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Synthesis and characterizations of arsine– and stibine–ligated Schiff base palladacycles and their applications in Suzuki–Miyaura cross-coupling reactions

Haozhen Wang and Jin Yang*

A series of arsine- and stibine-ligated Schiff base palladacycles were synthesized by the reaction of μ-Cl-bridged Schiff base palladacycles $[Pd(C_6H_4CH]NC_6H_2R)(\mu\text{-}Cl)]_2$ (R = 2,4,6-trimethyl or 2,6-diisopropyl) with $AsPh_3$ or $SbPh_3$. The new arsine- and stibine-ligated palladacycles were fully characterized using ^1H NMR, ^{13}C NMR and infrared spectroscopies, high-resolution mass spectrometry, elemental analysis and single-crystal X-ray diffraction. Further exploration of the catalytic application of the palladacycles for Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids was carried out. It was found that the new palladacycles are considerably active for these coupling reactions. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: Palladacycles; $AsPh_3$; $SbPh_3$; Suzuki–Miyaura cross-coupling

Introduction

Since the first cyclopalladacycles were initially isolated and characterized from the cyclopalladation of azobenzene derivatives in 1965,[1] cyclopalladacycles have attracted increasing attention and have been much explored in coordination and organometallic chemistry.[2] The applications of cyclopalladacycles in organic synthesis, organometallic catalysis and new molecular materials have been fully investigated.[3] In particular, palladacycles are encountered as the intermediate species in many palladium-catalyzed reactions.[4] 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.[2a] Recently, there has been a growing interest in the use of ancillary ligands for modification of palladacycles. In this regard, various functional ligands, such as N-heterocyclic carbene ligands,[5] phosphine derivatives[6] and nitrogen-donor compounds,[7] have been involved in coordination with palladacycles. The combination of palladacycles with N-heterocyclic carbenes and phosphine derivatives can effectively promote the catalytic performance, due to the inherent hybrid character of the mixed-ligand complexes which would be electronically more sensitive and tunable to the needs of the substrates. Among them, phosphine derivatives have attracted more attention since the phosphine compounds exhibit high efficiency in C–C bond forming reactions catalyzed by palladium.[8] With regard to imine-based palladacycles, Weissman and Milstein first reported the use of a dinuclear phosphine-free complex in the Suzuki coupling of aryl bromides.[9] Bedford and co-workers then reported that the phosphine adducts of imine-based palladacycles exhibited higher catalytic activities than dinuclear phosphine-free palladacycles in Suzuki coupling and further described the role played by the phosphine and the anionic ligand in terms of both catalyst activity and lifetime.[6a–c] Serrano and co-workers reported that phosphine adducts of the imine-based palladacycles with imidate anions also exhibit greater activity than phosphine-free palladacycles.[6g]

The original idea of our work came from the interesting reports of Bedford *et al.* Serrano *et al.* We thought that changing the ancillary ligand by replacing the P-donor with As-donor and Sb-donor may provide an opportunity to systematically study the catalytic activities of palladacycles since some derivatives of triarylarsine have been reported as more efficient ligands than their phosphorus analogues in transition-metal-catalyzed reactions. For example, Farina and co-workers have reported that in Stille reactions there is a large rate acceleration with $AsPh_3$ as palladium ligand, of two and three orders of magnitude, relative to PPh_3.[10a–c] Pringle and co-workers have reported that $AsPh_3$ is a more effective ligand for palladium-catalyzed Heck olefination than PPh_3.[10d] In sharp contrast to phosphines, reports of palladacycle fragments coordinated to arsine or stibine ligands are much rarer. As part of our program of exploring ligand synergism in catalysis, herein we report the synthesis and full characterization of well-defined mixed palladacycle/$AsPh_3$

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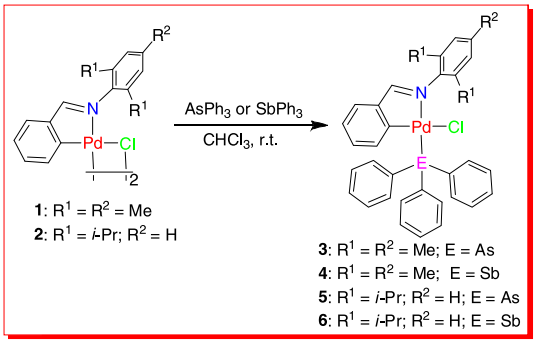


Scheme 1. Overview of preparation of $AsPh_3$- and $SbPh_3$-ligated Schiff base palladacycles.

or palladacycle/$SbPh_3$ systems and their catalytic performance in Suzuki–Miyaura cross-coupling reactions.

Results and discussion

Synthesis and characterization of palladacycles

The cleavages of Cl-bridged palladacycles by phosphines giving neutral or ionic complexes have been reported.[6a,f,g] Consequently, we examined the reactions of μ-Cl-bridged palladacycles [Pd($C_6H_4CH{=}NC_6H_2R$)(μ-Cl)]$_2$ (R = 2,4,6-trimethyl or 2,6-diisopropyl) with $AsPh_3$ or $SbPh_3$, as shown in 1. Treatment of Cl-bridged palladacycles **1** or **2** with 2 equiv. of $AsPh_3$ or $SbPh_3$ in $CHCl_3$ at ambient temperature produces yellow mononuclear palladacycles [Pd($C_6H_4CH{=}NC_6H_2R$)(L)(Cl)] (**3**–**6**; L = $AsPh_3$, $SbPh_3$). Palladacycles **3**–**6** were both air- and moisture-stable, and were fully characterized using ^{1}H NMR, ^{13}C NMR and Fourier transform infrared (FT-IR) spectroscopies, high-resolution mass spectrometry (HRMS), elemental analysis and X-ray crystallography. As evident from Table 1, the FT-IR spectra of **3**–**6** show strengthened stretching for $\nu_{C=N}$ in the range 1602–1613 cm^{-1}, which are similar to that of the Cl-bridged palladacycle **2** (1603 cm^{-1}).[11] The ^{1}H NMR spectra of **3**–**6** display the resonances for *H*C=N protons in the range 8.07–8.15 ppm, which are shifted downfield compared to the corresponding Cl-bridged palladacycle **2** (7.72 ppm). The ^{13}C NMR spectra show the expected signals in the appropriate regions. The chemical shifts of the C_{imine} atoms (HC=N) which appear in the range 155.5–157.5 ppm in the ^{13}C NMR spectra are comparable with the ^{13}C NMR signals of the C_{imine} atom in palladacycle **2** (155.4 ppm). In addition, the ^{13}C NMR spectra reveal the appearance of diagnostic Pd–*C* peaks (177.0–178.1 ppm) for **3**–**6**. These values are shifted slightly upfield when compared with palladacycle **2** (176.2 ppm) and the PCy_3-ligated palladacycle [Pd($C_6H_4CH{=}NC_6H_3$-2,6-iPr)(PCy_3)(Cl)] (176.1 ppm).[6f] Furthermore, the formation is further confirmed from the HRMS analysis where exclusive signals are observed for their respective [M − Cl$^-$]$^+$ fragments.

Crystal structures

Single crystals of **3**–**6** suitable for X-ray diffraction analysis were obtained from a chloroform–hexane solution, and the structures were unambiguously determined using X-ray crystallography. Complexes **3** and **4** crystallize as $CHCl_3$ solvates **3**·$CHCl_3$ and **4**·$CHCl_3$, respectively. Figure 1 displays ORTEP plots of **3**–**6**, and Table 1 summarizes selected bond distances and bond angles. As shown in Fig. 1, in all structures, the coordination of the Pd atom is essentially square-planar, containing a cyclometallated Schiff base ligand, a chloride moiety and an As or Sb donor with angles between adjacent ligands ranging from 80.50(16)° to 101.15(17)°. As expected, the As or Sb donor is located at a *trans*-position of the nitrogen atom. The five-membered chelate ring that contains the imine functionality defined by Pd1, N1, C1, C2 and C3, which are quasi-coplanar with the coordination planes defined by As1 (Sb1), C3, N1, Cl1 and Pd1, is oriented roughly perpendicular to the trimethylphenyl or diisopropylphenyl rings with the smallest dihedral angle of 76.05°, in accordance with a previous study. The Pd1–C1 (1.992(4) Å for **3**, 2.011(6) Å for **4**, 1.984(3) Å for **5** and 1.987(3) Å for **6**) and the Pd1–N1 (2.052(3) Å for **3**, 2.098(5) Å for **4**, 2.079(3) Å for **5** and 2.096(2) Å for **6**) bond lengths are within the expected range, relative to the corresponding palladacycle **2** (Pd–C bond: 1.965(2) Å; Pd–N bond: 2.022(1) Å)[11] and the PCy_3-ligated palladacycle [Pd($C_6H_4CH{=}NC_6H_3$-2,6-iPr)(PCy_3)(Cl)] (Pd–C bond: 2.016(2) Å; Pd–N bond: 2.109(2) Å).[6f] The Pd–As bond

Table 1. Selected FT-IR, ^{1}H NMR and ^{13}C NMR spectral data, bond lengths and angles for complexes **3**–**6**

	3	4	5	6
FT-IR $\nu_{C=N}$ (cm^{-1})	1612	1613	1602	1602
^{1}H NMR[a] $\delta_{CH=N}$ (ppm)	8.07	8.10	8.13	8.15
^{13}C NMR[a] $\delta_{CH=N}$ (ppm)	157.3	155.5	157.5	155.7
^{13}C NMR[a] δ_{Pd-C} (ppm)	178.1	177.7	177.4	177.0
Pd1–C3 (Å)	1.992(4)	2.011(6)	1.984(3)	1.987(3)
Pd1–N1 (Å)	2.052(3)	2.098(5)	2.079(3)	2.096(2)
Pd1–Cl1 (Å)	2.3587(9)	2.3904(17)	2.3606(10)	2.3648(8)
Pd1–E[b] (Å)	2.3668(14)	2.5195(7)	2.3533(7)	2.5007(3)
C1–Pd1–N1 (°)	80.50(16)	80.9(2)	80.74(11)	81.18(11)
C1–Pd1–E[b] (°)	101.02(12)	101.15(17)	94.94(9)	95.11(8)
E[b]–Pd1–Cl1 (°)	85.72(5)	82.91(5)	91.39(3)	89.21(2)
N1–Pd1–Cl1 (°)	92.95(11)	95.17(15)	92.83(7)	94.46(7)

[a] ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 298 K.
[b] E represents As or Sb donor.

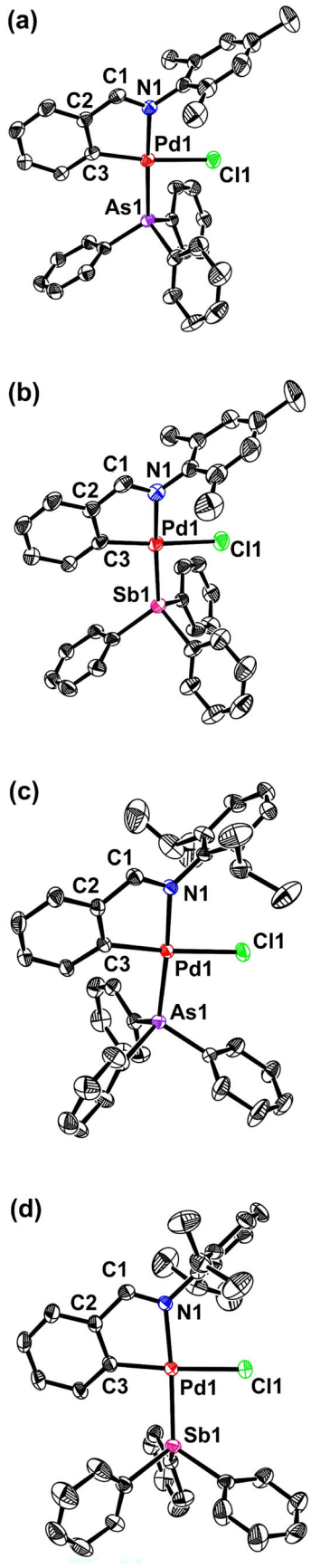


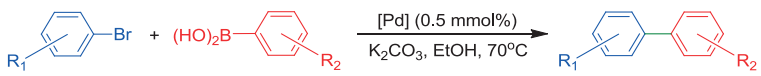
Figure 1. ORTEP diagrams of **3–6** with thermal displacement parameters drawn at 30% probability. The hydrogen atoms and solvent molecules ($CHCl_3$ for 3 and 4) have been omitted for clarity.

lengths in complexes **3** and **5** (2.3668(14) and 2.3533(7) Å) are longer than the Pd–P bond lengths in the related complexes, but are somewhat shorter than that in the arsine-stabilized N-heterocyclic carbene palladium complexes (2.4103(7) and 2.4676(7) Å).[12] A similar disparity can be observed when the $SbPh_3$-bearing complexes **4** and **6** are compared.

Catalytic study

Suzuki–Miyaura cross-coupling catalyzed by palladacycles has been researched extensively since the first well-known phosphine-derived palladacycles were developed by Herrmann and co-workers in 1995.[13] After that a variety of modified palladacycles containing functional groups have shown their efficiency in these coupling reactions.[14] Herein, the catalytic activities of the $AsPh_3$- and $SbPh_3$-ligated palladacycles (**3**–**6**) as catalysts in Suzuki–Miyaura cross-coupling were investigated. According to the general reaction conditions reported in the literature,[6f] the reactions were directly performed in EtOH in the presence of K_2CO_3 as base. The focus of the study was essentially to demonstrate the potential of $AsPh_3$ and $SbPh_3$ as ancillary ligands; the reaction conditions were not further optimized. In all instances the solvent was used as obtained commercially without further purification. The organic products were isolated by flash column chromatography and then analyzed using ^1H NMR and ^{13}C NMR spectroscopy. The activities of **3**–**6** were investigated in the Suzuki–Miyaura cross-coupling reactions of various aryl bromides with arylboronic acids yielding the corresponding biphenyl products. The results are summarized in Table 2. At the beginning of the determination of the aryl bromide substrate scope, phenylboronic acid was used as a model substrate, and several substituted aryl bromides were examined. Aryl bromides with both electron-drawing groups (4-OMe and 4-NO_2) and electron-donating group (4-Me) are able to effectively react with phenylboronic acid. The most facile reaction is that between 4-nitrobromobenzene and phenylboronic acid with yields of 93–98% (Table 2, entries 5–8). Also, the cross-coupling of arylboronic acids with 4-bromoanisole was evaluated. Under the given conditions, 4-chlorophenylboronic acid and 4-trifluoromethylphenylboronic acid are able to undergo the coupling reactions smoothly with 4-bromoanisole and generate the corresponding products in good yields. Meanwhile, it should be noted that the reaction can tolerate *ortho*-substituted groups, the reaction of 2,4-dimethoxyphenylboronic acid with 4-bromoanisole under identical reaction conditions giving good yields of the corresponding product (Table 2, entries 21–24). Unfortunately, the coupling reaction of aryl chlorides, such as 4-choloroanisole and 4-choloronitrobenzene, with phenylboronic acid gives poor results (Table 2, entries 25–28). Furthermore, the Suzuki–Miyaura cross-coupling reactions of 4-bromoanisole with phenylboronic acid conducted in aqueous media were carried out. The reactions using catalysts **3** and **4** were carried out in pure water (Table 2, entries 29 and 30). The rapid formation of palladium black was observed under these conditions, leading to limited conversions. When the catalytic activity results from the palladacycles are analyzed, it is found that the arsine and stibine adducts are very similar to each other and are both efficient precatalysts for the cross-coupling reactions tested. Small differences can be attributed to the chemical functions present on the substrate. Generally, electron-deficient aryl bromides react more easily than electron-rich ones and give products in good yields.

Table 2. Suzuki–Miyaura cross-coupling of aryl bromides with arylboronic acids catalyzed by **3–6**[a]



Entry	Catalyst	Aryl bromide	Arylboronic acid	Yield (%)[b]
1	**3**	R^1 = 4-MeO	R^2 = H	91
2	**4**			92
3	**5**			96
4	**6**			94
5	**3**	R^1 = 4-NO_2	R^2 = H	93
6	**4**			95
7	**5**			98
8	**6**			98
9	**3**	R^1 = 4-Me	R^2 = H	80
10	**4**			82
11	**5**			85
12	**6**			86
13	**3**	R^1 = 4-MeO	R^2 = 4-Cl	92
14	**4**			90
15	**5**			94
16	**6**			92
17	**3**	R^1 = 4-MeO	R^2 = 4-CF_3	91
18	**4**			93
19	**5**			90
20	**6**			94
21	**3**	R^1 = 4-MeO	R^2 = 2,4-di-MeO	92
22	**4**			90
23	**5**			93
24	**6**			95
25[c]	**3**	R^1 = 4-MeO	R^2 = H	22
26[c]	**4**			25
27[d]	**5**	R^1 = 4-NO_2	R^2 = H	30
28[d]	**6**			32
29[e]	**3**	R^1 = 4-MeO	R^2 = H	Trace
30[e]	**4**			Trace

[a]Reaction conditions: aryl bromide (0.50 mmol), arylboronic acid (0.60 mmol), catalyst (0.0025 mmol), K_2CO_3 (1.0 mmol) in EtOH (2.0 ml) at 70°C for 6 h.
[b]Isolated yield.
[c]Suzuki–Miyaura cross-coupling of 4-choloroanisole with phenylboronic acid.
[d]Suzuki–Miyaura cross-coupling of 4-choloronitrobenzene with phenylboronic acid.
[e]Reaction performed in aqueous media.

Conclusions

A series of arsine- and stibine-ligated Schiff base palladacycles have been synthesized and fully characterized using ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopies, HRMS and elemental analysis. The solid-state structures have been further confirmed using single-crystal X-ray diffraction. The catalytic behavior of the palladacycles in Suzuki–Miyaura cross-coupling reactions was investigated and good yields of the corresponding products were achieved. The results demonstrate that these complexes show high catalytic activity and good tolerance to various chemical functions.

Experimental

General remarks

The chemicals were purchased from commercial suppliers and were used without purification prior to use unless otherwise indicated. NMR spectra were recorded at 400 MHz (for ^{1}H NMR) and 100 MHz (for ^{13}C NMR) with a Bruker Avance 400 NMR spectrometer. ^{1}H NMR and ^{13}C NMR spectroscopy was performed in $CDCl_3$ with tetramethylsilane as an internal standard. C, H and N analyses were performed with a Vario El III Elementar. High-resolution mass spectra were recorded with an Agilent 6550 iFunnel Q-TOF MS system. FT-IR spectra were recorded with a Bruker IFS 120HR spectrometer using KBr discs. Flash column chromatography was carried out using 300–400 mesh silica gel. The μ-Cl-bridged palladacycles **1** and **2** were prepared according to the literature.[11]

Synthesis of complexes 3–6

A mixture of the μ-Cl-bridged palladacycles (0.10 mmol) **1** or **2** and the arsine or stibine ligand (0.20 mmol) was dissolved in $CHCl_3$ (5.0 ml). After stirring for 12 h at ambient temperature, the reaction mixture was reduced under vacuum and the resulting residue was

washed with ether to afford a yellow solid. Single crystals of complexes **3**–**6** suitable for X-ray diffraction analysis were obtained from the evaporation of $CHCl_3$–*n*-hexane solutions of the complexes.

*[Pd($C_6H_4CH{=}NC_6H_2$-2,4,6-Me_3)($AsPh_3$)(Cl)] (**3**)*

The procedure yielded 115 mg (86%) of pure product **3** as yellow crystals. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 8.07 (s, 1H, C*H*=N), 7.71–7.69 (m, 6H), 7.45–7.36 (m, 10H), 7.04–7.01 (m, 1H), 6.91 (s, 2H, NC_6H_2-2,4,6-Me_3), 6.70–6.62 (m, 2H), 2.41(s, 6H, *o*-CH_3), 2.29 (s, 3H, *p*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 178.1 (Pd–*C*), 157.3 (*C*H=N), 148.3 (N *C*), 145.1 (As *C*), 138.4, 135.8, 134.5, 133.4, 130.8, 130.4, 130.1, 128.9, 128.6, 128.3, 124.3, 21.0 (*p*-CH_3), 19.1 (*o*-CH_3). FT-IR (KBr, cm^{-1}): 3046, 2987, 2915, 1612 ($\nu_{C=N}$), 1577, 1481, 1436, 1199, 733. HRMS (ESI): calcd for $C_{34}H_{31}AsNPd$ $[M - Cl^-]^+$ 634.0707; found 634.0741. Anal. Calcd for [Pd($C_6H_4CH{=}NC_6H_2$-2,4,6-Me_3)($AsPh_3$)(Cl)]·$CHCl_3$ ($C_{35}H_{32}AsCl_4NPd$) (%): C, 53.23; H, 4.08; N, 1.77. Found (%): C, 53.48; H, 4.14; N, 1.93.

*[Pd($C_6H_4CH{=}NC_6H_2$-2,4,6-Me_3)($SbPh_3$)(Cl)] (**4**)*

The procedure yielded 132 mg (92%) of pure product **4** as yellow crystals. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 8.10 (s, 1H, C*H*=N), 7.79–7.77 (m, 6H), 7.47–7.40 (m, 10H), 7.08–6.92 (m, 4H), 6.72–6.69 (m, 1H), 2.47(s, 6H, *o*-CH_3), 2.35 (s, 3H, *p*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 177.7 (Pd–*C*), 155.5 (*C*H=N), 148.4 (N–*C*), 144.3 (Sb–*C*), 139.9, 136.7, 136.0, 131.4, 131.3, 130.5, 130.2, 129.6, 129.1, 128.6, 124.6, 21.1 (*p*-CH_3), 19.1 (*o*-CH_3). FT-IR (KBr, cm^{-1}): 3046, 2977, 1613 ($\nu_{C=N}$), 1575, 1555, 1479, 1433, 1199, 997, 730. HRMS (ESI): calcd for $C_{34}H_{31}NPdSb$ $[M - Cl^-]^+$ 680.0529; found 680.0557. Anal. Calcd for [Pd($C_6H_4CH{=}NC_6H_2$-2,4,6-Me_3)($SbPh_3$)(Cl)]·$CHCl_3$ ($C_{35}H_{32}Cl_4NPdSb$) (%): C, 50.25; H, 3.86; N, 1.67. Found (%): C, 50.37; H, 4.03; N, 1.75.

*[Pd($C_6H_4CH{=}NC_6H_3$-2,6-iPr_2)($AsPh_3$)(Cl)] (**5**)*

The procedure yielded 124 mg (87%) of pure product **5** as yellow crystals. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 8.13 (s, 1H, C*H*=N), 7.73–7.71 (m, 7H), 7.47–7.38 (m, 10H), 7.24–7.22 (m, 2H), 7.08–7.04 (m, 1H), 6.74–6.70 (m, 1H), 6.64–6.62 (m, 1H), 3.57(sept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 1.37 (br, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 177.4 (Pd–*C*), 157.5 (*C*H=N), 148.1 (N–*C*), 144.8 (As–*C*), 141.1, 138.0, 134.5, 133.9, 131.0, 130.0, 129.0, 128.6, 127.2, 124.4, 122.9, 28.7 (*C*H(CH_3)$_2$), 23.8 (CH(*C*H$_3$)$_2$). FT-IR (KBr, cm^{-1}): 3045, 2961, 2868, 1602 ($\nu_{C=N}$), 1589, 1575, 1550, 1480, 1465, 1436, 1225, 1179, 737. HRMS (ESI): calcd for $C_{37}H_{37}AsNPd$ $[M - Cl^-]^+$ 676.1177; found 676.1195. Anal. Calcd for [Pd($C_6H_4CH{=}NC6H_3$-2,6-iPr_2)($AsPh_3$)(Cl)] ($C_{37}H_{37}AsClNPd$) (%): C, 62.37; H, 5.23; N, 1.97. Found (%): C, 62.51; H, 5.44; N, 2.31.

*[Pd($C_6H_4CH{=}NC_6H_3$-2,6-iPr_2)($SbPh_3$)(Cl)] (**6**)*

The procedure yielded 131 mg (86%) of pure product **6** as yellow crystals. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 8.15 (s, 1H, C*H*=N), 7.81–7.77 (m, 7H), 7.50–7.41 (m, 10H), 7.37–7.35 (m, 1H), 7.26–7.24 (m, 1H), 7.11–7.07 (m, 1H), 6.93–6.91 (m, 1H), 6.74–6.71 (m, 1H), 3.60 (sept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 1.41 (br, 12H CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 177.0 (Pd–*C*), 155.7 (*C*H=N), 148.1 (N–*C*), 144.0 (Sb–*C*), 141.3, 139.7, 136.7, 131.7, 131.4, 130.1, 129.6, 129.1, 127.3, 124.5, 123.0, 28.7 (*C*H(CH_3)$_2$), 23.8 (CH(*C*H$_3$)$_2$). FT-IR (KBr, cm^{-1}): 3042, 2960, 2866, 1602 ($\nu_{C=N}$), 1577, 1553, 1478, 1464, 1433, 1178, 735. HRMS (ESI): calcd for $C_{37}H_{37}NPdSb$ $[M - Cl^-]^+$ 722.0999; found 722.1027. Anal. Calcd for [Pd($C_6H_4CH{=}NC_6H_3$-2,6-iPr_2)($SbPh_3$)(Cl)] ($C_{37}H_{37}ClNPdSb$) (%): C, 58.52; H, 4.91; N, 1.84. Found (%): C, 58.77; H, 5.16; N, 1.63.

General procedure for Suzuki–Miyaura cross-coupling reaction

A sealable reaction tube equipped with a magnetic stir bar was charged with aryl bromide (0.50 mmol), arylboronic acid (0.60 mmol), K_2CO_3 (1.0 mmol), palladacycle catalyst (0.0025 mmol) and EtOH (2.0 ml). The mixture was heated in an oil bath at 70°C and stirred for 6 h. After the reaction the mixture was cooled to room temperature, the filtrate was concentrated with a rotary evaporator and the residue was then subjected to purification via flash column chromatography with petroleum ether–EtOAc as eluent to give the corresponding pure products.

X-Ray crystallography

Data collection was performed with a Bruker-AXS SMART CCD area detector diffractometer at 296 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.[15] Structure solutions and refinements were performed with the SHELX-97 package.[16] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. The hydrogen atoms to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of carbon atoms. A summary of the crystallographic data, data collection and refinement parameters for complexes **3**–**6** is provided in Table S1. CCDC 1427408, 1427409, 1427410 and 1427411 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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