	Yield (%)[b]
1	**1a** (1%)	DMF	K_2CO_3	93
2	**1a** (1%)	DMA	K_2CO_3	92
3	**1a** (1%)	DMSO	K_2CO_3	80
4	**1a** (1%)	1,4-dixone	K_2CO_3	50
5	**1a** (1%)	THF	K_2CO_3	45
6	**1a** (1%)	DMF	Cs_2CO_3	96
7	**1a** (1%)	DMF	Na_2CO_3	90
8	**1a** (1%)	DMF	KOH	70
9	**1a** (1%)	DMF	NaOH	74
10	**1a** (1%)	DMF	KO^{t}Bu	72
11	**1a** (1%)	DMF	KOAc	85
12	**1a** (0.5%)	DMF	Cs_2CO_3	95
13	**1a** (0.25%)	DMF	Cs_2CO_3	70
14[c]	**1a** (0.5%)	DMF	Cs_2CO_3	72
15[d]	**1a** (0.5%)	DMF	Cs_2CO_3	90

[a]Reaction conditions: 4-bromoanisole (0.50 mmol), styrene (0.60 mmol), NHC–Pd (0.25–1.0% mol), base (0.75 mmol), solvent (2.0 mL) at 140 °C for 3 h.
[b]Isolated yield.
[c]The reaction was performed at 120 °C for 3 h.
[d]The reaction was performed at 120 °C for 8 h.

Initially, the effect of solvent on the reaction was examined, and a significant solvent effect was observed. High yields were obtained when the reactions were performed in DMF and DMA. Among the bases examined, all reactions took place smoothly to give product in moderate to good yields within 3 h; the best result can be achieved with Cs_2CO_3. To further examine the catalytic efficiency of **1a**, a variation of the catalyst loading from 1.0–0.5 to 0.25 mol% within 3 h was performed to give the product in 93, 91, and 80% yields, respectively. The reaction with low catalyst loading results in incomplete conversion. On the basis of the above preliminary optimized results, the next study focused on reaction temperature. Among the temperatures examined, 140 °C was the optimum reaction temperature. Reducing the temperature to 120 °C resulted in decreased product yield. However, the reaction can be also finished at 120 °C through increasing the reaction time to 8 h.

With the optimized reaction condition, catalytic results between a variety of aryl bromides and styrene are summarized in Scheme 2. In order to maintain consistency of the catalyst loading, 0.5 mol % for **1a**–**1c** and 0.25 mol % for **2a** and **2b** were used in the catalytic reactions. All of the catalysts displayed moderate to good outcomes in coupling reactions. Different substituents on aryl bromide were tolerated, and good yields of the products were obtained. The reactions of aryl bromides with electron-withdrawing groups such as CN and CF_3 at the *para*-position are more efficient. The *ortho*-substituents of aryl bromides, 2-bromotoluene proceeds well and generated the corresponding products in good yields. On the whole, the activities of the dinuclear NHC–Pd complexes as catalysts in the Mizoroki–Heck reactions are similar to those of related mononuclear complexes. This suggests that the catalytic activity of the NHC–Pd complexes is mainly dependent on the NHC ligand. The dinuclear complexes as catalysts do not display outstanding superiority. The reason may be that the distances between two palladium centers are too large for cooperative interactions.

To further compare the catalytic efficiency between mono- and dinuclear complexes, kinetic experiments for **1a** and **2a** were performed by GC analysis. As shown in Figure 2, the reactions turned over immediately and were complete within 3 h. Complexes **1a** and **2a**



Scheme 2. Mizoroki–Heck reactions catalyzed by **1a**–**1c** and **2a**–**2b**[a,b].
Notes: [a]Reaction conditions: 4-bromoanisole (0.50 mmol), styrene (0.60 mmol), NHC–Pd (0.25–0.5 % mol), Cs_2CO_3 (0.75 mmol), DMF (2.0 mL) at 140 °C for 3 h. [b]Isolated yield.

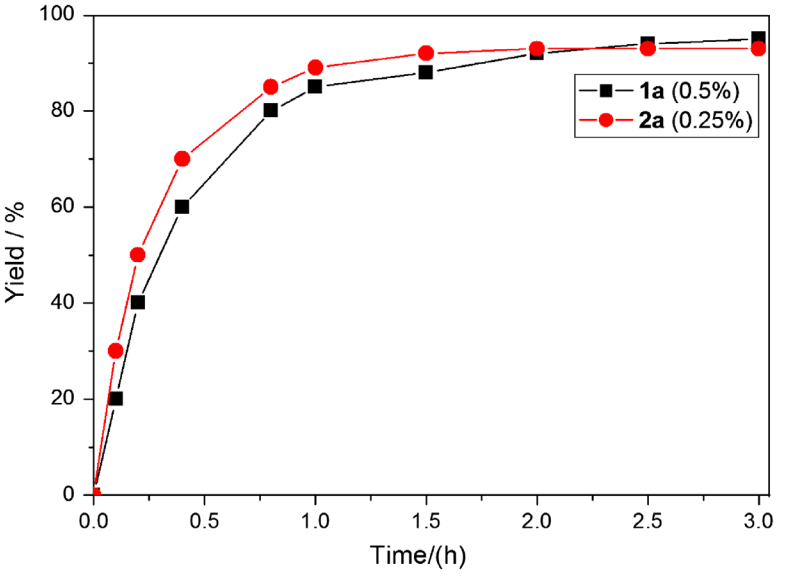


Figure 2. Reaction of 4-bromoanisole and styrene promoted by **1a** and **2a**.

demonstrated similar catalytic activities. However, the induction period for these complexes was slightly different, a short time was present for **2a** relative to **1a**, which may be related to reduction to the active Pd species. The observance of short induction period for **2a** possibly indicates cooperative effects to some extent. Although the complexes showed good catalytic activities, there is no obvious advantage in catalyst amount and reaction activity compared to recently reported NHC–Pd complexes. As ancillary ligands, the diazine ligands indeed adjust the σ-donation property of the NHC to some extent. However, the real role of the nitrogen donors in the catalytic process needs to be further investigated.

4. Conclusion

Five mono- and dinuclear heteroleptic palladium complexes containing NHC and diazines were synthesized and characterized. The catalytic performance of the complexes in the Mizoroki–Heck reaction exhibited good catalytic activities. Although mono- and dinuclear complexes display similar catalytic activities, dinuclear complexes introduce some benefits into the catalytic reaction with shorter induction periods than their mononuclear counterparts, which might be attributed to cooperative effects.

Supplementary material

CCDC 1520583–1520587 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Disclosure statement

No potential conflict of interest was reported by the author.

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