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Synthesis of Chlorinated Biphenyls by Suzuki Cross-Coupling Using Diamine or Diimine-Palladium Complexes

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Several novel diimines (Salen-type ligands) **2a**–**2i** and their reduced diamine counterparts **3b**,**3d**–**3g** and **3i** form complexes **4a**–**4i**, **5b**,**5d**–**5g**, and **5i** with $PdCl_2$ in DMF or methanol. Using 1 mol-% of the isolated complexes **4e** and **5f** many polychlorinated biphenyls (PCBs) can be prepared in moderate to excellent yields according to the Suzuki cross-coupling protocol with contact to air. Several 4-acetylbiphenyls prepared by this method can be converted in moderate yields into the corresponding biphenylcarboxylic acids (BCAs) by alkaline cleavage. An X-ray crystal structure determination confirms the structure of complex **5f**.

Introduction

For many years cross-coupling reactions catalyzed by transition metals have been most powerful and convenient tools in modern organic synthesis.[1] Although many different types of ligands have been discovered for these types of reactions, there is still a need for new creative innovations. For example, the development of catalysts not including phosphane ligands is of special interest due to environmental concerns. As reported in several scientific papers, it is very difficult to separate the remaining phosphane moiety during the work-up process.[2–7] Moreover, many ligands are often air-sensitive or expensive, which places significant limits on their synthetic applications.

In an effort to find an efficient metal complex that could promote the Suzuki reaction, we first decided to investigate the scope and limitations of several novel diimines (Salen-type ligands) complexed to Pd. As previously been published, Salen-ligands coordinate to a large variety of metals (Pd, Co, Cu, Ni, Mn, V, Zn, Cr, Al, Ru).[8–15] Due to this complexation-ability these ligands are currently most intensively studied classes of chiral Schiff bases. Moreover, Salen-type complexes often promote the reaction under very mild conditions[16] and are excellent catalysts for a large group of different reactions such as epoxidations of alkenes and styrenes,[9,15] alkylations,[16] oxidations,[13] cyclopropanations,[15] Michel reactions,[11] Diels–Alder reactions,[10] Strecker reactions,[17] and addition of Et_2Zn to benzaldehyde.[15] However, according to the best of our knowledge, only some complexes of this type have been tested for Suzuki cross-coupling reactions. Styring et al.[18] and Sarkar et al.[6] have obtained good results from studies on the use of Salen-type ligands in some reactions, but modifications to the structure have not further been performed. Spectroscopic data for these types of ligands cannot also be found in papers. Pd-Salen complexes have also not yet been used for the preparation of *p*oly*c*hlorinated *b*iphenyls (PCBs) or chlorinated *b*iphenyl*c*arboxylic *a*cids (BCAs). PCBs incur a number of human diseases. PCBs are well known industrial organochlorine chemicals that caused big environmental concern in the 1980s and 1990s.[19] Moreover, it is well known that PCBs are important environmental contaminants that have been implicated in a number of human diseases, such as cancer and cardiovascular disease. However, possible mechanisms of PCB toxicity are still poorly understand, mainly because there still are not efficient and easy method to prepare PCB compounds. Many literature reviews on synthesis and analyses of PCBs have previously been reported.[20–22] It is well known that for many BCAs, such as the environmental pollutants 3-chloro-4-

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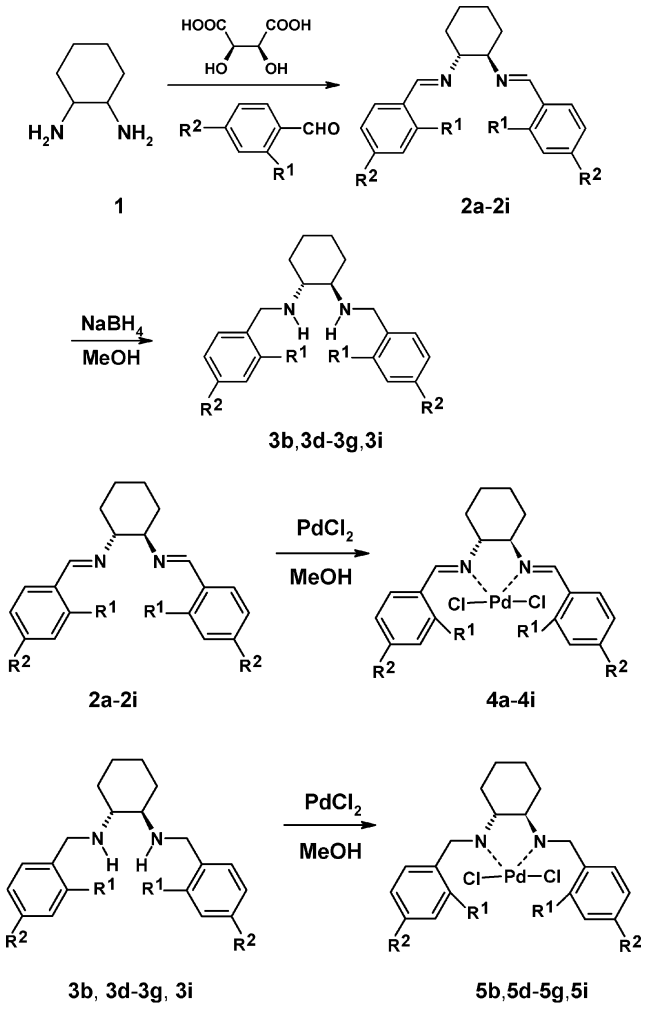
(2,4,5-trichlorophenyl)benzoic acid and 2-chloro-4-(2,4,6-trichlorophenyl)benzoic acid, there are no synthetic methods available until today.[23]

Belokon and North reported previously that the introduction of substituents onto the aromatic rings of the Salen ligand decreases the activity of the copper catalyst[24] but electron-donating groups, on the other hand (such as methoxy) and electron-withdrawing groups (like nitro and trifluoromethyl) in *para* position to the phenol oxygen decrease the enantioselectivity of the catalyst in the alkylation reaction.[25] This difference in catalytic ability between the Salen-ligand analogs prompted us to prepare first the novel Salen-type ligands **2a**–**2i** and their reduced counterparts **3b**, **3d**–**3g** and **3i** (Scheme 1). Secondly, the corresponding Pd complexes **4a**–**4i**, **5b**, **5d**–**5g**,**5i** were prepared in an effort to find an efficient catalyst for the Suzuki reaction. We recently developed a ligandless version of Suzuki reaction in water,[4] but this protocol was limited to the synthesis of biaryl phenols or carboxylic acids. With the new approach presented in this paper we try to overcome this problem by preparing biaryls using easily synthesized palladium-diimine or -diamine complexes instead.

The present initial study shows that our novel ligands[8–14,26] **2a**–**2i** and **3b**, **3d**–**3g**,**3i** can easily be prepared in good yield and with high purity and that their Pd complexes **4a**–**4i** and **5b**, **5d**–**5g**,**5i** (Scheme 1) promote the Suzuki reaction in the preparation of chlorinated biphenyls in moderate to excellent yields.



Ligand		Complex	Substituents	
2	**3**	**4-5**	R^1	R^2
a	-	**a**	H	H
b	**b**	**b**	OH	H
c	-	**c**	NO_2	H
d	**d**	**d**	OMe	H
e	**e**	**e**	CF_3	H
f	**f**	**f**	F	H
g	**g**	**g**	H	OMe
h	-	**h**	H	NMe_2
i	**i**	**i**	OMe	OMe

Scheme 1. Prepared Salen-type **2a**–**2i** and diamine-type ligands **3b**, **3d**–**3g**,**3i**. Structures of Pd complexes **4a**–**4i**, and **5b**, **5d**–**5g**,**5i**.

Results and Discussion

Ligands **2a**–**2i** and **3b**, **3d**–**3g** and **3i** form complexes **4a**–**4i** and **5b**, **5d**–**5g** and **5i** with Pd (see Scheme 1). Complexes **4e**, **5e**, **5f** and **5i** could be isolated as crystals but only those of complex **5f** were obtained with sufficient quality for a crystal structure analysis (Figure 1).

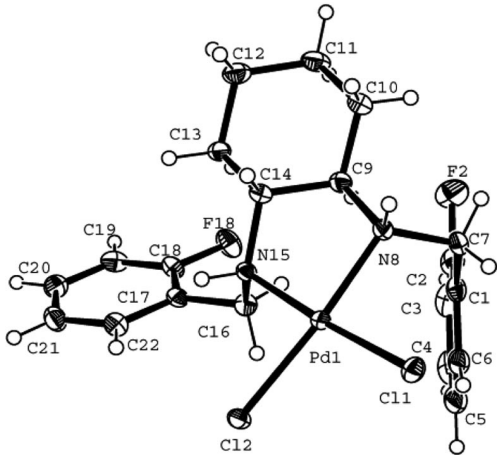
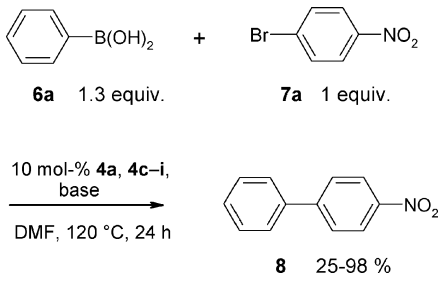


Figure 1. A plot of the X-ray structure of **5f** with atom labels. The thermal displacement parameters are shown at 50% probability level.

In the solid state **5f** shows an unsymmetrical twisted structure with the expected square-planar Pd coordination sphere. The Pd–N and Pd–Cl bond lengths are normal for this kind of Pd complex: Pd1–N8 2.068(2), Pd1–N15 2.030(2), Pd1–Cl1 2.3309(7) and Pd1–Cl2 2.3265(6) Å. Remarkably, **5f** forms a centrosymmetric dimer through hydrogen bonds from N8 and N15 to the Cl1 and Cl2 of the adjacent complex (the contact distance being 3.365 Å for N8···Cl2 and 3.279 Å for N15···Cl1).

Using all ligands **2a**–**2i** complexed to palladium we then initially studied the Suzuki reaction between phenylboronic acid **6a** and 4-bromonitrobenzene (**7a**) as the first model reaction in an effort to understand how our diimine-type ligands would promote this coupling reaction most efficiently. Results are collected in Table 1. Reactions proceeded in situ and we noticed that a ligand/Pd ratio of 5:1 should be used to completely form the palladium species. With large excess of ligand, we could conclude that all palladium was complexed. Our aim was then to further investigate the best complex alternatives and to study the scope and limitations for these in more demanding reactions.

Table 1. Pd-Salen-catalyzed Suzuki reaction of boronic acid **6a** with bromide **7a**.



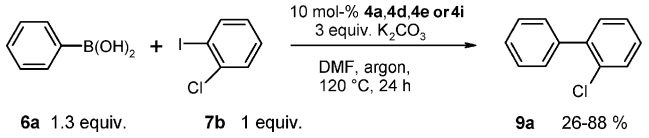
Entry	Catalyst	Base [mol-equiv.]	Yield (inert gas: Ar)	Yield (with contact to the air)
1	$PdCl_2$[a]	K_2CO_3(2.0)	53	57
		K_2CO_3 (3.0)	–	–
2	**4a**	K_2CO_3 (2.0)	57	62
		K_2CO_3 (3.0)	85	86
3	**4c**	K_2CO_3 (2.0)	39	25
		K_2CO_3 (3.0)	58	–
4	**4d**	K_2CO_3 (2.0)	63	95
		K_2CO_3 (3.0)	98	–
5	**4e**	K_2CO_3 (2.0)	54	41
		K_2CO_3 (3.0)	89	55
6	**4f**	K_2CO_3 (3.0)	67	75
		K_2CO_3 (2.0)	–	97
7	**4g**	K_2CO_3 (3.0)	97	–
		$NaHCO_3$ (3.0)	79	–
8	**4h**	K_2CO_3 (3.0)	70	53
		$NaHCO_3$ (3.0)	87	–
9	**4i**	K_2CO_3 (3.0)	72	61

[a] Ligandless $PdCl_2$ was used for the reaction. Complex **4b** gave yields less than 10% and are not reported in the Table. Yields determined by quantitative NMR analyses.[27]

As shown in Table 1, the catalysts formed in situ indeed catalyze the reactions because ligandless $PdCl_2$ promotes the reaction with only 49–57% yield. The reactions proceeded with moderate to excellent yields when performed under argon atmosphere. However, with the catalysts **4a**, **4d**, and **4f** good yields could also be obtained if the reactions were performed in the air. During ligand tuning it was rewarding to discover that catalysts containing both electron-donating (**4d** 98%, **4g** 97%) or -withdrawing (**4e** 89%, **4f** 75%) substituents gave excellent results.

2-Chlorobiphenyl (**9a**) could thereafter be synthesized using **2a**, **2d, 2e** and **2f** when complexed in situ with $PdCl_2$. Compound **9a** was synthesized starting from 1 equiv. of 1-chloro-2-iodobenzene (**7b**) and 1.3 equiv. of phenylboronic acid (**6a**) in DMF at 120 °C for 24 h under argon using different bases. The highest yield (88%) was obtained when 30 mol-% of complex **4e** was used. (Table 2). Reaction to prepare **9a** was successful, so we concluded that it would perhaps also be possible to synthesize other polychlorinated PCBs by this protocol.

Table 2. In situ synthesis of 2-chlorobiphenyl (**9a**) using 10 mol-% of Pd-Salen complexes.



Entry	Catalyst	Base [equiv.]	Yield (%)
1	$PdCl_2$[a]	K_2CO_3 (3)	46[b]
2		NaOH (3)	40
3	**4a**	K_2CO_3 (3)	59
4	**4d**	K_2CO_3 (3)	26
5		NaOH (3)	36
6	**4e**	K_2CO_3 (3)	74
7		K_2CO_3 (3)	88[c]
8	**4i**	K_2CO_3 (3)	30[d]

[a] Ligandless $PdCl_2$ as catalyst. [b] Pd amount 20 mol-%. [c] Pd amount 30 mol-%. [d] With contact to the air. Yields determined by quantitative NMR analyses.[27]

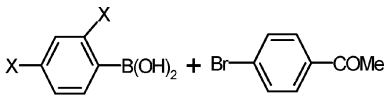
Ligands **2e**, **2f** and **2i** were reduced as previously shown in Scheme 1. The catalytic activity of reduced and non-reduced ligands complexed with $PdCl_2$ (to produce **4e**, **4f**, **4i**, **5e**, **5f**, and **5i**, respectively) were further examined in the syntheses of 4-acetylbiphenyls **10a**–**10c** (Table 3). Overall, reduced ligands gave better yields than their non-reduced counterparts. The most active complexes **4e**, **5e**, **5f** and **5i** were isolated resulting in same yields than in situ reactions.

Isolated catalysts **4e** and **5f** were chosen for more specific studies for preparing PCBs. As summarized in Table 4, 1 mol-% of complex **4e** and **5f** catalyzed the reaction between the corresponding chlorinated aryl halide and phenylboronic acid using 3 equiv. of K_2CO_3 in DMF giving moderate yields. When using the complex **5f** for the synthesis of pentachlorinated PCBs, the yields decreased [for example, 2,3,5,2′,3′-PCB (**9r**) (10%, X = Br); 2,4,5,2′,3′-PCB (**9s**) (9%, X = I). These results are not reported in Table 4.]

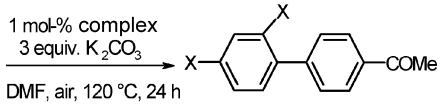
Finally we decided to use our newly designed diamine-type complex **5f** for the synthesis of chlorinated 4-acetylbiaryls. Reactions proceeded in moderate to excellent yields 23%–99% (Table 5). Alkaline cleavage of the produced ketones according Žabjek and Petrič[28] was also utilized in order to obtain BCAs in different yields.

Although the overall yields in the synthesis of compounds **11a**, **11b**, **11d**–**11j** remained low, the high purity and easy separation of the compounds can be seen as an advantage of the method.

Table 3. Preparation of 4-acetylbiphenyls. Reactions with **4f** and **4i** as catalysts are performed in situ. **4e**, **5e**, **5f** and **5i** are used as isolated complex.



6a–c 1.3 equiv. **7c** 1 equiv.

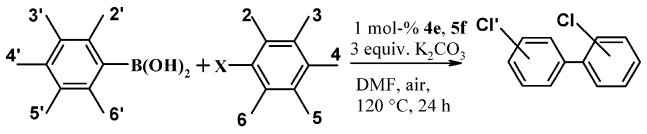


10a–c 25-98 %

		Product yield[a] (%)					
	X	**4e**	**4f**	**4i**	**5e**	**5f**	**5i**
10a	H	19	30	26	92	98	99
10b	Cl	11	1	1	94	98	46
10c	F	12	2	4	91	95	99

[a] All yields determined by quantitative NMR analyses.[27]

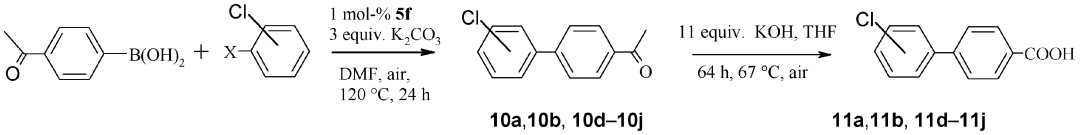
Table 4. Synthesis of PCBs using isolated catalysts **4e** and **5f**.



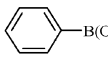
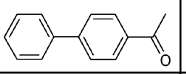
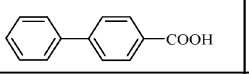
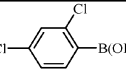
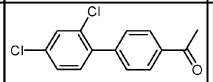
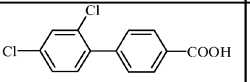
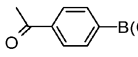
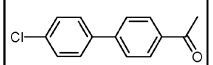
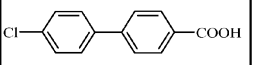
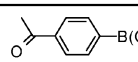
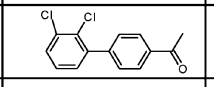
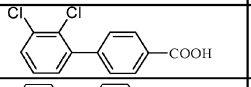
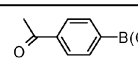
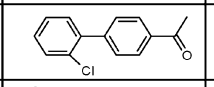
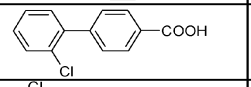
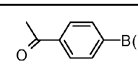
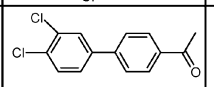
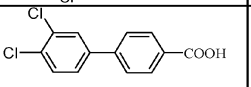
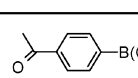
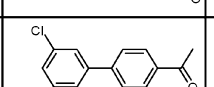
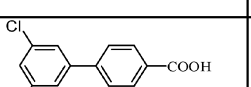
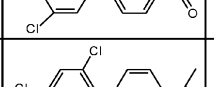
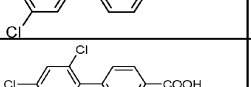
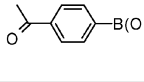
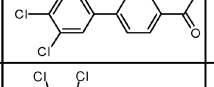
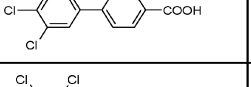
1.3 equiv. 1 equiv. **9b–s**

Entry	**9**	PCB	X	Catalyst	Yield (%)
1	**b**	4	I	**4e**	95
2	**c**	2,3	Br	**5f**	51
3	**d**	2′,4′	Br	**4e**	32
4	**e**	3,4	I	**4e**	87
5	**f**	3,5	Br	**5f**	35
6	**g**	2,3,5	Br	**5f**	10
7	**h**	2,4,5	I	**5f**	30
8	**i**	2,2′,3′	I	**5f**	23
9	**j**	2,2′,4′	I	**5f**	45
10	**k**	2,3,4′	I	**5f**	40
11	**l**	2,4,4′	I	**4e**	68
12	**m**	2,3,2′,4′	Br	**5f**	29
13	**n**	2,3,3′4′	I	**5f**	35
14	**o**	2,4,3′4′	I	**4e**	52
15	**p**	3,5,2′,3′	Br	**5f**	20
16	**q**	3,5,2′,4′	Br	**5f**	13

Table 5. Preparation of BCAs by alkaline cleavage of ketones synthesized via Suzuki cross-coupling using complex **5f**[a].



10a,**10b**, **10d–10j** **11a**,**11b**, **11d–11j**

Entry	Phenylboronic acid	Aryl halide	Product of Suzuki reaction	**10**	Yield [%]	Product of alkaline cleavage of ketones	**11**	Yield [%]	Total yield [%]
1				**a**	99		**a**	62	61
2				**b**	98		**b**	30	29
3				**d**	83		**d**	58	42
4				**e**	72		**e**	54	45
5				**f**	69		**f**	21	14
6				**g**	86		**g**	56	48
7				**h**	74		**h**	62	46
8				**i**	23		**i**	22	5
9				**j**	32		**j**	28	9

[a] All yields were determined by quantitative NMR analyses.[27]

Conclusions

Diimine-type ligands prepared form diaminocyclohexane **2a**–**2i** and their reduced analogs (diamines) **3b**, **3d**–**3g**,**3i** form metal complexes **4a**–**4i** and **5b**, **5d**–**5g**,**5i** with $PdCl_2$. When using the isolated complexes **4e** and **5f** several PCBs can be prepared in moderate to excellent yields. The novel ligands **2d** (including an electron-donating methoxy group at C-2′), **2e** and **3f** (including the electron-withdrawing substituents CF_3 and F at C-2′) give promising results in the Suzuki–Miyaura reaction when complexed to palladium. The isolated diamine complex **5f** appears to be a promising candidate for the synthesis of PCBs with a catalyst-loading of 1 mol-%. Using this complex several 4-acetylbiaryls can be synthesized. These products can conveniently be converted into the corresponding carboxylic acids.

Experimental Section

General: Solvents and reagents were purchased from Sigma–Aldrich or Merck and were used without further purification. Thin-layer chromatography (TLC) was performed on precoated (Kieselgel 60 F_{254}) aluminium plates and detected by UV light. Silica gel 100, particle size 0.063–0.2 mm, was used for column chromatography. ^1H and ^{13}C NMR spectra were measured with a Varian Mercury 300 MHz spectrometer using $CDCl_3$ or DMSO as solvent. Chemical shifts are reported as δ values (ppm) relative to tetramethylsilane which was used as internal standard except for NMR analyses that were performed in DMSO. In these cases chemical shifts are reported relative to DMSO the shift value. Yields for the Suzuki reactions were determined by quantitative NMR analyses[27] and TCE (1,1,1-trichloroethane) or nitromethane was used as standard. IR spectra of ligands were analyzed in the 450–4000 cm^{-1} range using KBr discs (with 1 wt-% ligand) with a Perkin–Elmer Spectrum One FT-IR spectrometer.

X-ray Crystallography:[29] Crystals of **5f** for the single-crystal X-ray diffraction analysis were grown in the mixture of dichloromethane and methanol 1:1 by slow solvent evaporation. Suitable crystals were selected and analysis were performed using Bruker Kappa Apex II diffractometer with graphite-monochromatized Mo-K_α (λ = 0.71073 Å) radiation. Collect software[30] was used for the data measurement and DENZO-SMN[31] for the processing. The structures were solved by direct methods with SIR97[32] and refined by full-matrix least-squares methods with WinGX software,[33] which utilizes the SHELXL-97 module.[34] All CH hydrogen positions were calculated using a riding-atom model with $U_H = 1.2 \times U_N$ or $1.2 \times U_C$.

Crystal Data for 5f: $C_{20}H_{24}Cl_2F_2N_2Pd{\cdot}CH_2Cl_2$, M = 342.30, orange prism, $0.20 \times 0.30 \times 0.40$ mm^3, triclinic, space group $P\bar{1}$, a = 9.4943(3) Å, b = 9.9187(3) Å, c = 12.8329(3) Å, α = 85.007(2), β = 79.830(2), γ = 86.151(2)°, V = 1183.34(6) $Å^3$, Z = 2, D_c = 1.663 $g\,cm^{-3}$, F_{000} = 596, μ = 1.263 mm^{-1}, T = 123.0(1) K, $2\theta_{max}$ = 50.0°, 4163 unique reflections, 3964 with $I > 2\sigma(I)$, R_{int} = 0.0208, 271 parameters, 0 restraints, GoF = 1.097, R_1 = 0.0361, wR_2 = 0.0562 [$I > 2\sigma(I)$], R_1 = 0.0383, wR_2 = 0.0575 (all data), $0.370 < \Delta\rho < -0.355$ $e\,Å^{-3}$.

General Procedure of Preparing Ligands 2a–2i: Ligands were synthesized by the modified Jacobsen method.[26] (*R*,*R*)-Cyclohexane-1,2-diammonium mono-(+)-tartrate (2.00 g, 7.54 mmol) and K_2CO_3 (2.1 g, 15.19 mmol) were dissolved in distilled water (10 mL), and ethanol (25 mL) was added and solution was heated to 80 °C. The aldehyde (15.00 mmol, 1.98 equiv.) was dissolved in ethanol (varied amounts, 25–70 mL, depending on the aldehyde's solubility in ethanol) and added to the reaction mixture during 30 min in a slow stream. After addition, the mixture was refluxed for 2 h, then water (10 mL) was added. The cooled reaction mixture was stirred with further cooling (below +5 °C) for 2 h. The product was extracted with dichloromethane and washed twice with distilled water and twice with brine and dried with $MgSO_4$. The product was filtered, evaporated and dried under vacuum.

General Procedure of Preparing Ligands 3b, 3d–3 g, 3i: To the ligands (10 mmol) **2b**, **2d**–**2g**, **2i** dissolved to methanol was added $NaBH_4$ (950 mg, 25 mmol) in small portions with vigorous stirring. Stirring was continued at room temp. overnight. Then water was added to the reaction mixture and the product was extracted with dichloromethane and dried with $MgSO_4$. The product was filtered, evaporated and dried under vacuum.

General Procedure of Complex Formation with $PdCl_2$ To Obtain 4e, 5f and 5i: Ligand **3f** or **3i** (2.00 mmol) and $PdCl_2$ (1.00 mmol) were dissolved in methanol and refluxed overnight. Mixtures were cooled to room temperature and filtered through glass sinter (type 3G), methanol was used for washing. The solid crude product was dissolved in dichloromethane and filtered through the sinter, the solvents were evaporated. Recrystallisation from dichloromethane/methanol (1:1) gave the complexes **5f** and **5i**. Complexes could be obtained as orange-yellow crystals; ligand **2e** (1 g, 2.35 mmol) and $PdCl_2$ (415 mg, 2.34 mmol) were refluxed under argon in acetonitrile for 14 h. The solvent was evaporated and the residue was redissolved in DCM. Filtration through a 3G glass sinter and slow evaporation gave little yellow crystals of **4e**.

General Procedure of Suzuki Reaction with the Isolated Crystalline Catalyst: Catalyst (0.0056 mmol), aryl bromide (0.56 mmol), phenylboronic acid (0.728 mmol), base (232 mg, 1.68 mmol, 3 equiv.) and DMF (1.5 mL) was added, either under argon or with contact to the air. Thereafter, the reaction mixture was stirred for 24 h at 120 °C (argon or air conditions). The mixture was cooled to room temperature. Ethyl acetate (ca. 20 mL) was added and the suspension filtered through a 3G glass sinter in order to remove most of the used catalyst. The organic layer was washed with distilled water (2×15 mL) and brine (2×15 mL) and then dried with $MgSO_4$. Evaporation of the solvents and purification of the residue by column chromatography (*n*-hexane as eluent for PCBs and hexane/EtOAc, 13:1 including 1% methanol as eluent for acetylbiphenyls and nitrobiphenyls). Thereafter, all yields were determined by quantitative NMR analyses[27] with either TCE or nitromethane as standards.

General Procedure of Suzuki Reaction with the in-situ-Generated Catalyst: The ligand (0.0028 mmol) and $PdCl_2$ (1 mg, 0.0056 mmol) were first dissolved in 1 mL of DMF and then stirred for 2 h under argon or air at 120 °C. Thereafter all reactants were added in one portion. The next synthetic steps were executed as described above.

General Procedure of Alkaline Cleavage of Ketones: According to Žabjek and Petrič[28] the 4-acetylbiphenyl (0.2 mmol, 1 equiv.) and KOH (62 mg, 1.11 mmol) were dissolved in THF (10 mL) and refluxed at 65 °C using a $CaCl_2$ tube. After stirring for further 4 h more KOH (62 mg, 1.11 mmol) was added, then the mixture was stirred at 65 °C for 90 h. Mixture was then cooled to room temperature, water (ca. 20 mL) was added and by-products were extracted with chloroform. After addition of aqueous HCl (3 M) followed by extraction to chloroform, the organic phase was dried with $MgSO_4$, filtered and evaporated to yield the carboxylic acid.

(*R*,*R*)-Cyclohexane-1,2-diammonium mono-(+)-tartrate[12] used for the synthesis of all ligands was prepared by a method developed by Jacobsen[26]; instead of drying the product at 40–45 °C it was dried under vacuum.

Supporting Information (see also the footnote on the first page of this article): Spectroscopic data of synthesized compounds; refs.[35–43] refer to data in the Supporting Information.

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