Inorganica Chimica Acta 363 (2010) 961–966

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Iminophosphinite pincer palladium complexes: Synthesis and application

Jake Yorke [a], Jessica Sanford [a], Andreas Decken [b], Aibing Xia [a,*]

[a] Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada B3M 2J6
[b] Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

ARTICLE INFO

Article history:
Received 29 October 2009
Received in revised form 7 December 2009
Accepted 11 December 2009
Available online 16 December 2009

Keywords:
Palladium complexes
Pincer types
Unsymmetrical ligands
Iminophosphinites
Cross-coupling reactions
The Suzuki reaction

ABSTRACT

Iminophosphinite pincer palladium complexes were synthesized and evaluated as potential catalysts in the Suzuki coupling reactions of phenylboronic acid and various aryl halides. The iminophosphinite ligands were synthesized through condensation reactions between 2-bromo-3-hydroxybenzaldehyde and 2,4,6-trimethylaniline and 2,6-diisopropylaniline, followed by phosphorylation with chlorodiphenylphosphine and chlorodicyclohexylphosphine. Oxidative addition of the pincer ligands to $Pd_2(dba)_3$ afforded palladium iminophosphinite complexes [(2-(CH=NR)-6-(OPR′$_2$)C_6H_3)PdBr] (R = 2,6-^{i}Pr$_2$$C_6H_3$, R′ = Ph (**2a**) or Cy (**2b**); R = 2,4,6-$Me_3C_6H_2$, R′ = Ph (**2c**) or Cy (**2d**)). Reaction of **2b** and silver trifluoroacetate gave the corresponding iminophosphinite palladium trifluoroacetate (**3**). The solid state structures of **2a**, **2d**, and **3** were determined by X-ray single crystal diffraction studies.

1. Introduction

Trident pincer-type transition metal complexes, which contain a central aryl ring with two *ortho*-substituted donor groups, have played an important role in organometallic synthesis and catalysis since Shaw's pioneering work [1]. Their steric and electronic features can be modified at the donor sites as well as the metal sites which may give rise to excellent stability and/or activity. The chemistry of the pincer complexes has been extensively reviewed recently [2–7]. Among the pincer ligands symmetrical pincer types (Fig. 1, $A^1 = A^2$ and/or $E^1 = E^2$), which contains two identical donors at the two *ortho*-positions, are the most common such as PCP and NCN types. However, the unsymmetrical ($A^1 \neq A^2$ and/or $E^1 \neq E^2$) type (e.g. PCN) pincer complexes have attracted increasing attention due to their bonding versatility and catalytic applications [8–16]. When the unsymmetrical ligands contain both soft and hard donors, they may exhibit hemilabile properties which could facilitate substrate interaction with the metal center and stabilize the intermediate in the catalytic cycles [9,10,17–21]. Herein we wish to describe the synthesis, characterization and catalytic application of novel PCN type iminophosphinite pincer palladium complexes.

2. Results and discussion

2.1. Synthesis

The synthetic routes for the palladium complexes were outlined in Scheme 1. Regioselective bromination of 3-hydroxybenzaldehyde in acetic acid gave 2-bromo-3-hydroxybenzaldehyde [22]. Refluxing of 2-bromo-3-hydroxybenzaldehyde with 2,6-diisopropylaniline or 2,4,6-trimethylaniline in ethanol afforded the desired imines **1a** or **1b** as pale yellow solids. The imines reacted readily with chlorodiphenylphosphine or chlorodicyclohexylphosphine at room temperature in the presence of *p*-*N*,*N*-dimethylaminopyridine (DMAP) in THF to afford the corresponding iminophosphinites. As the crude iminophosphinites were often viscous oils and difficult to handle, they were used directly without isolation to react with tris(dibenzylideneacetone)dipalladium(0), $Pd_2(dba)_3$, to give the novel palladium iminophosphinite pincer complexes **2a–2d** in quantitative yields. The formation of arylphosphinite complexes **2a** and **2c** required refluxing, whereas **2b** and **2d** could be obtained at room temperature. While washing the crude products with 30% ethyl acetate/hexane and subsequent recrystallization from CH_2Cl_2/hexane gave crystals of pincer complexes **2a–2c**, we found that **2d** co-crystallized with one equivalent of dba. This is likely due to the solubility similarity of the two compounds in the solvents. The approach to the pincer complex formation via aryl bromide oxidative addition proved to be straightforward and provided higher yields than the alternative approach using C–H activation of non-halogenated aryl ligands [8,9,23]. The reaction

* Corresponding author.
E-mail address: aibing.xia@msvu.ca (A. Xia).

0020-1693/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2009.12.031

of **2d** with silver trifluoroacetate (AgTFA) in THF at room temperature afforded the palladium iminophosphinite trifluoroacetate complex (**3**). The novel iminophosphinite PCN pincer complexes were air and moisture stable, allowing the complexes to be recrystallized with reagent grade solvents and handled in air. They are also thermally stable and have fairly high melting points (e.g. 286 °C for **2b**). The imines and palladium iminophosphinite complexes were characterized by ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR (where applicable) and infrared (IR) spectroscopy. The solid state structures of iminophosphinite PCN pincer complex **2a**, **2d**, and **3** were determined through X-ray diffraction studies. The elemental analysis results matched well with the expected values.

2.2. Characterization

The ^{1}H NMR spectra of imines **1a** and **1b** showed single resonances at 8.45 and 8.55 ppm for the protons of the imine CH=N groups and 5.86 and 5.89 ppm for the protons of O–H groups. The IR spectra showed strong absorptions at 1620 and 1630 cm^{-1}, respectively for **1a** and **1b**, which are typical for the C=N double bond. The ^{1}H NMR spectra of the iminophosphinite pincer complexes **2a–2d** showed an upfield chemical shifts of the imine group to 8.03–8.13 range, with newly acquired coupling to phosphorus (J_{PH} = 4.6 Hz). The methyl groups in the isopropyl moieties in the complexes (**2a**, **2b**, and **3**) split to two signals, compared to a single signal in the free imines **1**. The ^{31}P NMR signals of the complexes are in the range of 157–200 ppm. The IR spectra of the iminophosphinite complexes showed a red-shift of the imine C=N stretches to 1584 cm^{-1}. In **2d**·dba and **3**, strong absorptions were observed at 1680 and 1692 cm^{-1} for the carbonyl groups of dba and trifluoroacetate, respectively.

Suitable crystals of **2a**, **2d**, and **3** for X-ray analysis were grown from saturated solutions of dichloromethane and hexane. In the crystal structure of **2a** there are two independent molecules per asymmetric unit that differ in the orientation of the phenyl groups of the PPh_2 moiety. **2d** and dba molecules were co-crystallized in 1:1 ratio. The molecular structures of complex **2a**, **2d**, and **3** are shown in Figs. 2–4. Selected bond distances and angles are listed in Table 1. Crystal data and structure refinement data are listed in Table 2. The structures are similar and show strongly distorted square–planar geometry around the palladium ion, which bonded to the phosphinite P atom, the central C atom in the aryl ring, the imine N atom, and the Br or O atom. The bond angles of P–Pd–N are 159.0°, suggesting significant strain in the core. The trifluoroacetate complex **3** has a C–Pd–O bond angle of 170.8° whereas the C–Pd–Br bond angles of 176.2° and 179.3° in **2a** and **2d** are closer to linearity. The bond lengths for Pd–C (1.94–1.96 Å), Pd–N (2.14–2.17 Å), Pd–P (2.21–2.22 Å), and Pd–Br (2.48–2.50 Å), and Pd–O (2.09 Å) are comparable to the reported values in related palladium complexes [8–10,13,23–26].

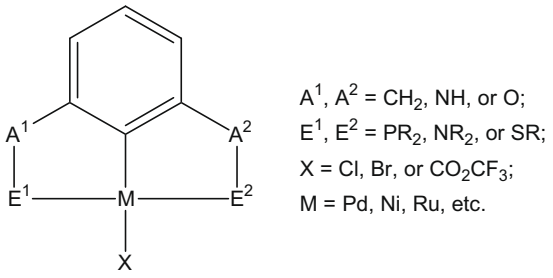
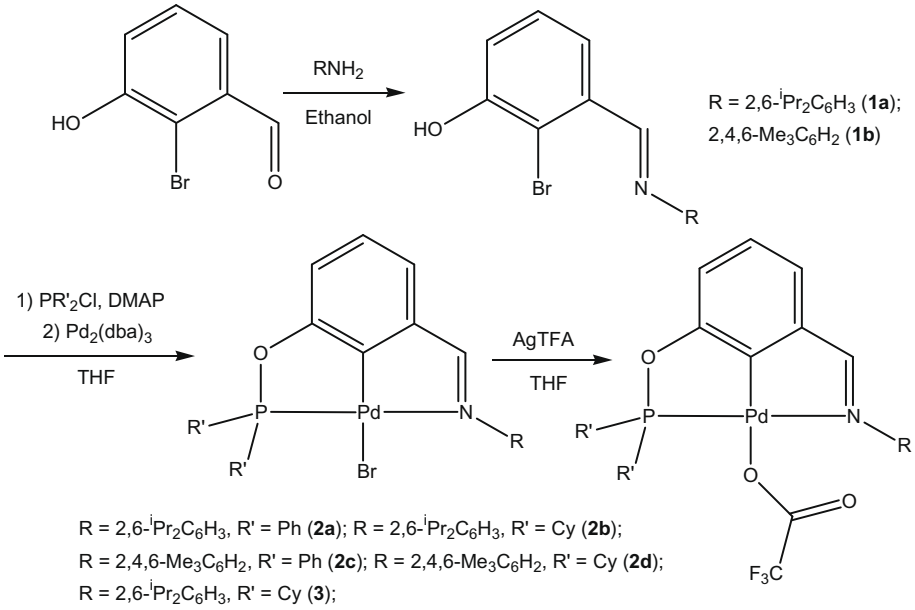


Fig. 1. Pincer complexes.

2.3. Catalytic studies

We evaluated the application of the palladium pincer complexes in the Suzuki coupling reaction, one of the most important palladium-catalyzed cross-coupling carbon–carbon bond forming reactions in organic synthesis [27–32]. The results were listed in Table 3. For screening purposes, we chose 4-bromoanisole, a rather inert aryl bromide, as the organic substrate and investigated a few common solvents and bases. The yields varied dramatically with different solvents and bases, with the combination of Cs_2CO_3 and dioxane affording the best yield when **2a** is used (entry 5). Under similar conditions, other palladium pincer complexes also gave excellent yields (entries 6–9). In addition, excellent yields (entries 7 and 8) were obtained when the experiments were carried out in air using **2c** and **2d**, suggesting the pincer complexes are rather robust in air. These results were comparable to the iminophosphinite



Scheme 1. Synthesis of iminophosphinite pincer palladium complexes.

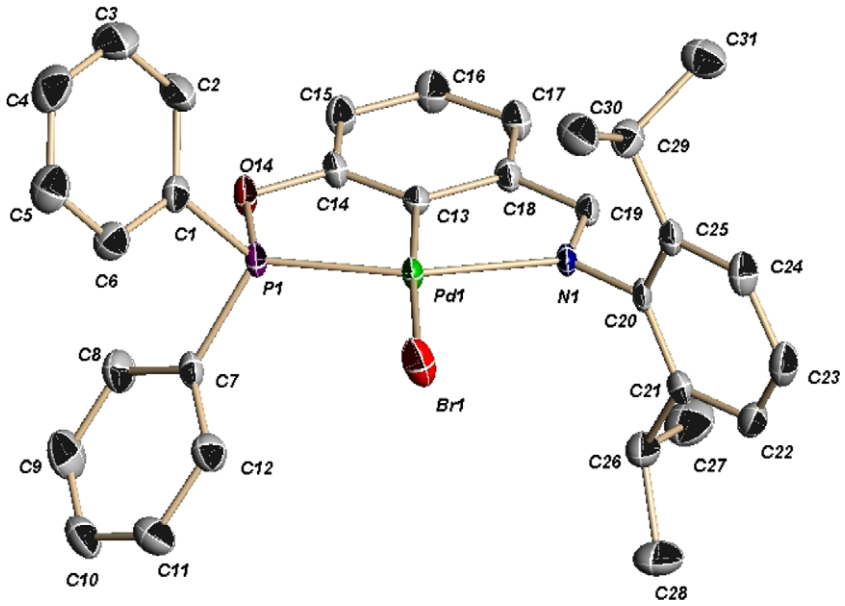


Fig. 2. Molecular structure of **2a** with 50% probability ellipsoids.

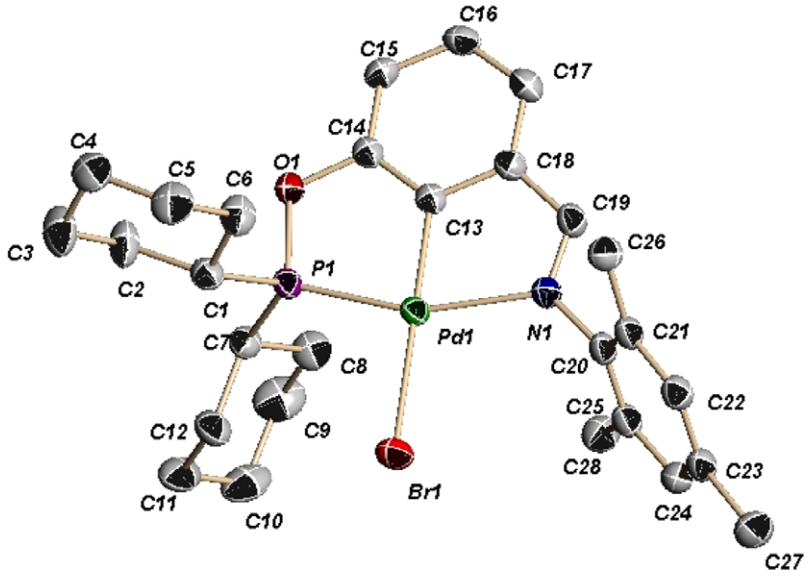


Fig. 3. Molecular structure of **2d** with 50% probability ellipsoids.

palladium chloride complexes Song reported very recently [8]. However, the palladium pincer complexes were not as effective towards aryl chlorides. Only moderate yields were obtained when 4′-chloroacetophenone was used (entries 11–12), while 4-chlorotoluene gave low yields (entries 13, 14). In comparison, recently reported palladium PCN complexes by Song coupled 4-chlorotoluene with moderate yields [10], whereas Dupont's palladium PCN complexes effectively coupled both activated and deactivated aryl chlorides [13]. The higher efficiency in the latter palladium PCN complexes may be attributed to their hemilabile properties, as they contain weakly bonded pyrazolyl or dialkylamino groups that may facilitate substrate interaction with the metal center.

2.4. Conclusion

In summary, we have synthesized and characterized a series of iminophosphinite pincer palladium complexes. The palladium complexes were easy to make, stable in air, and also thermally robust. They were found to be very active toward 4-bromoanisole and moderately active toward aryl chlorides in the Suzuki coupling reaction. The application of the palladium complexes in other catalytic transformations is underway.

3. Experimental

3.1. General procedures

All manipulations were performed under an argon atmosphere unless otherwise specified. All anhydrous solvents were purchased from Sigma–Aldrich Canada Ltd. and stored over 4Å molecular sieves prior to use. Diphenylchlorophosphine, dicyclohexylchlorophosphine, 3-hydroxybenzaldehyde, and 4-*N*,*N*-dimethylaminopyridine were purchased from Sigma–Aldrich Canada Ltd. and used as received. 2-Bromo-3-hydroxybenzaldehyde was prepared according to a literature procedure [22]. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AV-500 spectrometer and referenced

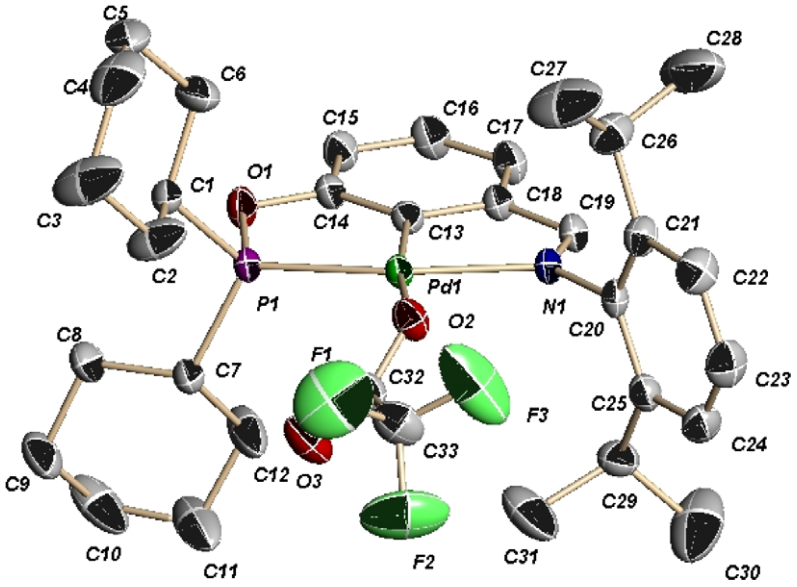


Fig. 4. Molecular structure of **3** with 50% probability ellipsoids.

Table 1
Selected bond lengths (Å) and angles (°) for **2a**, **2d**, and **3**.

Complexes	2a	2d	3
Pd1–C13	1.960(3)	1.961(2)	1.9400(18)
Pd1–N1	2.156(2)	2.1704(17)	2.1357(15)
Pd1–P1	2.2099(7)	2.2077(6)	2.2189(5)
Pd1–Br1	2.4807(4)	2.5012(3)	
Pd1–O2			2.0930(14)
C13–Pd1–N1	78.92(9)	78.84(7)	79.41(7)
C13–Pd1–P1	79.76(8)	79.91(6)	80.09(6)
N1–Pd1–P1	158.64(6)	158.75(5)	159.09(4)
P1–Pd1–Br1	103.80(2)	100.192(16)	
P1–Pd1–O2			108.20(4)
C13–Pd1–Br1	176.24(7)	179.29(6)	
C13–Pd1–O2			170.83(6)
N1–Pd1–Br1	97.55(6)	101.06(5)	
N1–Pd1–O2			92.54(6)

Table 2
Crystal data and structure refinement for **2a**, **2d**, and **3**.

	2a	2d·dba	3
CCDC Number	741752	741753	741754
Formula	$C_{31}H_{31}BrNOPPd$	$C_{45}H_{51}BrNO_2PPd$	$C_{33}H_{43}F_3NO_3PPd$
Formula weight	650.85	855.15	696.05
Crystal size (mm^3)	0.38 × 0.25 × 0.20	0.40 × 0.25 × 0.20	0.60 × 0.60 × 0.55
Space group	*P*2(1)/*n*	$P\bar{1}$	*P*2(1)/*c*
a (Å)	19.936(2)	12.1361(16)	12.8250(9)
b (Å)	14.5068(16)	12.1462(16)	16.3444(11)
c (Å)	20.066(2)	13.9274(18)	16.7050(12)
α (°)	90	87.047(2)	90
β (°)	106.873(1)	89.314(2)	110.031(1)
γ (°)	90	74.170(2)	90
V ($Å^3$)	5553.3(10)	1972.5(4)	3289.8(4)
Z	8	2	4
D_{calc} (g/cm^3)	1.557	1.440	1.405
μ (mm^{-1})	2.189	1.562	0.662
F(0 0 0)	2624	880	1440
θ For data collection (°)	1.27–27.50	1.46–27.50	1.69–27.50
Number of total reflections	37 987	13 611	22 614
Number of unique reflections	12 447	8574	7383
R (all data)	0.0303	0.0277	0.0282
R_w (all data)	0.0809	0.0742	0.0769

to $SiMe_4$ and 85% H_3PO_4, respectively. Infrared spectra were collected on a Nicolet Avatar 330 FT-IR spectrometer. Elemental analyses were carried out by Guelph Chemical Laboratories in Guelph, Ontario. Melting points were recorded on a Mel-Temp (Electrothermal) Apparatus and were uncorrected.

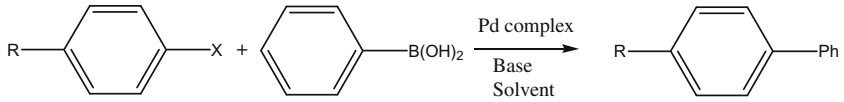
3.2. Synthesis of imines

General procedure: 2-bromo-3-hydroxybenzaldehyde (4.02 g, 20.0 mmol) and 2,6-diisopropylaniline or 2,4,6-trimethylaniline (20.0 mmol) were dissolved in 30 mL ethanol. Formic acid (6 drops) was added to the solution. The resultant yellow solution was refluxed with stirring for 24 h. After being cooled to room temperature, the reaction mixture was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated to dryness under reduced pressure, affording pale yellow solids of **1a** or **1b**.

2-Bromo-3-[(2,6-diisopropyl-phenylimino)methyl]phenol (***1a***): Yield: 5.76 g (82%). Mp 133-135 °C. *Anal.* Calc. for $C_{19}H_{22}BrNO$: C, 63.34; H, 6.15; N, 3.89. Found: C, 63.21; H, 6.45; N, 3.75%. ^1H NMR ($CDCl_3$, 500.13 MHz, ppm): δ 8.45 (s, 1H, C*H*═N), 7.75 (dd, 1H, *J* = 1.7, 7.9 Hz, Ar–H), 7.36 (t, 1H, *J* = 7.9 Hz, Ar–H), 7.10 (m, 4H, Ar–H), 5.86 (s, 1H, O*H*), 2.90 (sept, *J* = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.12 (d, *J* = 6.9 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 125.77 MHz, ppm) δ 161.66, 152.66, 148.72, 137.57, 135.03, 128.86, 124.51, 123.93, 120.93, 118.49, 113.76, 28.03, 23.54. IR (KBr, cm^{-1}): *v* 3367(m), 2959(s), 2866(m),1630(s), 1568(s), 1460(s), 1364(m), 1287(s), 1182(m), 1030(m), 779(m), 752(m), 713(w).

2-Bromo-3-[(2,4,6-trimethylphenylimino)methyl]phenol (***1b***): Yield: 4.762 g (75%). Mp 130–132 °C. *Anal.* Calc. for $C_{16}H_{16}BrNO$: C, 60.39; H, 5.07; N, 4.40. Found: C, 59.86; H, 4.78; N, 4.23%. ^1H ($CDCl_3$, 500.13 MHz, ppm): δ 8.55 (s, 1H, C*H*═N), 7.82 (dd, *J* = 1.5, 7.7 Hz, 1H, Ar–H), 7.32 (t, *J* = 7.7 Hz, 1H, Ar–H), 7.14 (dd, *J* = 1.5, 7.7 Hz, 1H, Ar–H), 6.90 (s, 2H, Ar–H), 5.89 (s, 1H, O*H*), 2.29 (s, 3H, *m*-Ar–CH_3), 2.14 (s, 6H, *o*-Ar–CH_3). ^{13}C NMR ($CDCl_3$, 125.77 MHz, ppm) δ 161.90, 152.68, 148.33, 135.21, 133.47, 128.83, 127.00,

Table 3
Suzuki reactions of selected halides.[a]



Entry	X	R	Base	Solvent	Pd complex	Yield[b] (%)
1	Br	OCH_3	K_2CO_3	Toluene	**2a**	45
2	Br	OCH_3	K_2CO_3	DMF	**2a**	11
3	Br	OCH_3	K_2CO_3	Dioxane	**2a**	53
4	Br	OCH_3	K_3PO_4	Dioxane	**2a**	79
5	Br	OCH_3	Cs_2CO_3	Dioxane	**2a**	97
6	Br	OCH_3	Cs_2CO_3	Dioxane	**2b**	90
7	Br	OCH_3	Cs_2CO_3	Dioxane	**2c**	99 (95)[c]
8	Br	OCH_3	Cs_2CO_3	Dioxane	**2d**·dba	95 (90)[c]
9	Br	OCH_3	Cs_2CO_3	Dioxane	**3**	82
10	Cl	$COCH_3$	Cs_2CO_3	Dioxane	**2b**	58
11	Cl	$COCH_3$	Cs_2CO_3	Dioxane	**2d**·dba	58
12	Cl	$COCH_3$	Cs_2CO_3	Dioxane	**3**	56
13	Cl	CH_3	Cs_2CO_3	Dioxane	**2b**	22
14	Cl	CH_3	Cs_2CO_3	Dioxane	**2d**·dba	29

[a] Aryl halide (1.0 mmol), 1.5 mmol phenylboronic acid, 2.0 mmol base, 0.010 mmol Pd complex, 5 mL solvent, 100 °C, 18 h.
[b] GC yields based on aryl halides.
[c] Experiments carried out in air.

120.69, 118.39, 113.39, 20.88, 18.32. IR (KBr, cm^{-1}): *v* 2949(m), 2774(w), 1637(m), 1567(s), 1462(s), 1359(m), 1235(w), 1202(m), 1027(m), 776(s).

3.3. Synthesis of palladium pincer complexes, [2-(CH=NR)-6-(OPR'_2)C_6H_3)PdBr]

General procedure: **1a** or **1b** (0.360 g, 1.00 mmol) and 4-*N*,*N*-dimethylaminopyridine (0.122 g, 1.00 mmol) were dissolved in THF (10 mL). To the solution was added diphenylchlorophosphine or dicyclohexylchlorophosphine (1.00 mmol) in THF (5 mL). The resultant mixture was stirred for 17 h and filtered. To the filtrate was added $Pd_2(dba)_3$ (0.458 g, 0.50 mmol) in THF (10 mL). The mixture was refluxed for 24 h and cooled to room temperature. After filtration, the volatiles were removed under reduced pressure to afford orange solids in quantitative yields, which were washed with 30% ethyl acetate/hexane (3 × 10 mL) to remove dba and then recrystallized from CH_2Cl_2/hexane.

2a *(R = 2,6-$^iPr_2C_6H_3$, R′ = Ph):* Yield: 0.472 g (73%). Mp 225 °C (dec). *Anal.* Calc. for $C_{31}H_{31}BrNOPPd$: C, 57.20; H, 4.80; N, 2.15. Found: C, 57.34; H, 4.71; N, 1.99%. ^{1}H NMR ($CDCl_3$, 500.13 MHz, ppm): *δ* 8.13 (d, J_{PH} = 5.2 Hz, 1H, C*H*=N), 8.06 (m, 4H, Ar–H), 7.50 (m, 6H, Ar-H), 7.25–7.19 (m, 5H, Ar–H), 7.08 (m, 1H, Ar–H), 3.24 (sept, *J* = 6.9 Hz, 2H, C*H*(CH_3)$_2$), 1.35 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)′(CH_3)″), 1.17 (d, *J* = 6.9 Hz, 6H, CH(CH_3)′(C*H*$_3$)″). ^{13}C NMR ($CDCl_3$, 125.77 MHz, ppm) *δ* 176.35, 161.68, 156.79, 145.47, 144.44, 140.32, 133.17, 132.73, 132.18, 132.06, 128.88, 127.27, 126.99, 123.05, 115.62, 28.55, 24.27, 22.98. ^{31}P NMR ($CDCl_3$, 202.47 MHz, ppm) *δ* 157.67. IR (KBr, cm^{-1}): *v* 2959(m), 1585(m), 1437(m), 1233(s), 1177(w), 1107(s), 1024(w), 746(m), 693(m), 525(m).

2b *(R = 2,6-$^iPr_2C_6H_3$, R′ = Cy):* Yield: 0.513 g (77%). Mp: 286–287 °C. *Anal.* Calc. for $C_{31}H_{43}BrNOPPd$: C, 56.16; H, 6.54; N, 2.11. Found: C, 5.74; H, 6.86; N, 2.12%. ^{1}H NMR ($CDCl_3$, 500.13 MHz, ppm): *δ* 8.09 (d, J_{PH} = 4.6 Hz, 1H, C*H*=N), 7.22–6.92 (m, 6H, Ar–H), 3.21 (sept, *J* = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 2.25–1.60 (m, 20H, Cy), 1.35–1.25 (m, 8H, ^{i}Pr and Cy), 1.17 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)′(CH_3)″). 13C NMR ($CDCl_3$, 125.77 MHz, ppm) *δ* 175.57, 155.76, 145.98, 144.95, 140.32, 127.19, 126.68, 123.33, 122.56, 38.42, 38.16, 28.64, 27.61, 26.58, 25.81, 24.26, 23.23. ^{31}P NMR ($CDCl_3$, 202.47 MHz, ppm) *δ* 201.24. IR (KBr, cm^{-1}): *v* 2959(m), 2929(s), 2858(m), 1584(m), 1458(m), 1383(w), 1324(m), 1234(s), 1178(m), 1043(w), 875(m), 798(s), 749(m).

2c *(R = 2,4,6-$Me_3C_6H_2$, R′ = Ph):* Yield: 0.389 g (64%). Mp: 210–212 °C. *Anal.* Calc. for $C_{28}H_{25}BrNOPPd$: C, 55.24; H, 4.14; N, 2.30. Found: C, 55.47; H, 4.23; N, 2.26%. ^{1}H NMR ($CDCl_3$, 500.13 MHz, ppm): *δ* 8.12 (d, J_{PH} = 4.6 Hz, 1H, C*H*=N), 8.03 (m, 4H, Ar–H), 7.50 (m, 6H, Ar–H), 7.19 (d, *J* = 4.4 Hz, 2H, Ar–H), 7.07 (m, 1H, Ar–H), 6.93 (s, 2H, Ar–H), 2.31 (s, 3H, *m*-Ar–C*H*$_3$), 2.30 (s, 6H, *o*-Ar–C*H*$_3$). ^{13}C NMR ($CDCl_3$, 125.77 MHz, ppm) *δ* 177.07, 162.18, 145.60, 144.71, 136.19, 133.32, 132.09, 131.97, 132.34, 129.56, 128.88, 128.78, 126.98, 122.82, 115.86, 21.02, 19.11. ^{31}P NMR ($CDCl_3$, 202.47 MHz, ppm) *δ* 157.40. IR (KBr, cm^{-1}): *v* 3051(w), 2967(w), 2913(w), 1586(m), 1433(s), 1422(m), 1226(s), 1157(m), 1107(s), 866(s), 754(m), 698(s).

2d *(R = 2,4,6-$Me_3C_6H_2$, R′ = Cy):* Recrystallization from CH_2Cl_2/hexane gave yellow crystals which contained a 1:1 mixture of the pincer complex and dba. *Anal.* Calc. for $C_{45}H_{51}BrNO_2PPd$ (**2d**·dba): C, 63.20; H, 6.01; N, 1.64. Found: C, 63.04; H, 6.24; N, 1.64%. ^{1}H NMR ($CDCl_3$, 500.13 MHz, ppm): *δ* 8.07 (d, J_{PH} = 4.6 Hz, 1H, C*H*=N), 7.76 (d, *J* = 16.1 Hz, 2H, CH=C*H*CO of dba), 7.65 (m, 4H, Ar–H of dba), 7.43 (m, 6H, Ar–H of dba), 7.12–7.09 (m, 5H, C*H*=CHCO of dba and Ar–H of **2d**), 6.91 (s, 2H, Ar–H), 2.30 (s, 3H, *m*-Ar–C*H*$_3$), 1.28 (s, 6H, *o*-Ar–C*H*$_3$), 2.10–1.31 (m, 22H, Cy). ^{31}P NMR ($CDCl_3$, 202.47 MHz, ppm) *δ* 200.37. IR (KBr, cm^{-1}): *v* 3043(w), 2928(s), 1680(s), 1648 (w), 1608(s), 1574(m), 1481(m), 1446(s), 1367(m), 1228(m), 1143(m), 1069(m), 1069(m), 866(s), 773(s), 698(s).

3.4. Synthesis of palladium trifluoroacetate complex (*3*)

To a solution of **2b** (0.133 g, 0.200 mmol) in THF (10 mL) was added a solution of AgTFA (0.044 g, 0.20 mmol) in THF (5 mL). The mixture was stirred at room temperature for 2 h and filtered through a 2-cm bed of celite. The volatiles were removed under vacuum to afford pale yellow solids. Yield: 0.220 g (79%). Mp: 194–196 °C. *Anal.* Calc. for $C_{33}H_{43}F_3NO_3PPd$: C, 56.94; H, 6.23; N, 2.01. Found: C, 56.99; H, 6.48; N, 1.99%. ^{1}H NMR ($CDCl_3$,

500.13 MHz, ppm): δ 8.05 (d, J_{PH} = 4.6 Hz, 1H, C*H*=N), 7.25–7.10 (m, 5H, Ar–H), 6.88 (d, J = 7.9 Hz, 1H, Ar–H), 3.19 (sept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 2.56–1.37 (m, 22H, Cy), 1.25 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)′(CH_3)″), 1.18 (d, J = 6.8 Hz, 6H, CH(CH_3)′(C*H*$_3$)″). ^{31}P NMR ($CDCl_3$, 202.47 MHz, ppm) δ 198.99. IR (KBr, cm^{-1}): ν 2959(m), 2928(s), 2851(m), 1692(s), 1595(m), 1460(m), 1423(m), 1324(w), 1236(m), 1199(s), 1027(w), 875(w), 799(m), 707(w).

3.5. X-ray structures

Crystals of **2a** and **2d** were grown by recrystallization method using dichloromethane and hexanes at −10 °C. Complex **3** was grown by slow evaporation of a dichloromethane/hexane solution under argon. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT) [33] and corrected for absorption (SADABS) [34]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) [35]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

3.6. General procedures for the Suzuki reactions

A 20 mL reaction tube was charged with an aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), palladium pincer complex (0.01 mmol), and a base (2.0 mmol) in 5 mL of solvent under argon and heated to 100 °C for 18 h. The mixture was then cooled to room temperature. The volatiles were removed under a reduced pressure. The organic product was extracted with ether and analyzed on an Agilent 6890 GC-FID instrument. The GC yields were calculated based on unreacted aryl halides and calibrated relative to standards containing authentic samples of aryl halides and their biphenyl products.

Supplementary material

CCDC 741752, 741753 and 741754 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.

Acknowledgements

We thank Natural Science and Engineering Research Council of Canada (NSERC) and Canada Foundation for Innovation (CFI) for financial support.

References

[1] C.J. Moulton, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1976) 1020.
[2] D. Morales-Morales, C.M. Jensen (Eds.), The Chemistry of Pincer Compounds, Elsevier, Amsterdam, 2007.
[3] D. Benito-Garagorri, K. Kirchner, Acc. Chem. Res. 41 (2008) 201.
[4] W. Leis, H.A. Mayer, W.C. Kaska, Coord. Chem. Rev. 252 (2008) 1787.
[5] D. Pugh, A.A. Danopoulos, Coord. Chem. Rev. 251 (2007) 610.
[6] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527.
[7] M.Q. Slagt, D.A.P. van Zwieten, A.J.C.M. Moerkerk, R.J.M.K. Gebbink, G. van Koten, Coord. Chem. Rev. 248 (2004) 2275.
[8] B. Zhang, C. Wang, J. Gong, M. Song, J. Organomet. Chem. 694 (2009) 2555.
[9] B. Ines, I. Moreno, R. SanMartin, E. Dominguez, J. Org. Chem. 73 (2008) 8448.
[10] J. Gong, Y. Zhang, M. Song, C. Xu, Organometallics 26 (2007) 6487.
[11] Y. Motoyama, K. Shimozono, H. Nishiyama, Inorg. Chim. Acta 359 (2006) 1725.
[12] F.S. Mancilha, B.A. Da Silveira Neto, A.S. Lopes, P.F. Moreira Jr., F.H. Quina, R.S. Goncalves, J. Dupont, Eur. J. Org. Chem. (2006) 4924.
[13] G.R. Rosa, C.H. Rosa, F. Rominger, J. Dupont, A.L. Monteiro, Inorg. Chim. Acta 359 (2006) 1947.
[14] B.A. Da Silveira Neto, A. Sant'Ana Lopes, G. Ebeling, R.S. Goncalves, V.E.U. Costa, F.H. Quina, J. Dupont, Tetrahedron 61 (2005) 10975.
[15] C.S. Consorti, G. Ebeling, F.R. Flores, F. Rominger, J. Dupont, Adv. Synth. Catal. 346 (2004) 617.
[16] G.R. Rosa, G. Ebeling, J. Dupont, A.L. Monteiro, Synthesis (2003) 2894.
[17] D. Vuzman, E. Poverenov, L.J.W. Shimon, Y. Diskin-Posner, D. Milstein, Organometallics 27 (2008) 2627.
[18] S.E. Angell, C.W. Rogers, Y. Zhang, M.O. Wolf, W.E. Jones, Coord. Chem. Rev. 250 (2006) 1829.
[19] E. Poverenov, M. Gandelman, L.J.W. Shimon, H. Rozenberg, Y. Ben-David, D. Milstein, Organometallics 24 (2005) 1082.
[20] P. Braunstein, F. Naud, Angew. Chem., Int. Ed. 40 (2001) 680.
[21] C.S. Slone, D.A. Weinberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233.
[22] W.A.L. Van Otterlo, J.P. Michael, M.A. Fernandes, C.B. De Koning, Tetrahedron Lett. 45 (2004) 5091.
[23] K. Takenaka, M. Minakawa, Y. Uozumi, J. Am. Chem. Soc. 127 (2005) 12273.
[24] M.C. Lipke, R.A. Woloszynek, L. Ma, J.D. Protasiewicz, Organometallics 28 (2009) 188.
[25] R. Johansson, M. Jarenmark, O.F. Wendt, Organometallics 24 (2005) 4500.
[26] R.B. Bedford, S.M. Draper, P. Noelle Scully, S.L. Welch, New J. Chem. 24 (2000) 745.
[27] S. Wuertz, F. Glorius, Acc. Chem. Res. 41 (2008) 1523.
[28] N. Marion, S.P. Nolan, Acc. Chem. Res. 41 (2008) 1440.
[29] K.C. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem., Int. Ed. 44 (2005) 4442.
[30] A. Suzuki, Chem. Commun. (2005) 4759.
[31] R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283.
[32] A.F. Littke, G.C. Fu, Angew. Chem., Int. Ed. 41 (2002) 4176.
[33] SAINT 7.23A, Bruker AXS, Inc., Madison, Wisconsin, USA, 2006.
[34] G. Sheldrick, SADABS 2004, Bruker AXS, Inc., Madison, Wisconsin, USA, 2004.
[35] G.M. Sheldrick, Crystallography A64 (2008) 112.