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Mono- and Dinuclear Palladium(II) N,S-Heterocyclic Carbene Complexes with N Spacers and their Suzuki Coupling Activities

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Mixed-ligand N,S-heterocyclic carbene (NSHC) complexes, *trans*-[$PdBr_2$(NSHC)(Py)] (NSHC = 3-benzyl- or 3-propyl-benzothiazolin-2-ylidene), have been obtained from bridge-cleavage reactions of the dinuclear complex, [Pd(μ-Br)Br(NSHC)]$_2$, in pyridine at room temperature. Use of neutral N-bidentate donors (L = pyrazine, 1,2-bis(4-pyridyl)ethane, 4,4′-bipyridine and *trans*-1,2-bis(4-pyridyl)-ethylene) yields the dinuclear spacer-bridged [Pd_2Br_4(NSHC)$_2$(μ-L)] complexes. The X-ray single-crystal structures of the pyridyl, bridging pyrazine and 1,2-bis(4-pyridyl)ethane complexes are reported. These air-stable complexes are active in the Suzuki–Miyaura coupling reactions of selected aryl bromides. The dinuclear complexes are generally more active than their mononuclear pyridyl analogues. The benzyl derivatives consistently outperform the *n*-propyl counterparts.

Keywords: C–C coupling · carbenes · ligand effects · palladium · PEPPSI

Introduction

The discovery of PEPPSI[1] to promote C–C bond formation is an important milestone in modern cross-coupling catalytic chemistry.[1] The major feature in the catalyst design is the combined use of a σ-donating N-heterocyclic carbene (NHC)[2] and a "throw-away" pyridyl ligand.[1] The former is expected to stabilize Pd^0 whilst the latter readily departs to create a vacant site. It is of interest to exploit these ideas on our current N,S-heterocyclic carbene (NSHC) work,[3] amidst a myriad of emerging NSHC systems.[4] We herein report a convenient one-step synthesis through a bridge-cleavage reaction of a known halide-bridged dinuclear NSHC complex.[3a,c] This methodology enables facile access to the NSHC analogue of PEPPSI and selected examples of other dinuclear complexes with mixed ligands of NSHC and bipyridyl or pyrazine-based heterocycles. The use of sp^2 nitrogen donors to support and activate the metal for catalysis is another emerging idea in coordination catalysis.[5] The use of nitrogen spacers with different labilities in a dinuclear framework also provides a model to test the catalytic benefits of dissociative ligand and non-interacting bimetallic catalytic sites.

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[1] The PEPPSI (Pyridine-enhanced precatalyst, preparation, stabilization and initiation) catalyst has been developed as an air-stable commercial catalyst to promote cross-coupling reactions. See Ref. [1].

Results and Discussion

Synthesis

The dinuclear carbene complexes **1–2**[3a,c] (Scheme 1) easily undergo bridge-cleavage reactions in a coordinating solvent such as CH_3CN and DMF to give the solvated monocarbene complexes.[3a] In the presence of an N ligand [viz. pyrazine (pyz), 1,2-bis(4-pyridyl)ethane (bpa), 4,4′-bipyridine (bpy) and *trans*-1,2-bis(4-pyridyl)ethylene (bpe)] at RT in CH_2Cl_2 or pyridine (Scheme 1), they give the corresponding di- and mononuclear complexes as yellow solids in moderate (53–80%) (**5–12**) to near-quantitative (~98%) yields (**3–4**) (Scheme 1). ^{1}H NMR analysis of the products is consistent with the mixed-ligand formulation. All the complexes are stable except **5** and **6**, the ^{1}H NMR spectra ($CDCl_3$ or CD_3OD) of which show resonances attributed to free pyrazine. Dissociation is even more significant in CD_3CN solution, which gives the solvento complex. The ^{13}C carbenoid resonance of **3** (δ = 195.7 ppm), **4** (δ = 193.3 ppm), **5** (δ = 191.8 ppm), **11** (δ = 195.8 ppm), and **12** (δ = 193.2 ppm) are

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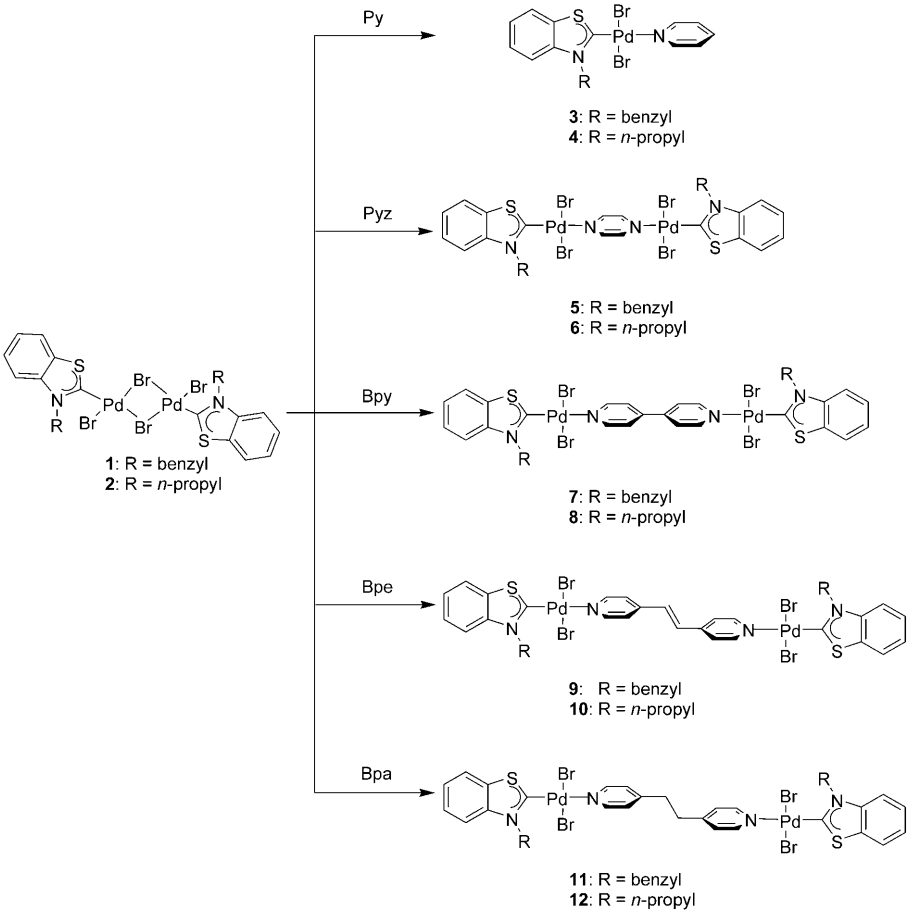

Scheme 1. Bridge-cleavage reaction of **1**–**2** to give mixed-ligand complexes **3**–**12**.

shifted down-field compared to the mononuclear solvated CH_3CN ($\delta = 191.5$ ppm) and DMF ($\delta = 191.9$ ppm) complexes,[3a] attributed probably to the inductive effect of pyridyl- or the N-heterocyclic rings. The carbene resonance was not detected in **6**, **7**, and **9** whereas the solubility of **8** and **10** was too poor to allow accurate measurement. ESI-MS analysis of these complexes generally show the parent and/or their fragment ions except for complexes **7**, **9**, and **10** that are too insoluble to exhibit any such signals.

Crystallographic Structures

X-ray single-crystal diffraction studies were carried out on **3**, **4**, **5**, and **11** (Figure 1 and Table 1). As expected, the Pd^{II} center is essentially square planar. In agreement with the spectroscopic data, the incoming N donor is invariably *trans* to the NSHC ligand. The complexes **3** and **4** are mononuclear and isostructural. The Pd–$C_{carbene}$ bonds (1.958(8) and 1.949(3) Å in **3** and **4**, respectively) are slightly longer and presumably weaker compared to those of the solvated DMF (1.921(2) Å) and CH_3CN (1.936(3) Å) complexes,[3a] suggesting a higher *trans*-influence of pyridine. They are closer to that of PEPPSI–IPr (1.969(3) Å),[1a] thus indicating similar strength. Those of **5** (1.941(3) Å) and **11** (1.947(4) and 1.959(4) Å) are marginally shorter than those of the 1,3-diisopropylbenzimidazolin-2-ylidene analogues (1.955(8)–1.959(7) Å),[6] probably as a result of the higher steric effect of the latter. The Pd–N lengths of these four complexes (2.110(7)–2.086(3) Å) are within the range of related complexes, PEPPSI–IPr and PEPPSI with N/O-functionalized NHCs (2.137(2)–2.089(3) Å).[1a,7] The complexes **5** and **11** are dinuclear with the spacer *trans* to the carbene donor. The two benzyl substitutents across the bridge are *anti* to each other in **5**, but *syn* in **11**. The non-interactive Pd···Pd separation increases from 6.98 Å in **5** to 13.40 Å in **11** without any apparent adverse effect on the key bond lengths in the coordination spheres. Both NSHC and the N-ring planes are twisted away from the Pd^{II} coordination planes to avoid inter-ligand conflicts, with the NSHC closer to perpendicular (65.1–79.8°) than the N ligand (43.7–67.0°) planes. The two pyridyl planes of the bpa spacer in **11** are also twisted away (55.1°) from each other.

Suzuki–Miyaura Coupling

Encouraged by the high activities shown by the PEPPSI precatalysts in Suzuki–Miyaura cross-coupling,[1a] we have examined the use of the present complexes in similar couplings of representative aryl bromides with phenylboronic acid in DMF in the presence of Cs_2CO_3 (Table 2). An advantage of these reactions is that they can be conveniently handled in air without the need for a glove-box or vigorous Schlenk techniques. The activities are sufficiently high in catalytic loadings from 0.5 to 2.0 mol%. The complexes **3**–**12** gave quantitative yields toward activated substrates such as 4-bromobenzaldehyde within 1 h at 100 °C (Table 2, Entries 1 and 4–14). Complexes **5–8** and **11** were able to maintain the quantitative yields even at RT, albeit with longer reaction periods (Table 2, Entries 19–23 and 27). This gave the first indication that, under ambient conditions, the dinuclear spacer-stabilised complexes, with the dpe complexes (**9** and **10**) being the notable exceptions, are more active than the mononuclear pyridine complexes (**3** and **4**) (Table 2, Entries 15–28 and Figure 2). The lower activities of **9** and **10**

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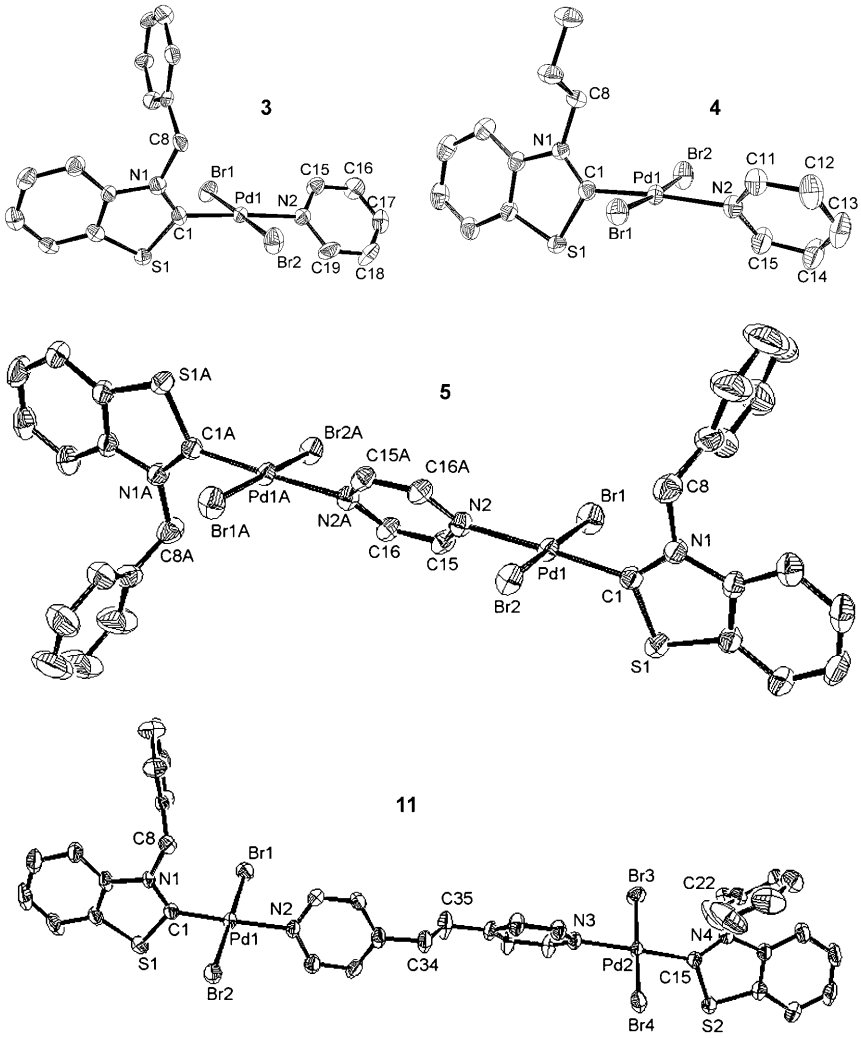

Figure 1. ORTEP view of complexes **3**, **4**, **5** and **11** with 50% thermal ellipsoids; hydrogen atoms are omitted for clarity.

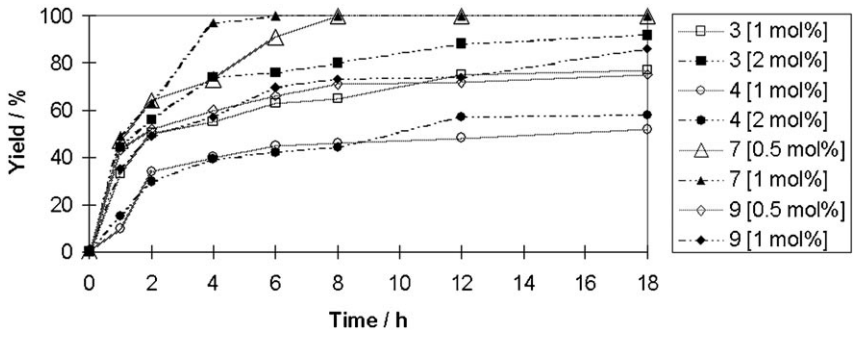

Figure 2. Suzuki coupling of 4-bromobenzaldehyde promoted by **3**, **4**, **7**, and **9** at RT with 0.5–2.0 mol% catalyst loading.

can be explained by their lower solubility in the catalytic mixtures.

Toward unactivated substrates such as 4-bromoanisole, these complexes were still active but began to show some differentiations (Table 2, Entries 29–38). Relatively poor yields were witnessed in the case of the mononuclear complexes, **3** and **4**, while the dinuclear complexes generally performed better, the only exception being **10**. The best performance (>90%) was found with **7** and **8**, which have the optimal separation between the two non-interactive Pd centers, minimum steric hindrance, and free rotation at the central bipy spacer. The more stable benzyl derivatives (viz. **3**, **5**, **7**, **9**, and **11**) consistently performed better with higher yields than their *n*-propyl (**4**, **6**, **8**, **10**, and **12**) counterparts. Similar observation has been reported in the literature.[3c] Under similar conditions, complex **7** was comparable with a mixture of $[PdBr_2(NSHC)(PPh_3)]$ with 3-benzylbenzothiazolin-2-ylidene or $[PdBr_2(PPh_3)_2]$.[3c] Toward 4-chlorobenzaldehyde, it gave a 38% yield of biphenyl-4-carbaldehyde.

As **7** could be easily prepared, was air stable, and was among the best catalysts in this series, it was chosen as a model for examination of responses toward different aryl boronic acids and under different catalyst loadings (Table 3). It is significant that phenyl boronic acid and *p*-tolylicboronic acid can still couple with near-quantitative yield at a low catalyst loading of 0.01 mol% (Table 3, Entries 1–2, 5–6, 9–10, and 13–14). It is also effective toward 3-(trifluoromethyl)phenylboronic acid, giving 84–99%, with 0.01–1.0 mol% catalyst loading (Table 3, Entries 3, 7, 11, and 15). It is also active toward 3-pyridylboronic acid (6–40%) with 0.01–1 mol% catalyst loadings, thus pointing a way toward heteroaryl-couplings.

This catalytic enhancement by a dinuclear core cannot simply be attributed to the presence of two active metal sites within a molecular complex. For example, increasing the load of **3** and **4** by two-fold (from 1 to 2 mol%) merely

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Table 1. Selected bond lengths and angles for complexes **3**, **4**, **5** and **11**.

	3	**4**	**5**	**11**
Bond Lengths [Å]				
Pd1-C1	1.958(8)	1.949(3)	1.941(3)	1.947(4)
Pd1-N2	2.110(7)	2.099(2)	2.102(2)	2.086(3)
Pd1-Br1	2.429(1)	2.425(3)	2.418(4)	2.434(6)
Pd1-Br2	2.421(1)	2.426(3)	2.436(4)	2.444(6)
Pd2-C15	–	–	–	1.959(4)
Pd2-N3	–	–	–	2.099(3)
Pd2-Br3	–	–	–	2.439(6)
Pd2-Br4	–	–	–	2.429(6)
S1-C1	1.697(9)	1.713(3)	1.713(3)	1.714(4)
N1-C1	1.332(10)	1.330(3)	1.324(4)	1.333(5)
N1-C8	1.481(10)	1.473(3)	1.466(4)	1.474(5)
N2-C15	–	–	1.344(4)	–
N2-C16	–	–	1.335(4)	–
S2-C15	–	–	–	1.712(4)
N4-C15	–	–	–	1.332(5)
N4-C22	–	–	–	1.482(6)
C34-C35	–	–	–	1.493(6)
Pd···Pd[a]	–	–	6.98	13.40
Angles [deg]				
C1-Pd1-N2	176.90(3)	175.23(10)	175.97(11)	177.11(17)
C15-Pd2-N3	–	–	–	178.01(17)
C1-Pd1-Br1	87.50(2)	89.26(8)	87.36(8)	90.45(13)
C15-Pd2-Br3	–	–	–	90.99(13)
C1-Pd1-Br2	89.90(2)	87.47(8)	89.52(8)	88.78(13)
C15-Pd2-Br4	–	–	–	89.09(13)
N2-Pd1-Br1	91.31(19)	91.27(6)	90.95(6)	89.67(10)
N3-Pd2-Br3	–	–	–	89.77(10)
N2-Pd1-Br2	91.25(19)	92.26(6)	92.37(6)	91.16(10)
N3-Pd2-Br4	–	–	–	89.77(10)
Br1-Pd1-Br2	177.44(4)	175.35(13)	175.47(15)	178.50(2)
Br3-Pd1-Br4	–	–	–	175.81(2)
C1-N1-C8	124.50(7)	122.80(2)	123.30(3)	122.80(3)
N1-C1-S1	111.10(6)	110.70(18)	111.30(2)	110.30(3)
N4-C15-S2	–	–	–	110.30(3)
N1-C1-Pd1	129.20(6)	130.19(19)	129.90(2)	126.50(3)
N4-C15-Pd2	–	–	–	129.60(3)
S1-C1-Pd1	119.70(5)	119.05(14)	118.73(17)	123.10(2)
S2-C15-Pd2	–	–	–	120.10(2)
C16A-N2-C15	–	–	117.00(2)	–
C16A-N2-Pd1	–	–	123.34(19)	–
C15-N2-Pd1	–	–	119.61(19)	–
Dihedral angle PdCNBr2/pyridine ring	43.7	53.8	45.2	59.3 67.0
Dihedral angle PdCNBr2/NSHC carbene plane	73.5	79.8	75.8	65.1 76.3

[a] intramolecular Pd···Pd distances.

raises the yields by ~20% (Table 2, Entries 15–18), which still falls short of the quantitative yields obtained with the dinuclear complexes (Table 2, Entries 19–23 and 27). To further examine the relationship between complex nuclearity and yield, we have selected **3**, **4**, **7**, and **9** as models for a time-conversion study (Figure 2). The bromobenzaldehyde reactions were performed at RT and the GC yields monitored over a period of 18 h with the catalyst loading of 0.5–2.0 mol%. In these conditions, only **7** was able to give quantitative yields within 6 h. Even when the loading was reduced by 2-fold to 0.5 mol%, under which **3** and **4** would be sluggish, it was able to achieve quantitative conversion within 8 h. The other dinuclear complex (**9**) was less impressive although it gave satisfactory yields (~80%) within 18 h. An advantage of **9** is that a reduction of loading to 0.5 mol% would not significantly affect its productivity. On the other hand, complex **4** was still inept when its load was doubled from 1 to 2 mol%. Complex **3** was better but the yield improvement was within 20%, and still could not reach a quantitative yield after 18 h, when the load was raised by 2-fold. These results suggest that, in this system, the mononuclear complexes cannot match the performance of the dinuclear species on the "per Pd" loading basis. This may be attributed to the higher stability of the latter rendered by the N-bidentate donors.

A distinct advantage of the current system is the use of a simple one-step method to enter into a range of dinuclear spacer-stabilized complexes that can in principle accommodate a range of bridging entities of different electronic and steric demands. Such versatility would significantly enhance our capability to search for the "universal" catalyst for C–C cross-couplings.

Conclusions

We have demonstrated that the PEPPSI-type chemistry can be extended to NSHC-carbene and other N ligands related to pyridyl. The use of NSHC as a support ligand, despite its single exocyclic substituent and lower steric protective ability compared to the more common NHC ligands, does not appear to have any adverse effects on the chemical stability of the complexes or their catalytic performance. These, together with our earlier work on the thiazole-2-ylidene catalysts,[3] as well as the similar findings of Grubbs on the Ru-based NHSC olefin metathesis catalysts,[8] suggest that NSHC-type ligands show good potential as phosphine and NHC-alternatives. The combinative use of dinuclear complexes, NSHC carbenes, and N-based spacers as the three main features of this system has presented a range of opportunities in our current exploration.

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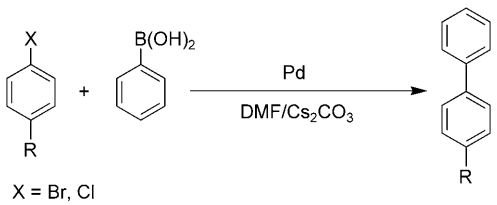
Table 2. Suzuki Coupling Reactions[a] catalyzed by complexes **3**–**12**.



X = Br, Cl
R = CHO, OCH_3

Entry	[Pd]	Aryl halide	*T*	Cat. loading [mol%]	*t* [h]	Yield[b] [%]
1	**3**	4-bromobenzaldehyde	100	1	1	100
2	**4**	4-bromobenzaldehyde	30	1	1	21
3	**4**	4-bromobenzaldehyde	70	1	1	98
4	**4**	4-bromobenzaldehyde	100	1	1	100
5	**3**	4-bromobenzaldehyde	100	2	1	100
6	**4**	4-bromobenzaldehyde	100	2	1	100
7	**5**	4-bromobenzaldehyde	100	1	1	100
8	**6**	4-bromobenzaldehyde	100	1	1	100
9	**7**	4-bromobenzaldehyde	100	1	1	100
10	**8**	4-bromobenzaldehyde	100	1	1	100
11	**9**	4-bromobenzaldehyde	100	1	1	100
12	**10**	4-bromobenzaldehyde	100	1	1	100
13	**11**	4-bromobenzaldehyde	100	1	1	100
14	**12**	4-bromobenzaldehyde	100	1	1	100
15	**3**	4-bromobenzaldehyde	RT	1	18	77
16	**3**	4-bromobenzaldehyde	RT	2	18	92
17	**4**	4-bromobenzaldehyde	RT	1	18	52
18	**4**	4-bromobenzaldehyde	RT	2	18	58
19	**5**	4-bromobenzaldehyde	RT	1	18	100
20	**6**	4-bromobenzaldehyde	RT	1	18	100
21	**7**	4-bromobenzaldehyde	RT	1	18	100
22	**7**	4-bromobenzaldehyde	RT	0.5	18	100
23	**8**	4-bromobenzaldehyde	RT	1	18	100
24	**9**	4-bromobenzaldehyde	RT	0.5	18	75
25	**9**	4-bromobenzaldehyde	RT	1	18	86
26	**10**	4-bromobenzaldehyde	RT	1	18	64
27	**11**	4-bromobenzaldehyde	RT	1	18	100
28	**12**	4-bromobenzaldehyde	RT	1	18	87
29	**3**	4-bromoanisole	100	1	65	27
30	**4**	4-bromoanisole	100	1	65	13
31	**5**	4-bromoanisole	100	1	65	62
32	**6**	4-bromoanisole	100	1	65	54
33	**7**	4-bromoanisole	100	1	65	94
34	**8**	4-bromoanisole	100	1	65	90
35	**9**	4-bromoanisole	100	1	65	33
36	**10**	4-bromoanisole	100	1	65	27
37	**11**	4-bromoanisole	100	1	65	58
38	**12**	4-bromoanisole	100	1	65	45
39	**7**	4-chlorobenzaldehyde	100	1	65	38

[a] 1 mmol of Ar-X, 2 mmol of Cs_2CO_3, 1.5 mmol of Ph-$B(OH)_2$. [b] GC/MS determination by using n-dodecane as the internal standard for an average of two runs.

Experimental Section

General

Unless otherwise stated, all manipulations, including the catalytic runs, were performed without taking precautions to exclude air and moisture. *N*,*N*-Dimethylformamide used for the Suzuki reaction was purchased from J. T. Baker ("Baker analyzed" ACS reagent). All solvents were used as received. Benzothiazole was purchased from Sigma–Aldrich and distilled prior to use. $Pd(OAc)_2$, pyrazine, *trans*-1,2-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridyl)ethane, 4,4′-bipyridine were purchased from Sigma–Aldrich and used as received. Dibromo(μ-dibromo)bis(3-benzylbenzothiazolin-2-ylidene)dipalladium(II) and dibromo(μ-dibromo)bis(3-propylbenzothiazolin-2-ylidene)dipalladium(II) were prepared according to the literature methods.[3a,c] ^{1}H and ^{13}C spectra were recorded on a Bruker AMX 500 spectrometer using Me_4Si as the internal standard. ESI mass spectra were obtained using a Finnigan LCQ spectrometer. The yields of C–C coupling products were determined by using a Hewlett–Packard Series 6890 GC (Santa Clara, CA, USA) coupled to a Hewlett Packard 5973 MS detector. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry of the National University of Singapore.

3: *trans*-Dibromo(3-benzylbenzothiazolin-2-ylidene)-(pyridine)palladium(II): Pyridine (5 mL) was added to complex **1** (60 mg, 0.06 mmol) and the mixture was stirred at RT overnight. The resulting clear yellow solution was evaporated under vacuum. The yellow solid obtained was dissolved in CH_2Cl_2, and Et_2O was added to induce precipitation. The product was washed with Et_2O and dried. Diffusion of Et_2O into a sample solution in CH_2Cl_2 yielded yellow crystals suitable for X-ray diffraction studies. Yield: 68 mg (0.12 mmol, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.01$ (m, 2H, Ar-H), 7.81 (d, $^3J_{HH} = 8.9$ Hz, 1H, Ar-H), 7.76 (tt, $^3J_{HH} = 1.6$ Hz, $^2J_{HH} = 7.9$ Hz, 1H, Ar-H), 7.57 (d, $^3J_{HH} = 6.9$ Hz, 2H, Ar-H), 7.44 (d, $^3J_{HH} = 8.2$ Hz, 1H, Ar-H), 7.40–7.31 (m, 7H, Ar-H), 6.54 ppm (s, 2H, CH_2); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 195.7$ (NCS), 162.7, 147.9, 142.8, 130.9, 129.6, 129.3, 129.1, 128.5, 128.2, 127.9, 127.6, 126.7, 125.1, 124.7, 124.5, 121.8, 115.1 (Ar-C), 60.1 ppm (CH_2); MS (ESI, positive mode) *m/z* (%): 571 (100) $[M+H]^+$; elemental analysis: calcd (%) for $C_{19}H_{16}Br_2PdN_2S.CH_2Cl_2.py$ (M = 734.67): C 40.87, H 3.16, N 5.72, S 4.36; found: C 40.99, H 3.19, N 5.72, S 4.96.

4: *trans*-Dibromo(3-propylbenzothiazolin-2-ylidene)-(pyridine)palladium(II): Complex **4** was prepared in analogy to **3** from **2** (79 mg, 0.089 mmol). Diffusion of Et_2O into a solution of **4** in CH_2Cl_2 yielded yellow crystals suitable for X-ray diffraction studies. Yield: 91 mg (0.178 mmol, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.04$ (d, $^3J_{HH}$ = 6.4 Hz, 2H, Ar-H), 7.82 (d, $^3J_{HH} = 8.0$ Hz, 1H, Ar-H), 7.79 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.68 (d, $^3J_{HH} = 8.2$ Hz, 1H, Ar-H), 7.51 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Ar-H), 7.42 (t, $^3J_{HH} = 7.6$ Hz, 1H, Ar-H), 7.37 (t, $^3J_{HH}$ = 6.9 Hz, 2H, Ar-H), 5.15 (t, $^3J_{HH} = 8.2$ Hz, 2H, $CH_2CH_2CH_3$), 2.35 (m, $^3J_{HH} = 7.9$ Hz, 2H, $CH_2CH_2CH_3$), 1.22 ppm (t, $^3J_{HH} = 7.6$ Hz, 3H, $CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 193.3$ (NSC), 154.4, 152.7, 149.8, 142.8, 138.1, 136.7, 126.7, 125.1, 124.7, 121.9, 113.8 (Ar-C), 56.9 ($CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_3$), 11.7 ppm ($CH_2CH_2CH_3$); MS (ESI, positive mode) *m/z* (%): 443 (40) $[M-Br]^+$; elemental analysis: calcd (%) for $C_{15}H_{16}Br_2N_2PdS$ (M = 522.59): C 34.47, H 3.09, N 5.36, S 6.14; found: C 35.65, H 2.98, N 5.54, S 6.09.

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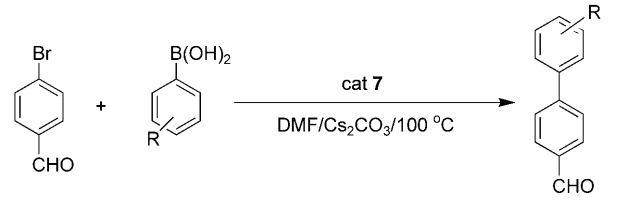
Table 3. Suzuki–Miyaura Coupling Reactions[a] catalyzed by complex **7** in different boronic acids.



Entry	Boronic acids	Cat. **7** [mol%]	*t* [h]	Yield[b] [%]
1	phenyl	1	0.5	100
2	4-tolyl	1	0.5	100
3	3-(trifluoro-methyl)phenyl	1	0.5	99
4	3-pyridyl	1	0.5	40
5	phenyl	0.5	0.5	100
6	4-tolyl	0.5	0.5	100
7	3-(trifluoro-methyl)phenyl	0.5	0.5	98
8	3-pyridyl	0.5	0.5	25
9	phenyl	0.25	5.0	100
10	4-tolyl	0.25	5.0	99
11	3-(trifluoro-methyl)phenyl	0.25	5.0	97
12	3-pyridyl	0.25	5.0	8
13	phenyl	0.01	5.0	98
14	4-tolyl	0.01	5.0	98
15	3-(trifluoro-methyl)phenyl	0.01	5.0	84
16	3-pyridyl	0.01	5.0	6

[a] 1 mmol of 4-bromobenzldehyde, 2 mmol of Cs_2CO_3, 1.5 mmol of boronic acids. [b] GC/MS determination by using n-dodecane as the internal standard for an average of two runs.

5: Dibromo(μ-pyrazine)bis(3-benzylbenzothiazolin-2-ylidene)dipalladium(II): A mixture of **1** (122 mg, 0.12 mmol) and pyrazine (9.9 mg, 0.12 mmol) was suspended in CH_2Cl_2 (5 mL) and stirred at RT overnight. Et_2O (15 mL) was added to give a yellow precipitate, which was collected by filtration. Diffusion of Et_2O into a CH_2Cl_2 solution of the complex yielded yellow crystals suitable for X-ray diffraction studies. Yield: 66 mg (0.062 mmol, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.22 (s, 4H, Ar-H), 7.83 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-H), 7.52 (d, $^3J_{HH}$ = 6.9 Hz, 4H, Ar-H), 7.46 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.41–7.33 (m, 10H, Ar-H), 6.46 ppm (s, 4H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 191.8 (NSC), 148.4, 147.6, 146.9, 146.4, 142.7, 136.7, 133.2, 129.2, 128.7, 127.6, 126.9, 125.4, 121.8, 115.2 (Ar-C), 60.2 ppm (CH_2); MS (ESI) *m/z* (%): 1080 (30) $[M+Na]^+$; elemental analysis: calcd (%) for $C_{32}H_{26}Br_4N_4Pd_2S_2$ (M = 1063.16): C 36.15, H 2.46, N 5.27, S 6.03; found: C 36.83, H 2.76, N 4.76, S 6.25.

6: Dibromo(μ-pyrazine)bis(3-propylbenzothiazolin-2-ylidene)dipalladium(II): Complex **6** was prepared in analogy to **5**, from **2** (127 mg, 0.14 mmol) and pyrazine (11.5 mg, 0.14 mmol). Yield: 73.4 mg (0.076 mmol, 53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.30 (s, 4H, Ar-H), 7.85 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.71 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar-H), 7.55 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Ar-H), 7.46 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-H), 5.10 (t, $^3J_{HH}$ = 8.2 Hz, 4H, $CH_2CH_2CH_3$), 2.32 (m, $^3J_{HH}$ = 7.8, 4H, $CH_2CH_2CH_3$), 1.22 ppm (t, $^3J_{HH}$ = 7.6, 6H, $CH_2CH_2CH_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 148.3, 146.9, 142.7, 136.6, 126.9, 125.3, 122.0, 113.9 (Ar-C), 57.2 ($CH_2CH_2CH_3$), 21.9 ($CH_2CH_2CH_3$), 11.6 ppm ($CH_2CH_2CH_3$); MS (ESI) *m/z* (%): 985 (10) $[M-Br+3CH_3OH]^+$; elemental analysis: calcd (%) for $C_{24}H_{26}Br_4N_4Pd_2S_2$ (M = 967.08): C 29.81, H 2.71, N 5.79, S 6.63; found: C 29.92, H 2.74, N 5.53, S 6.15.

7: Dibromo(μ-4,4′-bipyridine)bis(3-benzylbenzothiazolin-2-ylidene)dipalladium(II): Complex **7** was prepared in analogy to **5**, from **1** (122 mg, 0.12 mmol) and 4,4′-bipyridine (19 mg, 0.12 mmol). Yield: 89 mg (0.072 mmol, 60%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.03 (s, 3H, Ar-H), 8.76 (s, 5H, Ar-H), 8.18–8.02 (m, 4H, Ar-H), 7.89 (s, 2H, Ar-H), 7.75–7.51 (m, 8H, Ar-H), 7.37 (s, 4H, Ar-H), 6.63 ppm (s, 4H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): δ = 141.9, 134.9, 134.1, 128.6, 128.0, 127.1, 126.9, 125.5, 122.7, 115.8 (Ar-C), 58.2 ppm (CH_2); elemental analysis: calcd (%) for $C_{38}H_{30}Br_4N_4Pd_2S_2.CH_2Cl_2$ (M = 1224.19): C 38.26, H 2.63, N 4.58, S 5.24; found: C 39.69, H 2.46, N 4.69, S 5.39.

8: Dibromo(μ-4,4′-bipyridine)bis(3-propylbenzothiazolin-2-ylidene)dipalladium(II): Complex **8** was prepared in analogy to **5** from **2** (100 mg, 0.11 mmol) and 4,4′-bipyridine (17.2 mg, 0.11 mmol). Yield: 61 mg (0.058 mmol, 52%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.05 (m, 3H, Ar-H), 8.78 (s, 1H, Ar-H), 8.18 (m, 4H, Ar-H), 8.07 (m, 3H, Ar-H), 7.89 (s, 1H, Ar-H), 7.66 (t, $^3J_{HH}$ = 6.9 Hz, 2H, Ar-H), 7.56 (t, $^3J_{HH}$ = 6.9 Hz, 2H, Ar-H), 5.21 (br s, 4H, $CH_2CH_2CH_3$), 2.25 (broad s, 4H, $CH_2CH_2CH_3$), 1.14 ppm (br s, 6H, $CH_2CH_2CH_3$); MS (ESI) *m/z* (%): 964 (20) $[M-Br]^+$; elemental analysis: calcd (%) for $C_{30}H_{30}Br_4N_4Pd_2S_2$ (M = 1043.17): C 34.54, H 2.90, N 5.37, S 6.15; found: C 34.90, H 2.88, N 5.31, S 6.08.

9: Dibromo[μ-*trans*-1,2-bis(4-pyridyl)ethylene]bis(3-benzylbenzothiazolin-2-ylidene)dipalladium(II): Complex **2** was prepared in analogy to **5**, from **1** (215 mg, 0.22 mmol) and *trans*-1,2-bis(4-pyridyl)ethylene (40 mg, 0.22 mmol). Yield: 204 mg (0.175 mmol, 80%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.90 (s, 4H, Ar-H), 8.17 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.78 (s, 2H, C*H*=C*H*), 7.74–7.64 (m, 8H, Ar-H), 7.51–7.50 (m, 5H, Ar-H), 7.39–7.37 (m, 5H, Ar-H), 7.23 (s, 2H, Ar-H) 6.62 ppm (s, 4H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): δ = 153.0, 142.5, 136.1, 134.8, 132.3 (Ar-C), 129.2, 128.7 (CH_2=CH_2), 128.5, 128.3, 127.6, 127.5, 127.4, 126.0, 125.9, 123.2, 123.0, 116.3, 115.9 (Ar-C), 59.0 ppm (CH_2); elemental analysis: calcd (%) for $C_{40}H_{32}Br_4N_4Pd_2S_2$ (M = 1165.29): C 41.23, H 2.77, N 4.81, S 5.50; found: C 40.06, H 2.71, N 4.99, S 5.15.

10: Dibromo[μ-*trans*-1,2-bis(4-pyridyl)ethylene]bis(3-propylbenzothiazolin-2-ylidene)dipalladium(II): Complex **10** was prepared in analogy to **5**, from **2** (218 mg, 0.24 mmol) and *trans*-1,2-bis(4-pyridyl)ethylene (44 mg, 0.24 mmol). Yield: 184 mg (0.17 mmol, 70%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.91 (s, 4H, Ar-H), 8.17 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar-H), 7.81 (s, 4H, Ar-H), 7.72 (s, 2H, C*H*=C*H*), 7.66 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Ar-H), 7.56 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Ar-H), 5.20 (t, $^3J_{HH}$ = 7.3 Hz, 4H, $CH_2CH_2CH_3$), 2.24 (m, $^3J_{HH}$ = 7.4 Hz, 4H, $CH_2CH_2CH_3$), 1.14 ppm (t, $^3J_{HH}$ = 6.9 Hz, 6H, $CH_2CH_2CH_3$); elemental analysis: calcd (%) for $C_{32}H_{32}Br_4N_4Pd_2S_2$ (M = 1069.21): C 35.95, H 3.02, N 5.24, S 6.00; found: C 36.22, H 2.84, N 5.00, S 6.06.

11: Dibromo[μ-1,2-bis(4-pyridyl)ethane]bis(3-benzylbenzothiazolin-2-ylidene)dipalladium(II): Complex **11** was prepared in analogy to **5**, from **1** (100 mg, 0.101 mmol) and 1,2-bis(4-pyridyl)ethane (18.7 mg, 0.101 mmol). Diffusion of CH_2Cl_2 into a DMSO solution of the complex yielded orange crystals suitable for X-ray diffraction studies. Yield: 71 mg (0.06 mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.92 (d, $^3J_{HH}$ = 6.3 Hz, 4H, Ar-H), 7.81 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.71–7.69 (m, 2H, Ar-H), 7.57 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-H), 7.54–7.52 (m, 2H, Ar-H), 7.44 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.39–7.32 (m, 10H, Ar-H), 7.17 (d, $^3J_{HH}$ = 6.3 Hz, 2H, Ar-H), 6.53 (s, 4H, CH_2), 2.93 ppm (s, 4H, CH_2CH_2); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 195.8 (NSC), 167.8, 152.7, 151.8, 142.8, 136.8, 133.6, 132.5, 130.8, 129.1, 128.8, 128.5, 127.7, 126.7, 125.1, 124.5, 121.8, 115.1 (Ar-C), 60.1 (CH_2), 38.8 ppm (CH_2CH_2); MS (ESI) *m/z* (%): 1088 (50) $[M-Br]^+$; elemental analysis: calcd (%) for $C_{40}H_{34}Br_4N_4Pd_2S_2$ (M = 1167.31): C 41.16, H 2.94, N 4.80, S 5.49; found: C 41.06, H 2.76, N 4.66, S 5.53.

12: Dibromo[μ-1,2-bis(4-pyridyl)ethane]bis(3-propylbenzothiazolin-2-ylidene)dipalladium(II): Complex **12** was prepared in analogy to **5** from **2** (100 mg, 0.11 mmol) and 1,2-bis(4-pyridyl)ethane (21 mg, 0.11 mmol). Yield: 79 mg (0.07 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.91 (t, $^3J_{HH}$ = 6.3 Hz, 2H, Ar-H), 8.50 (d, $^3J_{HH}$ = 5.7 Hz, 4H, Ar-H), 7.82 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.68 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ar-H), 7.52 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.43 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 7.16 (d, $^3J_{HH}$ = 6.3 Hz, 2H, Ar-H), 7.10–7.07 (m, 4H, Ar-H), 5.14 (t, $^3J_{HH}$ = 7.9, 4H, $CH_2CH_2CH_3$), 2.94 (s, 4H, CH_2CH_2), 2.33 (m, $^3J_{HH}$ = 7.9 Hz, 4H, $CH_2CH_2CH_3$), 1.22 ppm (t, $^3J_{HH}$ = 7.5 Hz, 6H, $CH_2CH_2CH_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 193.2 (NSC), 152.7, 150.0, 149.8, 142.9, 126.7, 125.1, 124.7, 123.8, 123.7, 121.9, 113.8 (Ar-C), 56.9 ($CH_2CH_2CH_3$), 35.7 (CH_2CH_2) 21.9 ($CH_2CH_2CH_3$), 11.7 ppm ($CH_2CH_2CH_3$); MS (ESI): 990 (30) $[M-Br]^+$; elemental analysis: calcd (%) for $C_{32}H_{34}Br_4N_4Pd_2S_2$ (M = 1071.23): C 35.88, H 3.20, N 5.23, S 5.99; found: C 35.33, H 3.34, N 5.37, S 5.84.

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Table 4. Selected crystallographic data for complexes **3**, **4**, **5**, and **11**.

	3	**4**	**5**	**11**
Formula	$C_{19}H_{16}Br_2PdN_2S$	$C_{16}H_{17}Br_2Cl_3N_2PdS$	$C_{32}H_{26}Br_4N_4Pd_2S_2$	$C_{40}H_{34}Br_4N_4Pd_2S_2$
Formula weight	570.62	641.95	1063.13	1167.27
Color, habit	Yellow, thin plate	Yellow, block	Yellow, thin plate	Orange, plate
Crystal size [mm]	$0.14\times0.06\times0.04$	$0.40\times0.30\times0.18$	$0.60\times0.40\times0.02$	$0.20\times0.10\times0.04$
Temperature [K]	223(2)	223(2)	223(2)	223(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
a [Å]	8.9881(9)	8.3997(3)	17.4609(11)	9.1736(9)
b [Å]	11.7083(13)	9.4585(4)	7.4862(5)	13.8016(14)
c [Å]	17.762(2)	15.2011(6)	13.8481(9)	17.0404(17)
α [°]	90	98.7860(10)	90	69.345(2)
β [°]	90.917(3)	94.3620(10)	95.5070(10)	88.504(2)
γ [°]	90	114.3510(1)	90	89.441(2)
V [Å^3]	1869.0	1074.31(7)	1801.8(2)	2018.1(3)
Z	4	2	2	2
D_c [g cm^{-3}]	2.028	1.984	1.960	1.921
Radiation used	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
M [mm^{-1}]	5.385	5.056	5.577	4.989
Θ range [°]	2.08-24.99	1.37-27.49	2.34-27.50	1.58-27.49
unique data	10787	14104	22594	26455
R(int)	0.0684	0.0237	0.0556	0.0490
Max., min. transmission	0.8134, 0.5194	0.4630, 0.2369	0.8966, 0.1347	0.8254, 0.4353
Final R indices	$R1=0.0625$,	$R1=0.0267$,	$R1=0.0303$,	$R1=0.0454$,
$[I>2\sigma(I)]$	$wR2=0.1125$	$wR2=0.0676$	$wR2=0.0716$	$wR2=0.0936$
R indices (all data)	$R1=0.0903$,	$R1=0.0314$,	$R1=0.0409$,	$R1=0.0695$,
	$wR2=0.1211$	$wR2=0.0743$	$wR2=0.0757$	$wR2=0.1021$
Goodness-of-fit on F^2	1.132	1.074	0.997	1.006
Peak/hole [e Å^{-3}]	0.811/−0.573	0.846/−1.074	0.789/−0.551	1.042/−0.432

General Procedure for the Suzuki Reaction

Cs_2CO_3 (2 mmol), aryl halide (1 mmol) and phenyl boronic acid (1.5 mmol) were placed in a reaction flask equipped with a stirring bar. DMF (5 mL) was introduced and the resulting suspension heated to 100 °C for 10 min before the catalyst was added. After the desired reaction duration, the reaction mixture was cooled to ambient temperature. Water was added and the organic phase was extracted with CH_2Cl_2 (3× 4 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solution was analyzed by GC/MS by using dodecane as the internal standard.

X-ray Diffraction Studies

Single crystals of complexes **3**, **4**, **5**, and **11** were obtained from solvent diffusion experiments as described previously. Suitable crystals were mounted on quartz fibers and the X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). The collecting frames of data, indexing reflection and determination of lattice parameters and polarization effects were done with the SMART suite programs.[9] The integration of intensity of reflections and scaling was done by SAINT. The empirical absorption correction was done by SADABS.[10] The space group determination, structure solution and least-squares refinements on $|F|^2$ were carried out with the SHELXTL.[11] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions. A selected summary of crystal data for complexes **3**–**5** and **11** is found in Table 4.

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[1] a) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem. Eur. J.* **2006**, *12*, 4743; b) M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2006**, *12*, 4749; c) C. Valente, S. Baglione, D. Candito, C. J. O'Brien, M. G. Organ, *Chem. Commun.* **2008**, 735; d) M. G. Organ, M. Abdel-Hadi, S. Avola, N. Hadei, J. Nasielski, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2007**, *13*, 150; e) G. Shore, S. Morin, D. Mallik, M. G. Organ, *Chem. Eur. J.* **2008**, *14*, 1351; f) M. G. Organ, M. Abdel-Hadi, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. Sayah, C. Valente, *Chem. Eur. J.* **2008**, *14*, 2443.

[2] a) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768; b) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596; c) S. P. Nolan, *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH, Weinheim, **2006**; d) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348; e) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; f) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247; g) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239; h) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; i) K. J. Cavell, D. S. McGuinness, *Coord. Chem. Rev.* **2004**, *248*, 671; j) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

[3] a) S. K. Yen, L. L. Koh, F. E. Hahn, H. V. Huynh, T. S. A. Hor, *Organometallics* **2006**, *25*, 5105; b) S. K. Yen, L. L. Koh, H. V. Huynh,

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T. S. A. Hor, *Dalton Trans.* **2007**, 3952; c) S. K. Yen, L. L. Koh, H. V. Huynh, T. S. A. Hor, *Dalton Trans.* **2008**, 699.

[4] a) H. V. Huynh, N. Meier, T. Pape, F. E. Hahn, *Organometallics* **2006**, *25*, 3012; b) H. G. Raubenheimer, A. d. Toit, M. d. Toit, J. An, L. v. Niekerk, S. Cronje, C. Esterhuysen, A. M. Crouch, *Dalton Trans.* **2004**, 1173; c) H. G. Raubenheimer, S. Cronje, *J. Organomet. Chem.* **2001**, *617–618*, 170; d) V. Calò, A. Nacci, A. Monopoli, M. Spinelli, *Eur. J. Org. Chem.* **2003**, *8*, 1382; e) V. Calò, P. Giannoccaro, A. Nacci, A. Monopoli, *J. Organomet. Chem.* **2002**, *645*, 152; f) V. Calò, A. Nacci, L. Lopez, A. Napola, *Tetrahedron Lett.* **2001**, *42*, 4701; g) V. Calò, A. Nacci, A. Monopoli, L. Lopez, A. d. Cosmo, *Tetrahedron* **2001**, *57*, 6071; h) V. Calò, R. Del Sole, A. Nacci, E. Schingaro, F. Scorgari, *Eur. J. Org. Chem.* **2000**, 869; i) V. Calò, A. Nacci, L. Lopez, N. Mannarini, *Tetrahedron Lett.* **2000**, *41*, 8973; j) A. J. Arduengo III, J. R. Goerlich, W. J. Mashall, *Liebigs Ann.* **1997**, 365.

[5] a) J. Houghton, G. Dyson, R. E. Douthwaite, A. C. Whitwood, B. M. Kariuki, *Dalton Trans.* **2007**, 3065; b) H. Huang, T. Okuno, K. Tsuda, M. Yoshimura, M. Kitamura, *J. Am. Chem. Soc.* **2006**, *128*, 8716; c) A. Flahaut, J.-P. Baltaze, S. Roland, P. Mangeney, *J. Organomet. Chem.* **2006**, *691*, 3498; d) R. Hodgson, R. E. Douthwaite, *J. Organomet. Chem.* **2005**, *690*, 5822; e) R. E. Douthwaite, J. Houghtona, B. M. Kariukib, *Chem. Commun.* **2004**, 698; f) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, J. Houghton, B. M. Kariukib, S. Simonovic, *Dalton Trans.* **2004**, 3528.

[6] Y. Han, H. V. Huynh, G. K. Tan, *Organometallics* **2007**, *26*, 6447.

[7] L. Ray, M. M. Shaikh, P. Ghosh, *Dalton Trans.* **2007**, 4546.

[8] G. C. Vougioukalakis, R. H. Grubbs, *J. Am. Chem. Soc.* **2008**, *130*, 2234.

[9] SMART (Version 5.631) & SAINT (Version 6.63) Software Reference Manuals, Bruker AXS GmbH, Karlsruhe, Germany, **2000**.

[10] G. M. Sheldrick, SADABS: a Software for Empirical Absorption Correction; University of Göttingen: Göttingen Germany, **2001**.

[11] SHELXTL Reference Manual, Version 6.10; Bruker AXS GmbH, Karlsruhe, WI, **2000**.

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