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PAPER

Synthesis and characterization of dinuclear NHC–palladium complexes and their applications in the Hiyama reactions of aryltrialkyoxysilanes with aryl chlorides†

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Four linear dinuclear *N*-heterocyclic carbene (NHC)–palladium complexes $\{[PdCl_2(NHC)]_2(\mu\text{-L})\cdot xCH_2Cl_2\}$ (**1–4**, L = pyrazine, DABCO) were synthesized through one-pot reactions of imidazolium salts, $PdCl_2$ and various bidentate *N*-heterocycles under mild conditions. The compounds were fully characterized by NMR, FT-IR and elemental analysis. Among them, complexes $[PdCl_2L^{Mes}]_2(\mu\text{-pyrazine})\cdot CH_2Cl_2$ (**1**), $[PdCl_2L^{iPr}]_2(\mu\text{-pyrazine})$ (**2**), and $[PdCl_2L^{Mes}]_2(\mu\text{-DABCO})$ (**3**), were elucidated by single-crystal X-ray crystallography. Moreover, the catalytic activity of the NHC–palladium complexes was examined in the Hiyama reactions and the results showed that the dinuclear palladium complexes were the effective catalyst precursors for the reactions of aryltrialkyoxysilanes with aryl chlorides.

Introduction

Transition-metal-catalyzed coupling reactions have contributed greatly to the straightforward construction of carbon–carbon bonds in recent years. Significant progress in this area has been achieved with a variety of palladium catalysts.[1] Among them, the palladium-catalyzed Hiyama cross-coupling reactions of aryltrialkyoxysilanes with aryl halides have attracted much attention in organic synthesis.[2] Over the last few decades, considerable efforts have been made to develop more active catalysts for the Hiyama coupling reaction.[3] Generally, aryl iodides and bromides have been employed as substrate partners in the presence of palladium precursors and air-sensitive phosphine ligands. Despite the lower reactivity of aryl chlorides compared with the corresponding aryl iodides and bromides, aryl chlorides are the most desirable substrates because of their lower cost and ready availability. Therefore, the development of high-performance catalysts for Hiyama cross-couplings with aryl chlorides is still relatively unexplored.[4]

Since the successful isolation of the first stable carbene by Arguengo in 1991, *N*-heterocyclic carbenes (NHCs) have been extensively studied in the field of organometallics as ligands comparable to the conventional phosphine ligands capable of coordination with a wide range of transition metals.[5] Recently, it has been shown that *N*-heterocyclic carbene–palladium complexes offer distinctive advantages as possible alternatives to Pd–phosphine systems in C–C cross-coupling reactions.[6] Some highly active palladium systems with carbene ligands for the activation of aryl chlorides have been developed.[7] Recent studies have illustrated that the provision of functional ligands to complement the strongly binding NHCs could promote a reversible coordination and dissociation mechanism which is highly desirable for catalytic applications.[8] Among the known NHC–Pd complexes, most are tetracoordinate containing an ancillary ligand, such as pyridine, pyrazole, or imidazole, and adopt a square-planar geometry for stability.[9] Despite the great interest in *N*-heterocyclic carbene–palladium complexes as catalysts, very little research has been reported on dinuclear or multinuclear carbene complexes bearing bidentate or multidentate bridging ligands.[10] Recently, the design of regularly shaped molecules has aroused more and more interest as such a process can yield self-assembled architectures not only with regular, well-defined inner structures but also with tailored functionalities.[11] An emerging trend in coordination chemistry is to construct functionalized complexes that can enter into an array of di- and multinuclear systems which are versatile and generally constructed from simple mononuclear sources with bridging ligands. Both Stang and co-workers,[12] and Fujita and Ogura[13] have elegantly demonstrated the structural beauty arising from the application of diverse functional building blocks. Known as common bridging ligands, *N*-heterocycles such as 4,4′-bipyridine, pyrazine, and DABCO have been the most widely used linkers in this field. Herein, we reported the synthesis and structural characterization of four linear dinuclear *N*-heterocyclic carbene

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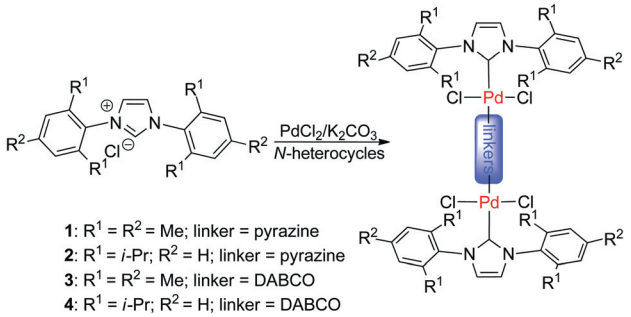


Scheme 1 Overview of the synthesis of the dinuclear *N*-heterocyclic carbene (NHC)–palladium complexes (**1–4**): imidazolium salts (1.0 mmol), $PdCl_2$ (1.0 mmol), K_2CO_3 (1.1 mmol) and bidentate *N*-heterocycles (0.6 mmol), THF, reflux, 6 h.

(NHC)–palladium complexes. The catalytic behavior of the complexes in Hiyama reactions of a range of aryl chlorides was also studied.

Results and discussion

Synthesis of NHC–palladium complexes

The synthesis of the NHC–palladium complexes **1–4** was achieved through the procedure shown in Scheme 1. The reactions of imidazolium salts, $PdCl_2$ and bidentate *N*-heterocycles (DABCO, and pyrazine) in the presence of K_2CO_3 afforded the corresponding NHC–palladium complexes in moderate to good yields. The compounds were fully characterized by NMR, FT-IR and elemental analysis. The elemental analysis results are consistent with the formation of dinuclear species of the general formula $[PdCl_2(NHC)]_2(\mu\text{-L})$ (L = DABCO or pyrazine), and there is no evidence of the occurrence of other stoichiometries. The ^{1}H-NMR spectrum of compounds **1–4** in $CDCl_3$ shows complete disappearance of the proton signal of N*CH*N from the imidazolium salts which appears at 10.73 ppm for L^{Mes}·HCl and 9.97 ppm for L^{iPr}·HCl. In addition, the formation of the dinuclear complexes was evident from the distinctive stoichiometric proton signal resonances of the bidentate *N*-heterocycles (Fig. 1). These spectra strongly support the formation of the dinuclear *N*-heterocyclic carbene–palladium complexes. Furthermore, the ^{13}C-NMR spectra revealed the appearance of a diagnostic Pd–$C_{(carbene)}$ peak at 149.9 ppm for **1**, 152.4 ppm for **2**, 150.6 ppm for **3** and 153.1 ppm for **4**, respectively. These values are significantly shifted downfield relative to that of the imidazolinium N*CH*N peak of the starting ligand precursor (141.0 ppm for L^{Mes}·HCl, 145.0 ppm for L^{iPr}·HCl).

The structures of compounds **1–3** were further investigated by single-crystal X-ray diffraction, and a summary of the crystallographic data is provided in Table 1. The crystal structures of **1–3** showed a dinuclear framework with bidentate *N*-heterocycle ligands bridging across two square planar Pd(II) units. Compounds **1** and **2** have similar compositions and structures, in which each palladium center is surrounded by an imidazolylidene, a pyrazine, and two chloro ligands in an almost square-planar fashion. Compound **1** crystallizes in the trigonal space group $R\bar{3}$ with a *trans*-configuration. As shown in Fig. 2, the

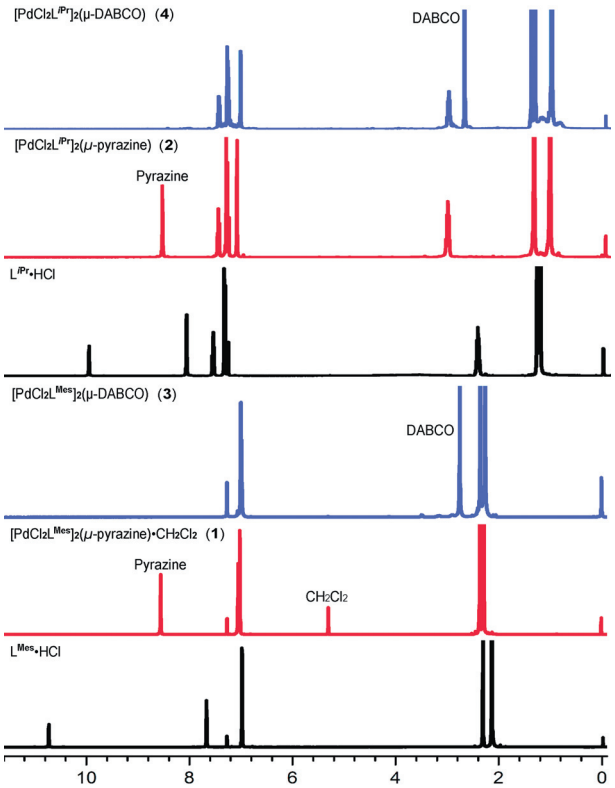


Fig. 1 ^{1}H NMR spectra of L^{Mes}·HCl, L^{iPr}·HCl and compounds **1–4** in $CDCl_3$ at room temperature.

$PdCNCl_2$ coordination plane of the compound **1** is oriented approximately perpendicularly to the carbene ring plane with dihedral angle of 76.97°, which is typical for NHC complexes to relieve steric congestion, and is twisted from the pyrazine ring plane by 26.43°. These values are significantly different from the mononuclear *N*-heterocyclic carbene–palladium complexes Pd-PEPPSI (66.70 and 40.48° for dichloro-(3-chloropyridine)-(1,3-dimesitylimidazol-2-ylidene)-palladium hexane solvate).[9a]

However, the Pd–$C_{(carbene)}$ bond (1.968(3) Å), Pd–N bond (2.151(2) Å) and Pd–Cl bonds (2.2863(9) and 2.3035(7) Å) in compound **1** are comparable to those found in the mononuclear *N*-heterocyclic carbene–palladium complexes Pd-PEPPSI (Pd–C: 1.962(3) Å, Pd–N: 2.117(3) Å, Pd–Cl: 2.290(1) and 2.298(1) Å for dichloro-(3-chloropyridine)-(1,3-dimesitylimidazol-2-ylidene)-palladium hexane solvate). The major difference in the structure of compound **1** from the mononuclear Pd-PEPPSI complex (dichloro-(3-chloropyridine)-(1,3-dimesitylimidazol-2-ylidene)-palladium hexane solvate) is that the dihedral angle between the carbene ring plane and the pyrazine ring plane (76.69°) is significantly bigger than that found in Pd-PEPPSI complex (27.57°).[9a]

The *i*Pr-substituted analogue **2** crystallizes in the monoclinic space group $P2(1)/c$ and the Pd–$C_{(carbene)}$ and Pd–N bonds are 1.959(7) and 2.116(6) Å, respectively, which are similar to those observed for compound **1** and other related mononuclear carbene–palladium Pd-PEPPSI analogues.[9a] As shown in Fig. 3, the dihedral angles between the carbene ring plane and the $PdCNCl_2$ coordination plane, and between the pyrazine ring

Table 1 Crystallographic data for compounds **1–3**

	1	**2**	**3**
Formula	$C_{46}H_{52}Cl_4N_6Pd_2$	$C_{58}H_{76}Cl_4N_6Pd_2$	$C_{48}H_{60}Cl_4N_6Pd_2$
F_w	1043.54	1211.85	1075.62
Crystal system	Trigonal	Monoclinic	Tetragonal
Space group	$R\bar{3}$	$P2_1/c$	$P4_2/n$
a /Å	21.2224(4)	11.785(5)	19.2748(5)
b /Å	21.2224(4)	19.420(8)	19.2748(5)
c /Å	28.0170(7)	14.692(6)	13.3673(6)
α /°	90.00	90.00	90.00
β/°	90.00	107.196(4)	90.00
γ /°	120.00	90.00	90.00
V/Å^3	10 928.0(4)	3212(2)	4966.2(3)
Z	9	2	4
D_{calc}/g cm^{-3}	1.427	1.253	1.439
$F(000)$	4770	1252	2200
μ/mm^{-1}	0.997	0.764	0.603
GOF	1.086	1.035	0.979
Reflections collected	23 441	19 415	9723
Independent reflections (R_{int})	4284 (0.0307)	5631 (0.1032)	4364 (0.0390)
Observed reflections [$I > 2\sigma(I)$]	3674	3051	2915
Refined parameters	268	324	272
R_1 [$I > 2\sigma(I)$]	0.0286	0.0588	0.0504
wR_2 (all data)	0.0795	0.1858	0.1110

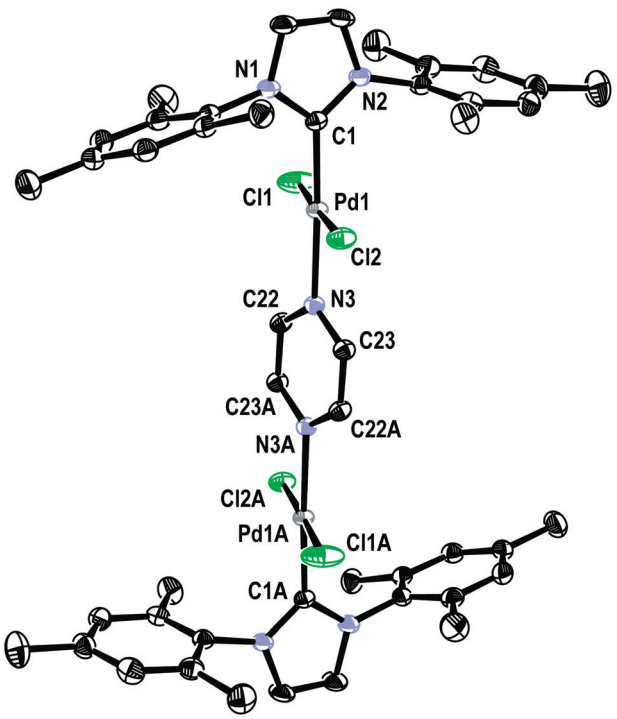


Fig. 2 ORTEP diagram of **1** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms have been omitted for clarity. The suffix A in **1** denotes symmetry operation 1.66667 − x, 1.33333 − y, 0.33333 − z. Selected bond lengths (Å) and angles (°) in **1**: Pd1–C1 1.968(3), Pd1–N3 2.151(2), Pd1–Cl1 2.2863(9), Pd1–Cl2 2.3035(7); C1–Pd1–Cl1 89.19(8), N3–Pd1–Cl1 90.02(6), C1–Pd1–Cl2 90.31(8), N3–Pd1–Cl2 90.55(6).

plane and the $PdCNCl_2$ coordination plane are 70.99 and 30.63°, respectively. These values are somewhat shorter than that in the mononuclear *N*-heterocyclic carbene–palladium complexes Pd-PEPPSI (79.07 and 32.61° for (1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene)-dichloro-(3-chloropyridine)-palladium dichloromenthane solvate).[9a] In addition, compared to the mononuclear *N*-heterocyclic carbene–palladium complex (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)-dichloro-(3-chloropyridine)-palladium dichloromenthane solvate) a dramatically decreased dihedral angle between the carbene ring plane and the pyrazine ring plane (from 69.16 to 41.15°) was observed.

The crystal structure of compound **3** confirmed a dinuclear complex bridged by DABCO (Fig. 4). Compound **3** crystallizes in the tetragonal space group $P4_2/n$ and also show a square-planar geometries around palladium center (largest deviation 0.080 Å), which are surrounded by an imidazolylidene, a DABCO, and two chloro anions in a *trans*-configuration. The Pd–$C_{carbene}$ and Pd–N distance are 1.970(5) and 2.184(3) Å, respectively, similar to that observed in compounds **1** and **2** and other related carbene–palladium analogues.[9a] The dihedral angle between the $PdCNCl_2$ coordination plane and the carbene ring is 76.97°, which is in the range of the compounds **1** and **2**.

Catalytic studies

The palladium-catalyzed Hiyama coupling reaction is a powerful method for the preparation of biaryl derivatives. Many efforts have been directed toward the development of efficient catalytic systems for the Hiyama reaction. Herein, compounds **1–4** were used as catalysts for Hiyama coupling reactions of aryltrialkyoxysilanes with aryl chlorides. The Pd-PEPPSI (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)-dichloro-(3-chloropyridine)-palladium)[9b] and palladium–NHC complexes, generated *in situ* from the corresponding imidazolinium salts and palladium acetate[14] were also examined as a comparison. The coupling reaction of phenyltrimethoxysilane with 4-chloroanisole was tested as the model reaction in toluene at 120 °C and the results are shown in Table 2. Upon treatment with TBAF, which is a well-known promoter of the Hiyama reaction, all the dinuclear

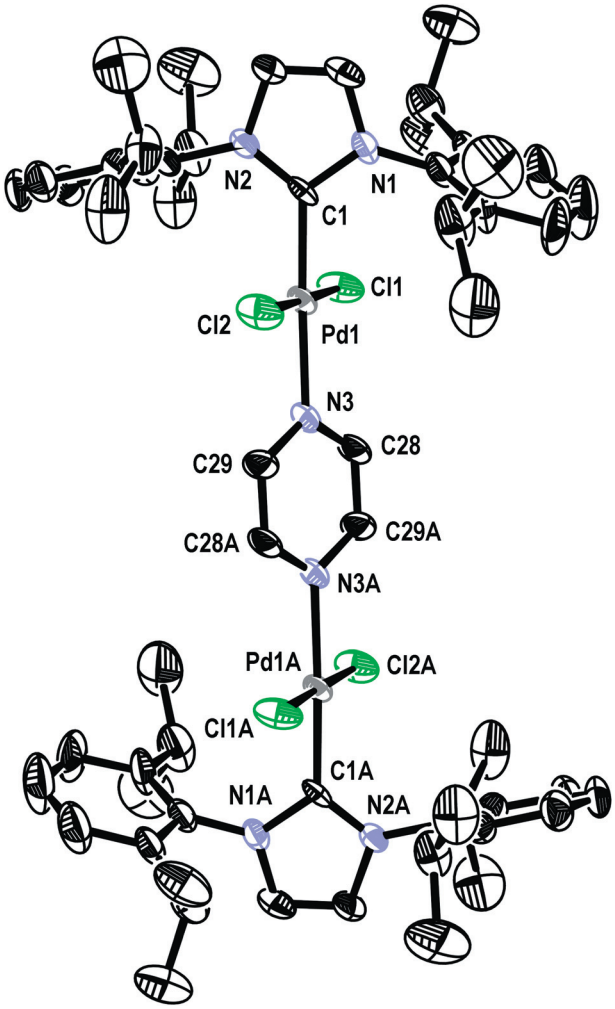


Fig. 3 ORTEP diagram of **2** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms have been omitted for clarity. The suffix A in **2** denotes symmetry operation $1 - x, -y, 1 - z$. Selected bond lengths (Å) and angles (°) in **2**: Pd1–C1 1.959(7), Pd1–N3 2.116(6), Pd1–Cl2 2.286(2), Pd1–Cl1 2.292(2); C1–Pd1–Cl2 88.5(2), N3–Pd1–Cl2 90.63(17), C1–Pd1–Cl1 90.6(2), N3–Pd1–Cl1 90.29(17).

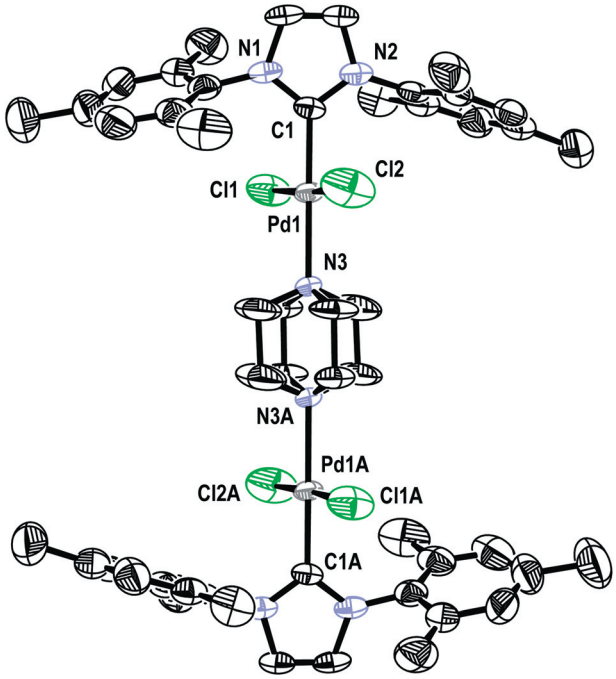
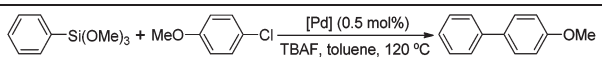


Fig. 4 ORTEP diagram of **3** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms have been omitted for clarity. The suffix A in **3** denotes symmetry operation $1 - x, 1 - y, -z$. Selected bond lengths (Å) and angles (°) in **3**: Pd1–C1 1.970(5), Pd1–N3 2.184(3), Pd1–Cl1 2.2842(17), Pd1–Cl2 2.2954(19); C1–Pd1–Cl1 89.14(16), N3–Pd1–Cl1 92.88(12), C1–Pd1–Cl2 86.90(16), N3–Pd1–Cl2 91.05(12).

Table 2 Hiyama reactions of phenyltrimethoxysilane with 4-chloroanisole in the presence of the NHC–palladium catalysts[a]



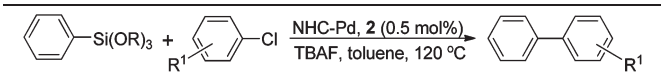
Entry	Catalyst	Yield[b] (%)
1	**1**	80
2	**2**	88
3	**3**	78
4	**4**	84
5	Pd-PEPPSI	86
6	$Pd(OAc)_2 + L^{Mes}{\cdot}HCl$	43
7	$Pd(OAc)_2 + L^{iPr}{\cdot}HCl$	51

[a] Reaction conditions: phenyltrimethoxysilane (0.75 mmol), 4-chloroanisole (0.50 mmol), palladium catalyst (containing Pd 0.0025 mmol), TBAF (1.0 mmol) in toluene (2.0 mL) at 120 °C for 5 h. [b] Isolated yield.

N-heterocyclic carbene (NHC)–palladium complexes showed high catalytic activities for the Hiyama reaction. The results show that the sterically bulkier catalysts **2** and **4** exhibited higher activity. This is mainly due to the different steric topography imparted by the NHC ligand around the palladium centre, which has an impact on the rate of transmetalation and/or reductive elimination. The sterically bulky ligands facilitate reductive elimination (or transmetalation) of the catalytic process, which results in the sterically bulkier catalysts displaying a higher conversion to product.[9a–c,15] Some multinuclear complexes exhibit cooperative reactivity between multiple metal centers and are far more catalytically active than their mononuclear counterparts.[16] Unfortunately, in our system, the dinuclear palladium complexes only demonstrated a similar level of catalytic activity compared with Pd-PEPPSI catalyst, but showed higher activities in comparison with the palladium–NHC complexes generated *in situ*. The Hiyama reactions of a wide range of aryl chlorides with aryltrialkyoxysilanes were further studied in the presence of compound **2** and the results are summarized in Table 3.

The results in Table 3 show that compound **2** is an effective catalyst for the Hiyama coupling of aryl chlorides with organosilanes. When 0.5 mol% of **2** was employed in the Hiyama reaction, both electron-rich and electron-deficient aryl chlorides generated moderate to good yields of the corresponding biphenyl products (Table 3, entries 1–11). It should be noted that the reaction could tolerate *ortho*-substituted groups, and a small

Table 3 Hiyama reactions of aryltrialkyoxysilanes with aryl chlorides[a]



Entry	Aryltrialkyoxysilane	Aryl chloride	Yield[b] (%)
1	R = CH_3	R^1 = 4-OCH_3	88
2	R = CH_3	R^1 = 3-OCH_3	80
3	R = CH_3	R^1 = 2-OCH_3	70
4	R = CH_3	R^1 = 4-NO_2	92
5	R = CH_3	R^1 = 3-OCH_3	89
6	R = CH_3	R^1 = 4-CN	90
7	R = CH_3	R^1 = 4-$COCH_3$	88
8	R = CH_3	R^1 = 4-$COOC_2H_5$	82
9	R = CH_3	R^1 = 4-F	85
10	R = CH_3	R^1 = 4-H	61[c]
11	R = CH_3	R^1 = 4-CH_3	54[c]
12	R = CH_3	2-chloropyridine	80
13	R = CH_3	3-chloropyridine	62
14	R = CH_2CH_3	R^1 = 4-OCH_3	86
15	R = CH_2CH_3	R^1 = 4-CN	89
16	R = CH_2CH_3	R^1 = 4-NO_2	87

[a] Reaction conditions: aryltrialkyoxysilane (0.75 mmol), aryl chloride (0.50 mmol), NHC–palladium catalyst (**2**, 0.0025 mmol), TBAF (1.0 mmol) in toluene (2.0 mL) at 120 °C for 5 h. [b] Isolated yields. [c] At 120 °C for 10 h.

ortho-position effect was observed (entry 3). The coupling reaction of activated 4-chloronitrobenzene and 4-chlorobenzonitrile proceeded smoothly to afford 92 and 90% yields, respectively (entries 4 and 6). For the less active chlorobenzene and 4-methylchlorobenzene, the yields of the products dropped to 61 and 54% even with prolonged reaction times (entries 10 and 11). In addition, the catalytic protocols were also extended to the cross-coupling of heteroaryl chlorides with phenyltrimethoxysilane. 2-Chloropyridine and 3-chloropyridine were able to undergo the coupling reactions and generated the corresponding products in moderate yields (entries 12 and 13). Meanwhile, phenyltriethoxysilane, as the organosilane substrate was employed to react with aryl chlorides under the identical reaction conditions, and good yields of the corresponding products were obtained (entries 14–16).

Conclusions

In summary, we have successfully prepared four linear dinuclear *N*-heterocyclic carbene (NHC)–palladium complexes **1–4** through the reaction of imidazolium salts, $PdCl_2$ and bidentate *N*-heterocycles. The catalytic behaviour of the *N*-heterocyclic carbene–palladium complexes **1–4** in Hiyama coupling reactions was investigated. Among **1–4**, NHC–Pd **2** exhibited the best activity in the Hiyama reaction of aryl chlorides with aryltrialkyoxysilanes. The reactions generated the corresponding products in moderate to good yields.

Experimental

General

The ligands L^{Mes}·HCl and L^{iPr}·HCl were prepared according to the literature.[17] The mononuclear *N*-heterocyclic carbene–palladium complex 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)-dichloro-(3-chloropyridine)-palladium dichloromenthane solvate was prepared according to the literature.[9a] Elemental analyses were performed on an Elementar VarioEL instrument. IR spectra were recorded on a Bruker IFS 120HR spectrometer as KBr disks. NMR spectra were recorded at ambient temperature on a Bruker Avance-400 MHz spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Commercially obtained reagents were used without further purification. Flash column chromatography was carried out using 300–400 mesh silica gel.

Synthesis

$[PdCl_2L^{Mes}]_2$(μ-pyrazine)·CH_2Cl_2 (1). A mixture of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (1.0 mmol), $PdCl_2$ (1.0 mmol), K_2CO_3 (1.1 mmol), and pyrazine (0.60 mmol) was stirred in anhydrous THF (5.0 mL) under reflux for 6 h. The solvent was removed under reduced pressure, and the residue was purified by a flash chromatography on silica gel (hexane/CH_2Cl_2 = 1 : 1) to give compound **1** as a yellow solid (0.88 g, 84% yield). The single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2 and diethyl ether. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 4H, pyrazine-*H*), 7.06 (s, 4H, Im-*H*), 7.02 (s, 8H, *m-ArH*), 2.37 (s, 12H, *p-*CH_3), 2.29 (s, 24H, *o-*CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.9, 146.1, 139.3, 136.2, 134.8, 129.3, 124.4, 21.2, 19.0. IR (KBr, cm^{-1}): 3179, 3124, 2949, 2916, 1606, 1483, 1420, 1409, 1380, 1328, 1280, 1227, 1162, 1133, 1060, 929, 861, 849, 914, 738. Anal. Calc. for $[PdCl_2L^{Mes}]_2$(μ-pyrazine) ($C_{46}H_{54}Cl_4N_6Pd_2$): C, 52.84; H, 5.21; N, 8.04%. Found: C, 52.51; H, 5.30; N, 8.18%.

$[PdCl_2L^{iPr}]_2$(μ-pyrazine) (2). Compound **2** was synthesized by a similar method for the preparation of **1** except that 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride was used instead of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride. Yield: 77%. The single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2 and ethyl acetate. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 4H, pyrazine-*H*), 7.47 (t, 4H, *J* = 8.0 Hz, *p-ArH*), 7.30 (d, 8H, *J* = 8.0 Hz, *m-ArH*), 7.12 (s, 4H, Im-*H*), 3.06 (heptet, 4H, *J* = 6.4 Hz, *CH*(CH_3)$_2$), 1.39 (d, 24H, *J* = 6.8 Hz, CH(*CH_3*)$_2$), 1.09 (d, 24H, *J* = 6.8 Hz, CH(*CH_3*)$_2$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.4, 146.6, 146.1, 134.8, 130.3, 125.2, 124.0, 28.7, 26.3, 23.2. IR (KBr, cm^{-1}): 3129, 2964, 2868, 1465, 1416, 1382, 1350, 1333, 1287, 1211, 1160, 1125, 1069, 946, 819, 802, 763, 757, 707. Anal. Calc. for $[PdCl_2L^{iPr}]_2$(μ-pyrazine) ($C_{58}H_{78}Cl_4N_6Pd_2$): C, 57.39; H, 6.48; N, 6.92%. Found: C, 57.41; H, 6.27; N, 6.98%.

$[PdCl_2L^{Mes}]_2$(μ-DABCO) (3). Compound **3** was synthesized by a similar method for the synthesis of **1** except that DABCO was used instead of pyrazine. Yield: 82%. The single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2 and diethyl ether. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.01 (s, 8H, *m-ArH*), 6.99 (s, 4H, Im-*H*), 2.76 (s, 12H, DABCO-*H*), 2.36 (s, 12H, *p-*CH_3), 2.27 (s, 24H, *o-*CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.6, 139.0, 136.2, 135.1, 129.1, 124.1, 48.8, 21.1, 19.2. IR (KBr, cm^{-1}): 3146, 3108, 3092, 2959, 2918, 1608, 1484, 1468, 1411, 1379, 1331, 1298, 1228, 1185, 1054,

1035, 849, 812, 706. Anal. Calc. for $[PdCl_2L^{Mes}]_2$(μ-DABCO) ($C_{48}H_{62}Cl_4N_6Pd_2$): C, 53.49; H, 5.80; N, 7.80%. Found: C, 53.51; H, 5.38; N, 7.67%.

$[PdCl_2L^{iPr}]_2$(μ-DABCO) (4). Compound **4** was synthesized by a similar method for the preparation of **2** except that DABCO was used instead of pyrazine. Yield: 54%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.47 (t, 4H, J = 7.6 Hz, *p-ArH*), 7.30 (d, 8H, J = 7.6 Hz, *m-ArH*), 7.05 (s, 4H, Im-*H*), 3.04 (heptet, 4H, J = 6.8 Hz, *CH*(CH_3)$_2$), 2.74 (s, 12H, DABCO-*H*), 1.38 (d, 24H, J = 6.4 Hz, CH(*CH*$_3$)$_2$), 1.06 (d, 24H, J = 6.8 Hz, CH(*CH*$_3$)$_2$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.1, 146.7, 135.1, 130.0, 124.9, 123.8, 49.0, 28.9, 26.2, 23.2. IR (KBr, cm^{-1}): 3131, 3069, 2965, 2869, 1696, 1591, 1465, 1446, 1416, 1381, 1364, 1349, 1330, 1286, 1268, 1212, 1161, 1124, 1068, 1059, 946, 820, 801, 757, 746, 705. Anal. Calc. for $[PdCl_2L^{iPr}]_2$(μ-DABCO) ($C_{60}H_{86}Cl_4N_6Pd_2$): C, 57.84; H, 6.96; N, 6.74%. Found: C, 57.98; H, 6.64; N, 7.02%.

General procedure for the NHC–Pd (2) catalyzed Hiyama reactions

A sealable reaction tube equipped with a magnetic stir bar was charged with aryl chloride (0.50 mmol), phenyltrialkyoxysilane (0.75 mmol), TBAF (1.0 mmol), NHC–Pd complex (**2**, 3.0 mg, 0.5 mmol%), and anhydrous toulene (2.0 mL). The mixture was heated in an oil bath at 120 °C and stirred for 5 h. The organic phase was evaporated under reduced pressure and the product was purified by column chromatography using silica gel.

X-Ray crystallography

Data collection was performed on a Bruker-AXS SMART CCD area detector diffractometer at 293 K using ω rotation scans with a scan width of 0.3° and Mo Kα radiation (λ = 0.71073 Å). Multi-scan corrections were applied using SADABS.[18] Structure solutions and refinements were performed with the SHELX-97 package.[19] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. The hydrogen atoms were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of carbon and nitrogen atoms. In compound **1**, the unit cell includes a disordered solvent CH_2Cl_2 molecule (it can be also observed from the ^{1}H-NMR), which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent CH_2Cl_2 molecule and, thereby, to produce a set of solvent-free diffraction intensities. Crystallographic data for the compounds are summarized in Table 1.

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