

Pyridin-, Quinolin- and Acridinylidene Palladium Carbene Complexes as Highly Efficient C–C Coupling Catalysts

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Abstract: A series of four new complexes bearing N-heterocyclic carbene ligands (NHCs) as well as four compounds bearing N-heterocyclic carbene ligands with remote heteroatoms (*r*NHCs) of the general types [(NHC)(PPh₃)₂PdCl]⁺BF₄[−] and [(*r*NHC)(PPh₃)₂PdCl]⁺BF₄[−], respectively, have been prepared in high yields. Crystal and molecular structures have been determined for four representative examples. These compounds proved to be efficient catalysts for aryl coupling reactions of the Heck and Suzuki types (reaching TONs of as high as 6,200,000). Both aryl bromides and aryl chlorides can be used as substrates. Like the well known mixed, standard (NHC)(phosphine) compounds, the new six-num-

bered, one-N-heterocyclic carbene complexes (and in particular certain *r*NHC-containing ones) also combine the advantageous stability of bis(carbene) and the high activity of bis(phosphine) complexes. Furthermore, their good catalytic performance and, especially, their easy synthesis based on cheap and commercially available starting materials, make them by far superior when compared to the mixed (NHC)(phosphine) catalysts known thus far.

Keywords: C–C coupling; N-heterocyclic carbenes; palladium; phosphine; remote heteroatom N-heterocyclic carbenes

Introduction

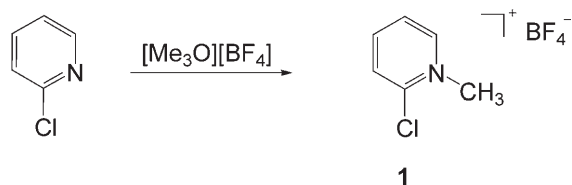
Carbon-carbon bond formation in the presence of a transition metal catalyst is a key step in many synthetic protocols for organic chemicals, natural products, as well as in a variety of industrial processes.^[1–3] Important examples of such catalytic transformations are found in the Suzuki^[4] and Heck reaction types.^[5] As palladium complexes are especially active in this regard, there has been long-standing interest in their properties. Current studies mainly deal with the use of new kinds of ligands as well as the collection of mechanistic information. Initially, phosphines have been the ligands of choice^[6] but now numerous investigations are being undertaken in order to overcome their limitations. Despite their high catalytic activity, the overall efficiency of such complexes suffers due to a lack of stability, especially at high reaction temperatures.^[1,7] Recent results indicate that N-heterocyclic carbenes (NHCs) as ligands in the precursor complexes^[8–10] lead to increased stability but,

unfortunately, this is accompanied by a loss of activity. In a recent communication we proposed that this problem could be overcome by introducing a new type of carbene ligand with remote heteroatoms (*r*NHC).^[11] These promising early results gave rise to a more detailed study of related one-N, six-membered carbene complexes, albeit derived from simple, commercially available pyridine, quinoline and acridine precursors, that still contain two phosphine ligands.

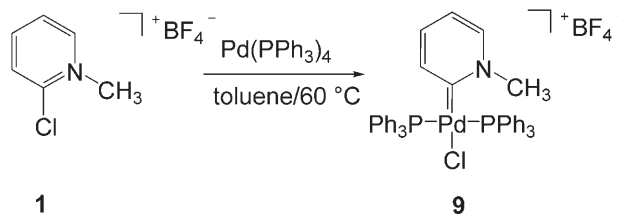
Results and Discussion

Synthesis and Characterization of Pyridinium and Quinolinium Precursors

Existing literature procedures were followed or slightly modified to prepare the target ligand precursors **1–8**. Compound **1**, for example, was prepared according to Scheme 1.^[12]



Scheme 1. Alkylation of chloropyridines according to Stone.^[12]



Scheme 2. Synthesis of complex **9** by oxidative addition.

The cations of **2–8** were synthesized similarly by alkylating the corresponding chloropyridine (**2**), chloroquinoline (**3–7**) or chloroacridine (**8**) substrates with one equivalent of Meerwein's salt in a dichloromethane/acetonitrile (3/1) mixture (Figure 1).

Washing with THF yielded compounds **2–7** as colourless and **8** as brownish powders in an average yield of approximately 90%. The synthesis of **2** first necessitated the generation of the free precursor 4-chloropyridine from the commercially available hydrochloride by treatment with aqueous NaOH.^[13] Compounds **1–8** were characterised by NMR spectroscopy, mass spectroscopy and elemental analysis.

Syntheses and Characterization of Pyridin- and Quinolinylidene Pd(II) Complexes

Cationic complexes of Pd(II) were obtained by oxidative addition when the ligand precursors **1–8** were reacted overnight with Pd(PPh₃)₄ at 60 °C in toluene according to Scheme 2. Filtration through Celite and precipitation with pentane afforded the compounds **9–16** (Figure 2) in good to excellent yields. Elemental

analyses and solution NMR spectra confirmed the expected compositions and structures.

The single resonance observed for each complex in the ³¹P NMR spectrum in a narrow range between 20.87 and 24.48 ppm, clearly shows the equivalence of the two phosphorus ligands in each compound, indicating *trans* positioning of these ligands in solution. Complex connectivities and bond properties derived from single crystal X-ray diffraction studies of the compounds **9**, **10**, and **15** confirmed this observation. For compound **11**, however, a *cis* orientation of the two phosphine ligands was also found in the solid state (*vide infra*), indicating that a *trans-cis*-isomerisation equilibrium is established during the crystallisation process. The room temperature ³¹P NMR spectrum of recrystallised **11-cis** from CD₂Cl₂-pentane exhibits only one signal at $\delta = 22.33$ indicating exclusively a *trans* isomer in solution. After cooling down, two additional weak doublets for the *cis* isomer at $\delta = 31.3$ and 21.0 appear only below -20°C .

The carbene carbon atoms in the complexes of **9–16** resonate at $\delta = 189.5$, 197.3, 200.1, 202.9, 198.9, 205.7, 202.9 and 216.8 in their ¹³C NMR spectra. All of them show a downfield shift of approximately 40 to 60 ppm compared to previously reported Pd(II)

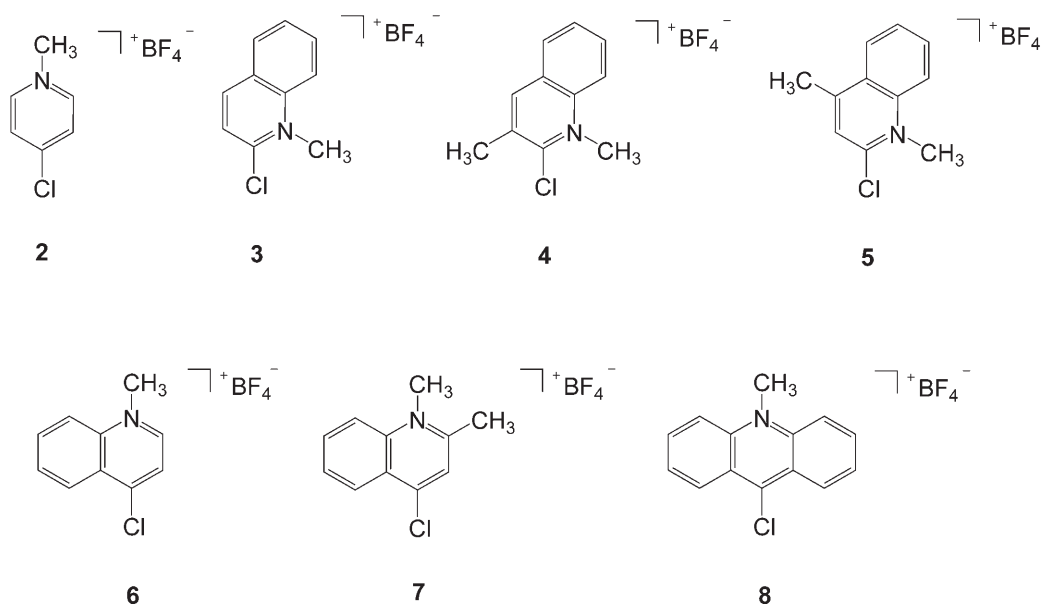


Figure 1. New ligand precursors **2–8**.

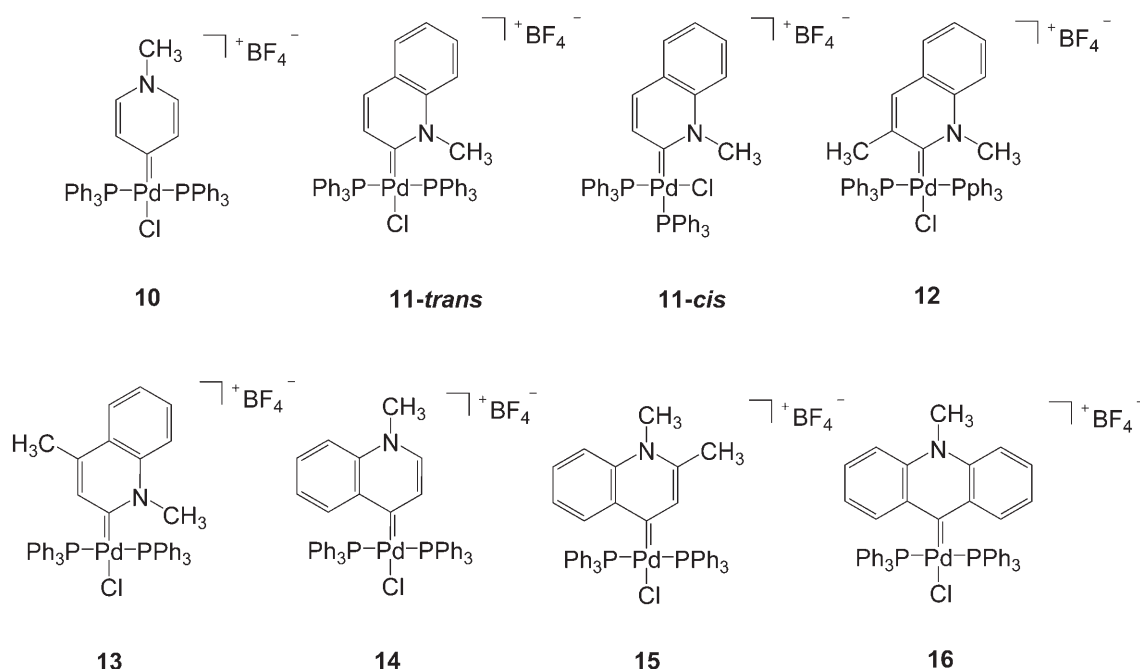


Figure 2. Carbene complexes 10–16.

carbene complexes.^[8a,b] All carbene carbon signals appear as triplets with coupling constants of about 5 to 8 Hz, again indicating the *trans* arrangement of the two phosphines in solution.

The NMR signals for 9–16 appear upfield-shifted with respect to the corresponding values of their ligand precursors.

With the exception of 11, all the FAB-MS of compounds 9–16 show the cationic complex peaks, $[M]^+$, with weak intensity. The base peaks are always due to an $[M-PPh_3]^+$ fragment. The ions $[M-PPh_3-Cl]^+$ were also present in each spectrum. In addition, the $[M-Cl-(2 \times PPh_3)]^+$ fragment is detected for compound 16.

It should be mentioned that the easy preparation of compounds 9–16 using cheap and commercially available starting materials, short reaction times as well as a straightforward work-up procedure are major advantages compared to most other palladium carbene complexes used before in related catalytic applications.

Crystal Structures of Complexes 9, 10, 11-*cis*, 11-*trans* and 15

Colourless needles of the two compounds chloro(*N*-methylpyridine-2-ylidene)-bis(triphenylphosphine)palladium(II) tetrafluoroborate (9, space group *P1*) and chloro(*N*-methylpyridine-4-ylidene)-bis(triphenylphosphine)palladium(II) tetrafluoroborate (10, space group *P1*) crystallised from dichloromethane-pentane mixtures at -20°C . Unexpectedly, cubic crystals of

the *cis*-isomer (space group *P1*) of chloro(*N*-methylquinoline-2-ylidene)-bis(triphenylphosphine)palladium(II) tetrafluoroborate, 11-*cis*, were obtained similarly. Needle-like crystals, suitable for a single crystal X-ray diffraction study of the *trans*-isomer, (space group *Pca2*₁) 11-*trans*, were grown from a saturated CH_2Cl_2 solution of the colourless microcrystalline synthetic product carefully layered with pentene and kept at room temperature for two weeks. The complex chloro(*N*-methyl-2-methylquinoline-4-ylidene)-bis(triphenylphosphine)palladium(II) tetrafluoroborate, 15, crystallised from acetonitrile as colourless platelets (space group *P2*₁2₁2₁).

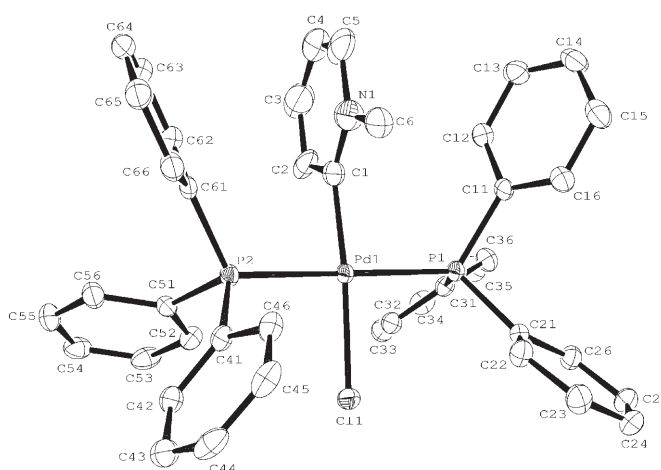


Figure 3. Molecular structure of the NHC complex in 9, showing the crystallographic numbering scheme (hydrogens and BF_4^- counteranion omitted for clarity).

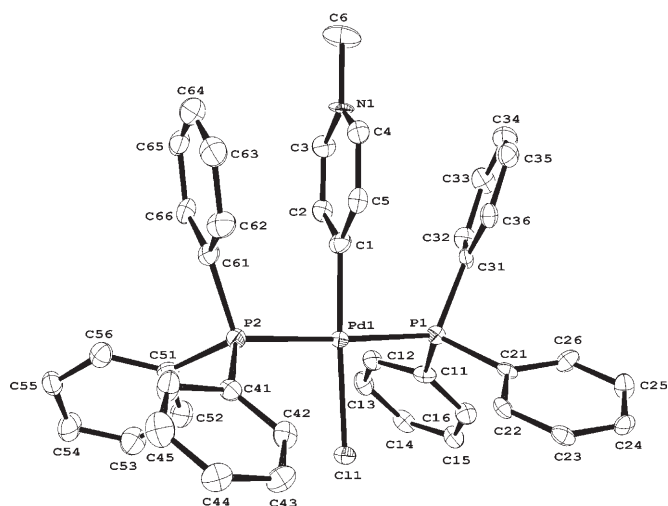


Figure 4. Molecular structure of the *r*NHC complex **10**, showing the crystallographic numbering scheme (hydrogens and BF_4^- counteranion omitted for clarity).

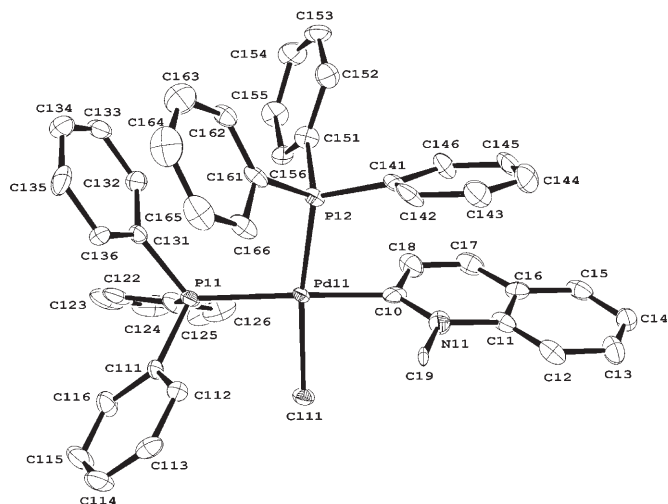


Figure 5. Molecular structure of the cationic complex in **11-cis**, showing the crystallographic numbering scheme (hydrogens and BF_4^- counteranion omitted for clarity).

The molecular structures of the cationic complexes in compounds **9** (Figure 3), **10** (Figure 4), **11-cis** (Figure 5), **11-trans** (Figure 6) and **15** (Figure 7) are depicted below. Crystal data and experimental details are given in the Experimental Section, and selected bond distances and bond angles in Table 1.

All cationic complexes of **9**, **10**, **11-trans** and **15** contain the Pd(II) in a square planar environment while the two PPh_3 ligands occupy *trans* positions. In **11-cis**, however, a *cis* arrangement of the two phosphine groups occurs. This is probably due to energy advantages during crystal packing, as only the *trans*-isomer is present in solution (^{31}P NMR). Even redi-

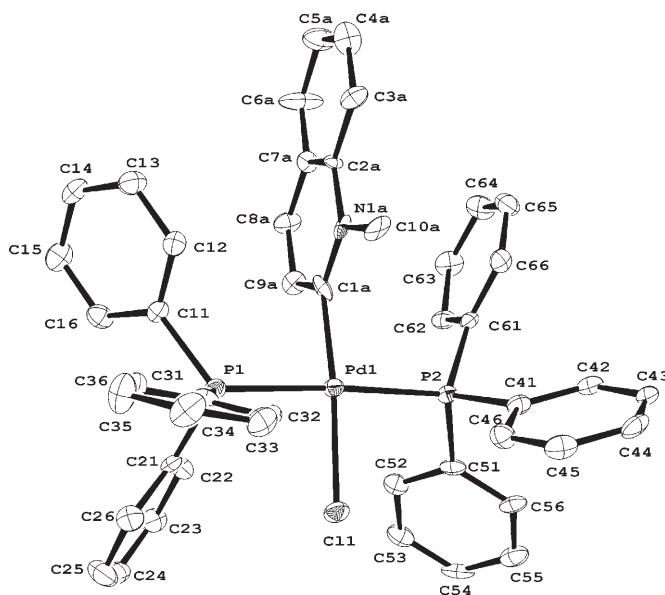


Figure 6. Molecular structure of cationic complex in **11-trans**, showing the crystallographic numbering scheme (hydrogens and BF_4^- counteranion omitted for clarity).

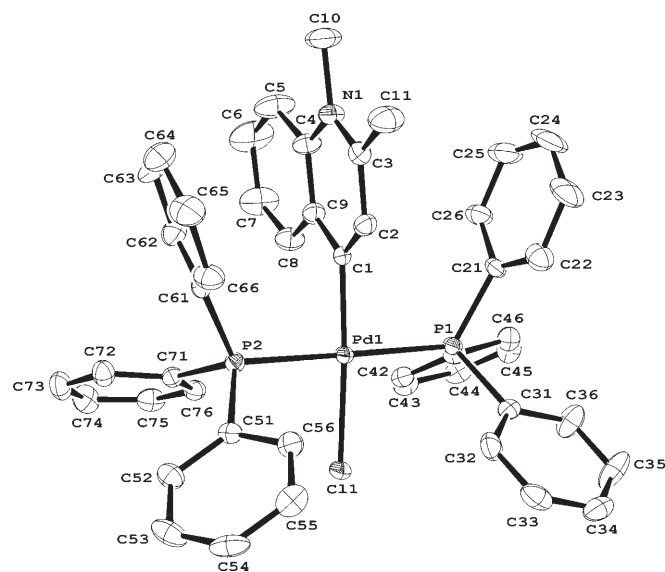


Figure 7. Molecular structure of the cationic complex in **15**, showing the crystallographic numbering scheme (hydrogens and BF_4^- counteranion omitted for clarity).

solution of the **11-cis** crystals in CD_2Cl_2 afforded again only the *trans*-isomer.

The Pd–C(carbene) distances in the cationic complexes of **9**, **10**, **11-trans** and **15** are similar [1.997(3), 1.979(7), 1.985(11) and 1.986(2) Å] and all fall comfortably within the previously obtained range (1.91–2.10 Å) for palladium(II) carbene complexes.^[14] With the two phosphines *cis* arranged in **11-cis**, the greater *trans* influence of phosphine compared to chloride is

Table 1. Selected bond lengths [Å] and angles [°] for complexes **9**, **10**, **11-cis**, **11-trans** and **15**.

	9	10	11-cis	11-trans ^[a]	15
Pd–C _{carbene}	1.997(3)	1.979(7)	2.029(9)	1.985(11)	1.986(2)
Pd–P1	2.3406(9)	2.3453(19)	2.388(2)	2.3197(13)	2.3206(7)
Pd–P2	2.3340(9)	2.3634(19)	2.268(2)	2.3286(12)	2.3334(7)
Pd–Cl	2.3632(9)	2.3938(17)	2.346(0)	2.3465(11)	2.3916(6)
C _{carbene} –Pd–Cl	169.20(12)	175.3 (2)	85.7(2)	170.4(3)	176.92(17)
P1–Pd–P2	179.29(3)	177.43(7)	100.61(8)	176.17(4)	178.21(7)
C _{carbene} –Pd–P1	88.91(9)	87.7 (2)	165.8(2)	93.05(4)	89.33(15)
C _{carbene} –Pd–P2	90.96(9)	89.7(2)	87.0(2)	90.3(4)	178.21(7)
Cl–Pd–P1	91.46(4)	87.89(6)	87.84(7)	86.52(4)	90.66(5)
Cl–Pd–P2	88.91(9)	94.65(6)	170.34(8)	90.10(4)	88.37(5)

^[a] The carbene ligand in **11-trans** is disordered; average values are reported.

clearly shown in the longer (2.032 Å) Pd–C(carbene) separation.

Comparing the *trans* complexes in **9**, **10**, **11-trans** and **15**, the Pd–Cl distances in **10** (ca. 2.39 Å), and **15** (ca. 2.39 Å) are somewhat longer than those in **9** (ca. 2.36 Å) and **11-trans** (ca. 2.35 Å), indicating a stronger *trans* influence by *r*NHC ligands compared to those with a neighbouring heteroatom. In recent work that involved related Ni compounds, we quantum mechanically calculated that *r*NHCs derived from pyridine are indeed better π -acceptors than related NHC ligands.^[15]

The structure of the quinolin-4-ylidene Pd(II) complex cation in **15** is very similar to that of the previously reported palladium(II) carbene complex carrying a 2-methoxy-*N*-methylquinolin-ylidene ligand [Pd–C(carbene) distance 1.986(3) Å],^[16] except that it contains a methyl instead of a methoxy group in the 2-position. The known complex is also a very active precatalyst for C–C coupling reactions^[11] and it is not too surprising that compound **15** also turned out to be the most active one in the present study.

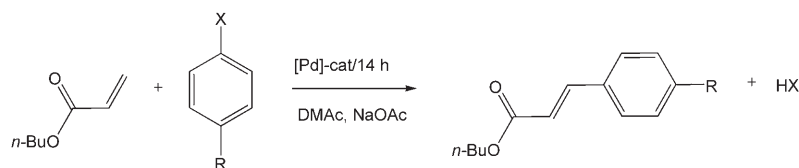
Catalysis

The catalyst compounds **9–16** (Figure 1) as well as a chosen simple imidazol-2-ylidene benchmark, compound **17** [*trans*-dimethylimidazol-2-ylidene(triphenylphosphine)palladium(II) iodide]^[10a] with a comparable steric demand should allow comparison of the role played by electronic effects in these complex types],^[10a] were all screened for their activity and efficiency in well-known Mizoroki–Heck and Suzuki–Miyaura reactions and the results obtained are summarised in Table 2 and Table 3. It can clearly be seen that all the new palladium complexes with pyridinylidene-, quinolinylidene- and acridinylidene-derived ligands are useful precatalysts for carbon-carbon coupling reactions. Under the reported conditions and with an extremely low catalyst loading of only 10^{–5}

mol %, compounds **9–16** give good yields and TONs as high as 6.2 × 10⁶ (Table 2, entry 17) in the Mizoroki–Heck reaction using bromo acetophenone as substrate. At the same time, no by-products were detected. Non-activated (Table 2, entries 20–27) and deactivated bromoarenes (Table 2, entries 28–35) couple successfully when using 0.1 mol % of the catalyst. Even aryl chlorides (Table 2, entries 36–43) can be used in the Mizoroki–Heck reaction, now with somewhat higher catalyst concentrations (0.5 mol %) and effecting diminished yields. The high activity and selectivity of these catalysts in Heck-type coupling is especially remarkable, as the standard mixed imidazole-2-ylidene/phosphine palladium(II) compounds described earlier are known rather for their good performance in Suzuki reactions but paired with a lack of activity in Heck conversions.^[10a]

In the Suzuki–Miyaura coupling TONs of 2.6 × 10⁶ (Table 3, entry 11) could be reached for activated bromo arenes, again using low catalyst concentrations (10^{–5} mol %). Non-activated (Table 3, entries 18–31) and deactivated bromoarenes (Table 3, entries 33–42) couple, even with relatively low amounts of catalyst present. It is especially remarkable that bromoanisole couples completely within 13 h using 0.1 mol % of **15** as catalyst (entry 40), and that even 0.01 mol % of **15** gives a yield of 82 % (entry 41). Activated aryl chlorides react successfully at a 0.1 mol % loading level of the catalyst, showing no evidence of palladium black formation even after reaction times of 14 h and more, with compound **16** being the most effective. Like in the Mizoroki–Heck reaction, compounds **13** and **15** are the most active ones as far as their overall performance is concerned whereas the standard NHC complex in **12** is again the worst precatalyst.

An even better picture of the relative catalyst activities is given by the time-conversion curves depicted in Figure 8 (Mizoroki–Heck reaction) and Figure 9 (Suzuki–Miyaura reaction). The reaction of bromobenzene with *n*-butyl acrylate was employed for the Mizoroki–Heck coupling using a catalyst concentra-

Table 2. Catalytic results for the Mizoroki–Heck reaction.

No. ^[a]	X	R	mol % Pd	Catalyst	T [°C]	Conversion [%] ^[b]	Yield [%] ^[b]	TON
1	Br	C(O)CH ₃	0.001	9	145	> 99.99	98	98,000
2	Br	C(O)CH ₃	0.0001	9	145	57	57	570,000
3	Br	C(O)CH ₃	0.001	10	145	> 99.99	98	98,000
4	Br	C(O)CH ₃	0.0001	10	145	56	56	560,000
5	Br	C(O)CH ₃	0.001	11	145	> 99.99	99	98,600
6	Br	C(O)CH ₃	0.0001	11	145	> 99.99	99.8	998,000
7	Br	C(O)CH ₃	10 ⁻⁵	11	145	50	50	5,000,000
8	Br	C(O)CH ₃	0.001	12	145	> 99.99	99.8	99,800
9	Br	C(O)CH ₃	0.0001	12	145	34	34	340,000
10	Br	C(O)CH ₃	0.001	13	145	> 99.99	99	99,000
11	Br	C(O)CH ₃	0.0001	13	145	99.4	99.1	991,000
12	Br	C(O)CH ₃	10 ⁻⁵	13	145	55	55	5,500,000
13	Br	C(O)CH ₃	0.001	14	145	> 99.99	99.8	99,800
14	Br	C(O)CH ₃	0.0001	14	145	66	66	660,000
15	Br	C(O)CH ₃	0.001	15	145	> 99.99	99.8	99,800
16	Br	C(O)CH ₃	0.0001	15	145	> 99.99	99.3	993,000
17	Br	C(O)CH ₃	10 ⁻⁵	15	145	62	62	6,200,000
18	Br	C(O)CH ₃	0.001	16	145	> 99.99	99.8	99,800
19	Br	C(O)CH ₃	0.0001	16	145	56	56	560,000
20	Br	H	0.1	9	145	82	81	810
21	Br	H	0.1	10	145	81	80	800
22	Br	H	0.1	11	145	89	87	870
23	Br	H	0.1	12	145	72	71	710
24	Br	H	0.1	13	145	77	76	760
25	Br	H	0.1	14	145	74	73	730
26	Br	H	0.1	15	145	96	94	940
27	Br	H	0.1	16	145	81	80	800
28	Br	OCH ₃	0.1	9	145	69	67	670
29	Br	OCH ₃	0.1	10	145	68	66	660
30	Br	OCH ₃	0.1	11	145	70	69	690
31	Br	OCH ₃	0.1	12	145	57	56	560
32	Br	OCH ₃	0.1	13	145	87	86	860
33	Br	OCH ₃	0.1	14	145	53	52	520
34	Br	OCH ₃	0.1	15	145	57	56	560
35	Br	OCH ₃	0.1	16	145	64	63	630
36	Cl ^[c]	C(O)CH ₃	0.5	9	150	27	23	46
37	Cl ^[c]	C(O)CH ₃	0.5	10	150	30	27	54
38	Cl ^[c]	C(O)CH ₃	0.5	11	150	33	29	58
39	Cl ^[c]	C(O)CH ₃	0.5	12	150	33	29	58
40	Cl ^[c]	C(O)CH ₃	0.5	13	150	35	30	60
41	Cl ^[c]	C(O)CH ₃	0.5	14	150	24	22	44
42	Cl ^[c]	C(O)CH ₃	0.5	15	150	47	43	86
43	Cl ^[c]	C(O)CH ₃	0.5	16	150	40	35	70

^[a] Mole ratio of aryl halide:olefin:NaOAc = 1 : 1.5 : 1.5; solvent: DMAc (dimethylacetamide); reaction time 14 h.

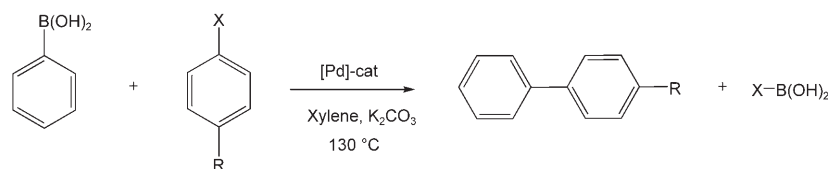
^[b] GC yield and conversion using diethylene glycol/di-*n*-butyl ether as internal standard.

^[c] 0.2 mole equivalents of [R₄N]Br added to the reaction mixture.

tion of 0.1 mol%. In the Suzuki–Miyaura case, the coupling of bromoanisole with phenylboronic acid in the presence of 0.1 mol% catalyst was studied. In both conversion types, compounds **9–16** exhibit rather similar catalytic performances. In both instances, the *r*NHC-compound, **15**, again has the highest activity whereas **12** performs poorly. Furthermore, compounds

9–16 all show a significantly higher initial activity as well as overall yield than compound **17**. The fact that the worst of the present group, **12**, a six-membered, single-N heterocyclic carbene complex, is much more active than a standard five-membered, two-N NHC-containing compound, **17**,^[10a] indicates a huge potential for these new type of ligands in C–C coupling cat-

Table 3. Catalytic results for the Suzuki–Miyaura reaction.



No. ^[a]	X	R	mol % Pd	Catalyst	<i>t</i> [h]	Yield [%] ^[b]	TON
1	Br	C(O)CH ₃	0.001	9	13	> 99.99	100,000
2	Br	C(O)CH ₃	0.0001	9	13	81	810,000
3	Br	C(O)CH ₃	0.001	10	13	> 99.99	100,000
4	Br	C(O)CH ₃	0.0001	10	13	62	620,000
5	Br	C(O)CH ₃	0.001	11	13	> 99.99	100,000
6	Br	C(O)CH ₃	0.0001	11	13	71	710,000
7	Br	C(O)CH ₃	0.001	12	13	> 99.99	100,000
8	Br	C(O)CH ₃	0.0001	12	13	57	570,000
9	Br	C(O)CH ₃	0.001	13	13	> 99.99	100,000
10	Br	C(O)CH ₃	0.0001	13	13	> 99.99	1,000,000
11	Br	C(O)CH ₃	10 ^{−5}	13	13	26	2,600,000
12	Br	C(O)CH ₃	0.001	14	13	> 99.99	100,000
13	Br	C(O)CH ₃	0.0001	14	13	76	760,000
14	Br	C(O)CH ₃	0.001	15	13	> 99.99	100,000
15	Br	C(O)CH ₃	0.0001	15	13	87	870,000
16	Br	C(O)CH ₃	0.001	16	13	> 99.99	100,000
17	Br	C(O)CH ₃	0.0001	16	13	82	820,000
18	Br	H	0.01	9	13	> 99.99	10,000
19	Br	H	0.001	9	13	87	87,000
20	Br	H	0.01	10	13	> 99.99	10,000
21	Br	H	0.001	10	13	77	77,000
22	Br	H	0.01	11	13	> 99.99	10,000
23	Br	H	0.001	11	13	79	79,000
24	Br	H	0.01	12	13	89	8,900
25	Br	H	0.01	13	13	> 99.99	10,000
26	Br	H	0.001	13	13	97	97,000
27	Br	H	0.01	14	13	> 99.99	10,000
28	Br	H	0.001	14	14	42	42,000
29	Br	H	0.01	15	13	> 99.99	10,000
30	Br	H	0.001	15	13	49	49,000
31	Br	H	0.01	16	13	96	9,600
33	Br	OCH ₃	0.1	9	13	72	720
34	Br	OCH ₃	0.1	10	13	77	770
35	Br	OCH ₃	0.1	11	13	84	840
36	Br	OCH ₃	0.1	12	13	45	450
37	Br	OCH ₃	0.1	13	13	> 99.99	1000
38	Br	OCH ₃	0.01	13	13	51	5,100
39	Br	OCH ₃	0.1	14	13	88	880
40	Br	OCH ₃	0.1	15	13	> 99.99	1000
41	Br	OCH ₃	0.01	15	13	82	8,200
42	Br	OCH ₃	0.1	16	13	60	600
43	Cl ^[c]	C(O)CH ₃	0.1	9	14	35	350

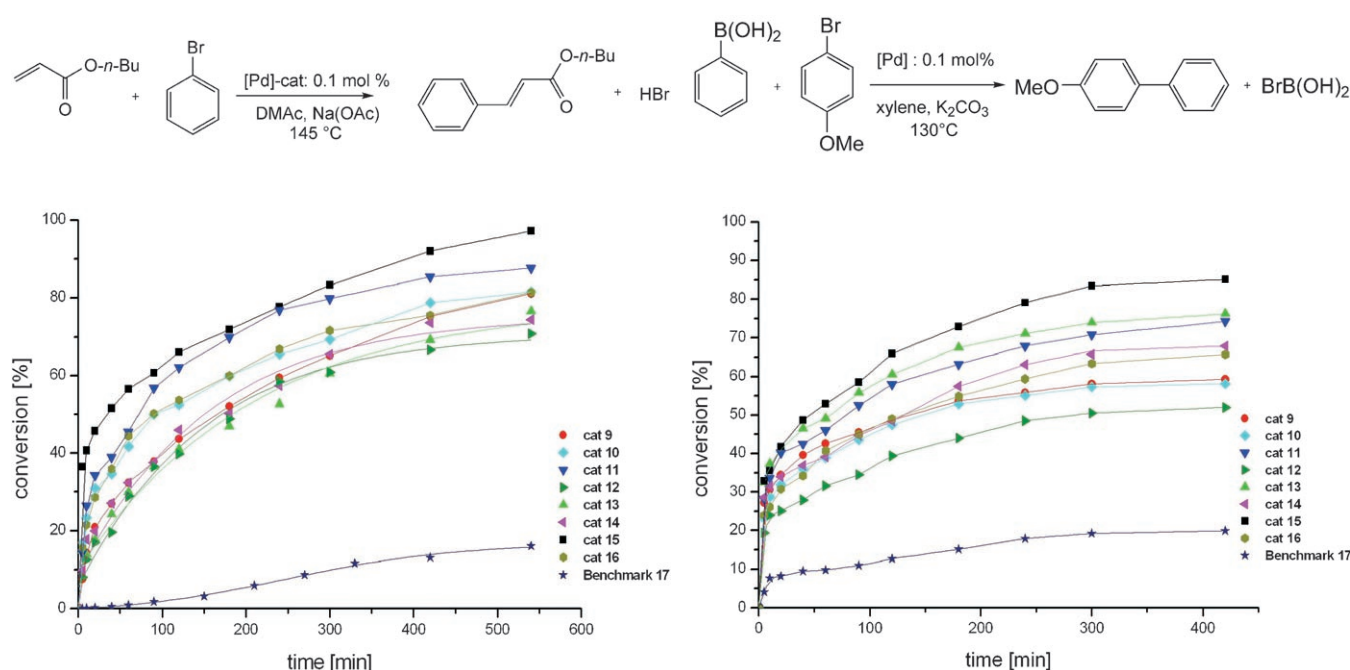
Table 3. (Continued)

No. ^[a]	X	R	mol % Pd	Catalyst	t [h]	Yield [%] ^[b]	TON
44	Cl ^[c]	C(O)CH ₃	0.1	10	14	34	340
45	Cl ^[c]	C(O)CH ₃	0.1	11	14	36	360
46	Cl ^[c]	C(O)CH ₃	0.1	12	13	25	250
47	Cl ^[c]	C(O)CH ₃	0.1	13	14	43	430
48	Cl ^[c]	C(O)CH ₃	0.1	14	13	29	290
49	Cl ^[c]	C(O)CH ₃	0.1	15	13	37	370
50	Cl ^[c]	C(O)CH ₃	0.1	16	13	57	570

^[a] Mole ratio of aryl halide:phenylboronic acid:K₂CO₃ = 1:1.2:1.5.

^[b] GC-yield using diethylene glycol/di-*n*-butyl ether as the internal standard.

^[c] Using Cs₂CO₃ as the base.

**Figure 8.** Time-conversion curves: Mizoroki–Heck reaction.**Figure 9.** Time-conversion curves: Suzuki–Miyaura reaction.

alysis in particular but possibly also for homogeneous catalysis in general. It is also remarkable that, unlike the situation with other NHC-containing catalysts,^[10a] no induction period was observed thus indicating a quick formation of the catalytically active Pd species.

These promising results encourage further studies in order to optimise the catalyst design without complicating the straightforward synthesis of the compounds. Tailoring the pyridin-, quinolin- and acridinylidene palladium complexes, especially by increasing steric bulk and replacing the aromatic phosphines by aliphatic or more sterically hindered ones, could increase their catalytic activity even further.

Conclusions

Our studies have demonstrated that the known increase in activity and stability of catalytically active Pd(II) compounds in C–C coupling brought about by the presence of both NHC and phosphine ligands is even more accentuated in such mixed carbene-phosphine complexes when the former ligand contains only one N and is derived from pyridine, quinoline or acridine. We have shown that these new compounds are well suited as catalysts for Heck-type as well as Suzuki-type couplings. No unambiguous activity differentiation between comparable six-membered NHC- and *r*NHC-containing complexes is yet possible. It is especially noteworthy that the syntheses of all new ligands and catalysts presented in this work are extraordinarily simple and only cheap and commercially available precursors were used in the process. There-

fore, we expect that this new class of ligands will find applications in other important catalytic processes and should, individually, be considered as useful alternatives to classical NHCs as we ourselves will show in future reports. Experiments in this regard are already underway.

Experimental Section

General Procedures

NMR spectra (^1H , ^{13}C , ^{31}P) were recorded either on a Jeol JMX-GX 400, on a Jeol JMX-GX 270 or on a Bruker DPX 400 instrument. Chemical shifts are given in ppm. The spectra were calibrated to the residual protons of the solvent (^1H) or to the carbon signals of the solvent (^{13}C). FAB-MS were measured at the TU Munich Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer (xenon/*p*-nitrobenzyl alcohol). Elemental analyses were carried out by the Microanalytical Laboratory at the TU Munich. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques. All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. Other chemicals were obtained from commercial sources and used without further purification.

4-Chloro-*N*-methylpyridinium Tetrafluoroborate (2)

4-Chloropyridine (735 mg, 6.47 mmol), obtained by treatment of the commercial available 4-chloropyridinium hydrochloride with base,^[17] was dissolved in a mixture of dichloromethane (30 mL) and acetonitrile (10 mL). $[\text{Me}_3\text{O}][\text{BF}_4]$ (957 mg, 6.47 mmol) was added over a period of 1.5 h at room temperature. After stirring overnight, the solvent was removed under vacuum. The residue was washed twice with THF (50 mL), filtered and dried under vacuum; yield: 91 %.

2-Chloro-*N*-methylquinolinium Tetrafluoroborate (3)

Compound **3** was prepared in the same manner as **2**, with the same amounts of $[\text{Me}_3\text{O}][\text{BF}_4]$ using 2-chloroquinoline as the organic substrate (white powder; yield: 95 %).

2-Chloro-3-methyl-*N*-methylquinolinium Tetrafluoroborate (4)

Compound **4** was prepared in the same manner as **2**, with the same amounts of $[\text{Me}_3\text{O}][\text{BF}_4]$ but with 2-chloro-3-methylquinoline as the organic substrate (white powder; yield: 92 %).

2-Chloro-4-methyl-*N*-methylquinolinium Tetrafluoroborate (5)

Compound **5** was prepared in the same manner as **2**, with the same amounts of $[\text{Me}_3\text{O}][\text{BF}_4]$ but with 2-chloro-4-methylquinoline as the organic substrate (yield: 98 %).

4-Chloro-*N*-methylquinolinium Tetrafluoroborate (6)

Compound **6** was prepared in the same manner as **2**, with the same amounts of $[\text{Me}_3\text{O}][\text{BF}_4]$ but with 4-chloro-*N*-methylquinoline as the organic substrate (white powder; yield: 93 %).

4-Chloro-2-methyl-*N*-methylquinolinium Tetrafluoroborate (7)

Compound **7** was prepared in the same manner as **2**, with the same amounts of $[\text{Me}_3\text{O}][\text{BF}_4]$ but with 4-chloro-2-methylquinoline as the organic substrate (white powder; yield: 90 %).

9-Chloro-*N*-methylacridinium Tetrafluoroborate (8)

Compound **8** was prepared in the same manner as **2**, with the same amounts of $[\text{Me}_3\text{O}][\text{BF}_4]$ but with 9-chloroacridine as the organic substrate (brown powder; yield: 78 %).

Chloro-(*N*-methylpyridin-2-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (9)

$\text{Pd}(\text{PPh}_3)_4$ (459 mg, 0.397 mmol) was dissolved in toluene (40 mL), 1 mole equivalent of **1** (85.6 mg, 0.397 mmol) was added and the reaction mixture stirred overnight at 60 °C. After cooling to room temperature, the precipitate was filtered off, washed with cold toluene, dissolved in dichloromethane and filtered through Celite. Precipitation with pentane afforded complex **9** as a white powder; yield: 274 mg (82 %).

Chloro-(*N*-methylpyridin-4-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (10)

Compound **10** was prepared in the same manner as **9**, with the same amounts of $\text{Pd}(\text{PPh}_3)_4$ but with **2** as the organic substrate (white powder; yield: 73 %).

Chloro-(*N*-methylquinolin-2-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (11)

Compound **11** was prepared in the same manner as **9**, with the same amounts of $\text{Pd}(\text{PPh}_3)_4$ but with **3** as the organic substrate (white powder; yield: 78 %).

Chloro-(*N*-methyl-3-methylquinolin-2-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (12)

Compound **12** was prepared in the same manner as **9**, with the same amounts of $\text{Pd}(\text{PPh}_3)_4$ but with **4** as the organic substrate (light yellow powder; yield: 72 %).

Chloro-(*N*-methyl-4-methylquinolin-2-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (13)

Compound **13** was prepared in the same manner as **9**, with the same amounts of $\text{Pd}(\text{PPh}_3)_4$ but with **5** as the organic substrate (pinkish powder; yield: 80 %).

Chloro-(*N*-methylquinolin-4-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (14)

Compound **14** was prepared in the same manner as **9**, with the same amounts of Pd(PPh₃)₄ but with **6** as the organic substrate (white powder; yield: 73 %).

Chloro-(*N*-methyl-4-methylquinolin-2-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (15)

Compound **15** was prepared in the same manner as **9**, with the same amounts of Pd(PPh₃)₄ but with **7** as the organic substrate (pinkish powder; yield: 77 %).

Chloro-(*N*-methylnacridin-9-ylidene)bis(triphenylphosphine)palladium(II) Tetrafluoroborate (16)

Compound **16** was prepared in the same manner as **9**, with the same amounts of Pd(PPh₃)₄ but with **8** as the organic substrate. The complex was dissolved in acetonitrile for filtering through Celite (green-yellow powder; yield: 53 %).

Heck Reaction

A constant ratio of sodium acetate (246 mg, 3.00 mmol) and aryl halide (2.00 mmol, for example, 315 mg bromobenzene) as well as 100 mL diethylene glycol/di-*n*-butyl ether were placed in a Schlenk tube equipped with a stirring bar under an argon atmosphere. Then 0.43 mL (3.00 mmol) of *n*-butyl acrylate and 2 mL degassed DMAc were added at 130 °C.

Table 4. Crystallographic data for complexes **9**, **10**, **11-*cis***, **11-*trans*** and **15**.

Complex	9	10	11-<i>cis</i>	11-<i>trans</i>	15
Chemical Formula	C _{44.5} H ₄₂ BCl ₆ F ₄ NP ₂ Pd	C ₄₃ H ₃₉ BCl ₃ F ₄ NP ₂ Pd	C _{46.5} H ₄₀ BCl ₂ F ₄ NP ₂ Pd	C ₄₇ H ₄₁ BCl ₃ F ₄ NP ₂ Pd	C ₅₁ H ₄₇ BClF ₄ N ₃ P ₂ Pd
MW (g mol ⁻¹)	1058.64	931.25	938.85	981.31	992.52
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	11.897(2)	9.359(3)	14.562(3)	31.977(3)	13.6471(6)
<i>b</i> (Å)	13.008(3)	11.552(3)	16.041(3)	12.8745(13)	15.3640(7)
<i>c</i> (Å)	17.193(3)	19.987(5)	18.605(3)	10.7781(11)	22.4549(11)
α (°)	73.05(3)	90.159(4)	94.746(3)	90	90
β (°)	76.83(30)	94.623(4)	95.891(3)	90	90
γ (°)	65.23(3)	106.670(4)	92.326(3)	90	90
Volume (Å ³)	2293.8(8)	2026.7(10)	4302.8(13)	4437.2(8)	4708.2(4)
<i>Z</i>	2	2	4	4	4
<i>d</i> _{calc} (g cm ⁻³)	1.533	1.499	1.449	1.469	1.400
Temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)
μ (mm ⁻¹)	0.873	0.772	0.681	0.722	0.573
Transmission (min)	0.7588	0.7252	0.7433	0.6866	0.8469
Transmission (max)	0.8801	0.9268	0.9350	0.9313	0.9190
θ (°)	1.25 ≤ θ ≤ 26.73	2.28 ≤ θ ≤ 25.68	1.28 ≤ θ ≤ 25.35	2.03 ≤ θ ≤ 25.68	2.19 ≤ θ ≤ 26.73
Crystal size (mm ³)	0.30 × 0.15 × 0.15	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.30 × 0.25 × 0.15
Index range	−15 ≤ <i>h</i> ≤ 15 −16 ≤ <i>k</i> ≤ 16 −21 ≤ <i>l</i> ≤ 21	−11 ≤ <i>h</i> ≤ 11 −13 ≤ <i>k</i> ≤ 14 −24 ≤ <i>l</i> ≤ 24	−17 ≤ <i>h</i> ≤ 17 −19 ≤ <i>k</i> ≤ 19 −22 ≤ <i>l</i> ≤ 22	−38 ≤ <i>h</i> ≤ 25 −15 ≤ <i>k</i> ≤ 15 −12 ≤ <i>l</i> ≤ 13	−17 ≤ <i>h</i> ≤ 16 −19 ≤ <i>k</i> ≤ 15 −25 ≤ <i>l</i> ≤ 28
Number of reflections collected	25172	17347	42527	23605	28510
Number of reflections used	9657	7716	15711	8144	10001
Number of reflections [<i>I</i> > 2 σ (<i>I</i>)]	9159	5289	11413	7173	8960
Refinement	Full matrix on <i>F</i> ² (SHELXL)	Full matrix on <i>F</i> ² (SHELXL)	Full matrix on <i>F</i> ² (SHELXL)	Full matrix on <i>F</i> ² (SHELXL)	Full matrix on <i>F</i> ² (SHELXL)
Parameters	607	497	1068	635	619
<i>F</i> ₀₀₀	1070	944	1908	1992	2032
<i>R</i> ₁ (<i>F</i> _o > 2 σ <i>F</i> _o)	0.0405	0.0695	0.0863	0.0440	0.0371
<i>wR</i> ₂ (all data)	0.0973	0.1788	0.1828	0.0941	0.0845

After 10 min the catalyst solution was added against a positive stream of nitrogen. To terminate the reaction the mixture was allowed to cool to room temperature and 3 mL of dilute HCl were added. The water phase was extracted twice with 2 mL of dichloromethane and the organic fraction dried over MgSO_4 . Conversions and yields were determined by GC-MS using diethylene glycol-di-*n*-butyl ether as internal standard.

Suzuki Reaction

Phenylboronic acid (2.40 mmol, 293 mg) and potassium carbonate (415 mg, 3.00 mmol) were placed in a Schlenk tube equipped with a stirring bar under argon. 2.00 mmol aryl halide (e.g., 374 mg bromoanisole), 100 mg diethylene glycol-di-*n*-butyl ether and 2 mL degassed xylene were added. After thermostating at 130 °C for 10 min, the catalyst solution was added against a positive stream of nitrogen. To terminate the reaction, the mixture was allowed to cool to room temperature and 3 mL of water were added. The water phase was extracted three times with 2 mL of diethyl ether and the combined organic phases dried over MgSO_4 .

Crystallography for the Complexes 9, 10, *trans*-11, *cis*-11 and 15

The crystal data collection and refinement details for compounds 9, 10, 11-*trans*, 11-*cis* and 15 are summarised in Table 4. All data sets were collected on a Bruker SMART Apex CCD diffractometer^[18] using a gamma scan with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction was carried out with standard methods from the software package Bruker SAINT.^[19] Empirical corrections were performed using SCALEPACK^[20] and SMART data were treated with SADABS.^[21,22] The structures were solved by direct methods (9, 11-*trans*, 11-*cis* and 15), the partial structure expansion method which yielded the position of the metal atoms (10), and conventional Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares calculations on F^2 using SHELXL-97^[23] within the X-Seed environment.^[24] The hydrogen atoms were fixed in calculated positions. ORTEP-III for Windows^[25] was used to generate the various figures of the three complexes at the 50 % probability level.

The structure of compound 15 was refined as a racemic twin with contributions of 0.63(2) and 0.37(2) of the two specimens. The crystal lattices of two complexes contained CH_2Cl_2 molecules that are disordered over two positions (the respective site occupancy factors are given in parenthesis): compound 9 contains two CH_2Cl_2 molecules (0.60 and 0.40 for both molecules) and 11-*cis*, one (0.51 and 0.49 for one Cl only). Contributions of another disordered CH_2Cl_2 in the unit cell of 11-*cis* were taken into account by the SQUEEZE method.^[26] Some atoms in the BF_4^- counterion in complex *cis*-11 (the B atom and one F atom, site occupancy factors 0.62 and 0.38) and the BF_4^- counterion in the unit cell of 15 (site occupancy factors 0.60 and 0.40) are disordered over two positions.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-289849 (11-*cis*), CCDC-289850 (10), CCDC-289851 (9), CCDC-289852 (15), and CCDC-

289853 (11-*trans*). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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