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Dichloro-Bis(aminophosphine) Complexes of Palladium: Highly Convenient, Reliable and Extremely Active Suzuki–Miyaura Catalysts with Excellent Functional Group Tolerance

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Abstract: Dichloro-bis(aminophosphine) complexes are stable depot forms of palladium nanoparticles and have proved to be excellent Suzuki–Miyaura catalysts. Simple modifications of the ligand (and/or the addition of water to the reaction mixture) have allowed their formation to be controlled. Dichlorobis[1-(dicyclohexylphosphanyl)piperidine]palladium (**3**), the most active catalyst of the investigated systems, is a highly convenient, reliable, and extremely active Suzuki catalyst with excellent functional group tolerance that enables the quantitative coupling of a wide variety of activated, nonactivated, and deactivated and/or sterically hindered functionalized and heterocyclic aryl and benzyl bromides with only a slight excess (1.1–1.2 equiv) of arylboronic acid at 80 °C in the presence of 0.2 mol % of the catalyst in technical grade toluene in flasks open to the air. Conversions of >95 % were generally achieved within only a few minutes. The reaction protocol presented herein is universally applicable. Side-products have only rarely been detected. The catalytic activities of the aminophosphine-based systems were found to be dramatically improved compared with their phosphine analogue as a result of significantly faster palladium nanoparticle formation. The decomposition products of the catalysts are dicyclohexylphosphinate, cyclohexylphosphonate, and phosphate, which can easily be separated from the coupling products, a great advantage when compared with non-water-soluble phosphine-based systems.

Keywords: C–C coupling · cross-coupling · nanoparticles · palladium · phosphorus

Introduction

The Suzuki–Miyaura reaction nowadays belongs to an indispensable set of palladium-catalyzed cross-coupling reactions and is one of the most important methods for the formation of symmetric and nonsymmetric biaryls[1–3] which are found in polymers,[4] biologically active compounds,[5] ligands,[6] and other materials.[7] Similarly, a powerful synthetic route to biarylmethanes, which are frequently found in biologically active compounds and pharmaceuticals,[8,9] involves the cross-coupling of benzyl halides with arylboronic acids (Scheme 1).[10] However, even though recent developments have led to a considerable increase in the activity of Suzuki catalysts, some of which are very efficient and allow the use of sterically hindered substrates and even aryl chlorides at low catalyst loadings and occasionally at room temperature, their syntheses are often time consuming, difficult, and/or require the use of expensive starting materials. Furthermore, many of these catalysts suffer from poor thermal stability, low functional group tolerance, and/or sensitivity towards both air and moisture and hence require inconvenient inert-atmosphere techniques for their successful use, which strongly limits their application in industrial processes.[11–14]

We report herein the catalytic activities of simple dichlorobis(aminophosphine)palladium complexes of the type $[(P\text{-}\{(NC_5H_{10})_{3-n}(C_6H_{11})_n\}_2Pd(Cl)_2]$ in Suzuki reactions performed with various aryl bromides and show that they are extremely active and reliable catalysts with outstanding functional group tolerance. Aminophosphines were expected to be ideal ligand systems for such transformations as they slowly degrade in the presence of water and hence promote the formation of palladium nanoparticles.[15] Moreover, their formation is accompanied by the generation of dicyclohexylphosphinate, cyclohexylphosphonate, and phosphate, which can easily be separated from the coupling products, a great advantage compared with most of the phosphine-

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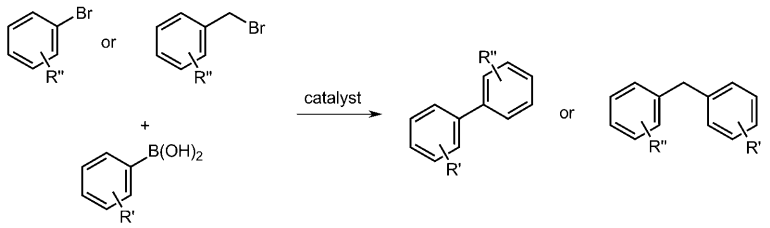
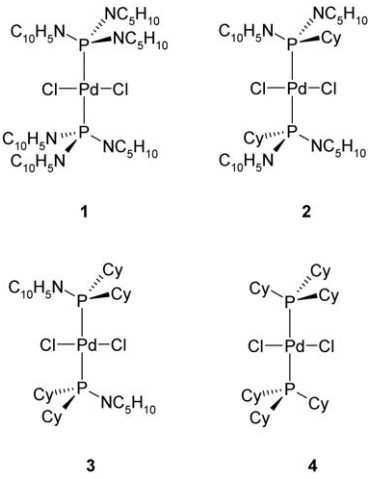


Scheme 1. Suzuki–Miyaura cross-coupling reaction between aryl or benzyl bromides with arylboronic acids.

based systems. However, we have demonstrated that dichloro-bis(aminophosphine) complexes are excellent depot forms of nanoparticles and show that simple modification of the ligand (and/or the addition of water to the reaction mixture) allow their formation to be controlled. We present a highly convenient, simple, and universally applicable reaction protocol for the high-yielding synthesis of biaryls and diarylmethanes within only a few minutes and show that aminophosphine-based complexes are significantly more active than their phosphine analogue under the chosen reaction conditions.

Results and Discussion

The addition of 2 equiv of 1,1′,1″-(phosphinetriyl)tripiperidine to a suspension of $[Pd(Cl)_2(cod)]$ (cod = cycloocta-1,5-diene) in toluene under N_2 at room temperature exclusively yielded the dichloro{bis[1,1′,1″-(phosphinetriyl)tripiperidine]}palladium complex $[\{P(NC_5H_{10})_3\}_2Pd(Cl)_2]$ (**1**) within a few minutes (Scheme 2).[15a] Removal of the volatiles under reduced pressure and the addition of pentane followed by filtration afforded the analytically pure **1** in almost quantitative yield. Dichlorobis[1,1′-(cyclohexylphosphanediyl)dipiperidine]palladium (**2**) and dichlorobis[1-(dicyclohexylphosphanyl)piperidine]palladium (**3**) were prepared accordingly.[16]



Scheme 2. Dichloro{bis[1,1′,1″-(phosphanetriyl)tripiperidine]}palladium (**1**), dichloro{bis[1,1′-(cyclohexylphosphanediyl)dipiperidine]}palladium (**2**), and dichloro{bis[1-(dicyclohexylphosphanyl)piperidine]}palladium (**3**), and dichloro[bis(tricyclohexylphosphane)]palladium (**4**).

The dichloro-bis(aminophosphine) complexes **1–3** are excellent Suzuki catalysts that enable the coupling of various activated, nonactivated, and deactivated and/or sterically hindered, functionalized and heterocyclic aryl and benzyl bromides with only a slight excess (1.1–1.2 equiv) of arylboronic acid. The catalytic reactions were carried out at 80 °C in the presence of 0.2 mol % of the catalyst in technical grade toluene in flasks open to the air to give the coupling products with conversions of >95 % within a few minutes. Whereas **3** was found to have the highest catalytic activity, a dramatically lower activity (compared with the aminophosphine-based systems) was found for the tricyclohexylphosphine complex **4** (see Scheme 2).[17] The results obtained with catalyst **3** are given in the Tables 1–3.[18]

For example, when electronically activated, nonactivated, or deactivated substrates such as 1-bromo-4-nitrobenzene, phenyl bromide, 1-bromo-4-ethenylbenzene, 9-bromoanthracene, and 4-bromoaniline were coupled with phenylboronic acid, complete product formation was achieved in almost all reactions examined within 15 min in the presence of 0.2 mol % of **3** (Table 1, entries 1–16). The same conversion rates and yields were observed with sterically hindered 1-bromo-2-methylbenzene, 1-bromo-2-methylnaphthalene, and 2-bromo-1,3-dimethylbenzene (entries 17–19). Smooth product formation was also observed with 2′-bromo-2,6-dimethoxybiphenyl as the coupling partner (entry 20). Although very high conversion rates and yields were achieved with 1-bromo-2-methoxybenzene and 2-bromo-1,3,5-trimethoxybenzene, only a moderate yield was observed with 2-bromo-*N*,*N*-dimethylaniline (Table 1, entries 21–23). Complete phenylation was obtained within only 15 min with 1,2-dibromobenzene, 1,4-dibromo-2,5-dimethoxybenzene, bis(4-bromophenyl)methanone, and 1,3,5-tribromobenzene, for example (Table 1, entries 24–34). Excellent conversion rates, product yields, and selectivities were also found for other halides, for example, 1-bromo-4-chloro-2-methylbenzene, 1-bromo-2,6-dichlorobenzene, and 2-bromo-4-chloro-1-methoxybenzene, which exclusively yielded the chlorobiphenyls in conversions between 89 and 100 % (Table 1, entries 35–40). Impressively, whereas only moderate conversion rates and yields were observed with pyridyl halides such as 2-bromopyridine and 3-bromopyridine, excellent rates and product yields were found for 2,6-dibromopyridine and 5-bromopyrimidine as well as thiophenes and thioanisoles (Table 1, entries 41–54). Exemplary results were obtained with 2-bromothiophene, 3-bromothiophene, 2,5-dibromothiophene, tetrabromothiophene,[19] 2-bromo-5-chlorothiophene, 5-bromothiophene-2-carbaldehyde, 4,5-dibromothiophene-2-carbaldehyde,[20] 5,5′-dibromo-2,2′-bithiophene, as well as 4-bromothioanisole, which demonstrates that **3** is nowadays the catalyst of choice

Table 1. Suzuki–Miyaura cross-coupling reactions between aryl bromides and phenylboronic acid catalyzed by **3**.[a]

Entry	Aryl halide	Conv. [%][b,c]	*t* [min]
1	1-bromo-4-nitrobenzene	100 (97)	15
2	4-bromobenzonitrile	100 (96)	5
3	methyl 4-bromobenzoate	100 (98)	5
4	methyl 3-bromobenzoate	100 (97)	5
5	methyl 2-bromobenzoate	100 (96)	10
6	1-(4-bromophenyl)ethanone	100 (97)	10
7	5-bromo-2-benzofuran-1(3*H*)-one	100 (97)	5
8	3-bromobenzaldehyde	100 (95)	5
9	phenyl bromide	100 (94)	5
10	1-bromo-4-ethenylbenzene	94 (89)	10
11	9-bromoanthracene	100 (96)	5
12	1-bromo-4-methoxybenzene	96 (90)	10
13	4′-bromo-2‘-methylacetanilide	99 (94)	10
14	1-bromo-2-(diethoxymethyl)benzene	99 (92)	5
15	4-bromoaniline	99 (96)	5
16	4-bromo-*N*,*N*-dimethylaniline	94 (89)	30
17	1-bromo-2-methylbenzene	100 (94)	5
18	1-bromo-2-methylnaphthalene	97 (91)	10
19	2-bromo-1,3-dimethylbenzene	100 (95)	10
20	2′-bromo-2,6-dimethoxybiphenyl	63 (52)	60
21	1-bromo-2-methoxybenzene	96 (91)	10
22	2-bromo-*N*,*N*-dimethylaniline	44 (29)	60
23	2-bromo-1,3,5-trimethoxybenzene	97 (87)	15
24	9,10-dibromoanthracene	100 (97)	5
25	2,7-dibromofluorene	100 (95)	5
26	1,4-dibromobenzene	100 (96)	10
27	1,3-dibromobenzene	100 (96)	10
28	1,2-dibromobenzene	100 (98)	10
29	1,4-dibromo-2,5-dimethoxybenzene	100 (98)	10
30	bis(4-bromophenyl)methanone	100 (95)	5
31	2,2‘-dibromobenzophenone	100 (96)	60
32	2,6-dibromo-4-methylaniline	90 (78)	30
33	2,4-dibromo-1,3,5-trimethylbenzene	100 (99)	15
34	1,3,5-tribromobenzene	99 (92)	15
35	1-bromo-3-chlorobenzene	91 (84)	10
36	1-bromo-4-chloro-2-methylbenzene	90 (85)	5
37	1-bromo-2,4-dichlorobenzene	94 (81)	10
38	1-bromo-2,5-dichlorobenzene	92 (85)	10
39	1-bromo-2,6-dichlorobenzene	89 (81)	15
40	2-bromo-4-chloro-1-methoxybenzene	100 (92)	5
41	2-bromopyridine	45 (32)	60
42	3-bromopyridine	64 (51)	60
43	2,6-dibromopyridine	100 (94)	10
44	5-bromopyrimidine	97 (89)	10
45	2-bromothiophene	100 (95)	5
46	3-bromothiophene	100 (94)	5
47	2,5-dibromothiophene	100 (97)	10
48	tetrabromothiophene	91 (82)	180
49	2-bromo-5-chlorothiophene	99 (92)	5
50	5-bromothiophene-2-carbaldehyde	100 (93)	15
51	4,5-dibromothiophene-2-carbaldehyde	94 (81)	15
52	5,5′-dibromo-2,2′-bithiophene	100 (92)	5
53	4-bromothioanisole	96 (91)	10
54	2-bromothioanisole	30 (18)	180
55	4-bromophenol	89 (78)	120
56	4-bromo-2,6-di-*tert*-butylphenol	100 (94)	30
57	1-(5-bromo-2-hydroxyphenyl)ethanone	99 (92)	120
58	5-bromo-2-hydroxybenzaldehyde	90 (82)	180
59	4-bromo-3-methylphenol	97 (87)	120
60	4-bromo-3,5-dimethylphenol	100 (88)	300
61	2-bromo-4-chlorophenol	100 (95)	30
62	4-bromobenzoic acid	93 (82)	240
63	(bromomethyl)benzene	100 (93)	15
64	methyl 4-(bromomethyl)benzoate	98 (92)	10
65	1-(bromomethyl)-4-methoxybenzene	96 (88)	15
66	1-(bromomethyl)-2-methylbenzene	100 (94)	10
67	1,3-bis(bromomethyl)benzene	99 (94)	20
68	1-bromo-3-(bromomethyl)benzene	94 (85)	15
69	1-(bromomethyl)-3-chlorobenzene	97 (92)	15
70	1-bromo-3-(chloromethyl)benzene	96 (87)	5

[a] Reaction conditions: 2.0 mmol aryl bromide, 1.1–1.2 equiv phenylboronic acid (rel. bromide), 1.1 equiv K_3PO_4 (rel. bromide), 2.5 mL of toluene, catalyst (0.2 mol%) added in solution, 80°C, air. [b] Determined by GC–MS, based on aryl halide. [c] Isolated yields are given in parentheses.

for coupling reactions performed with bromothiophenes. However, a lower yield was noticed with 2-bromothioanisole. Quantitative product formation was also achieved with various (also sterically hindered) bromophenols and even 4-bromobenzoic acid (entries 55–62).

Excellent performances were also observed with benzyl bromides as coupling partners (Table 2, entries 1–8). Reactions performed with (bromomethyl)benzene, methyl 4-(bromomethyl)benzoate, 1-(bromomethyl)-4-methoxybenzene, or 1-(bromomethyl)-2-methylbenzene cleanly yielded the corresponding coupling products in conversions of $>95\%$. Whereas complete phenylation was achieved with 1,3-bis(bromomethyl)benzene and 1-bromo-3-(bromomethyl)benzene, selective quantitative formation of 1-benzyl-3-chlorobenzene and 3-(chloromethyl)biphenyl, respectively, was observed with 1-(bromomethyl)-3-chlorobenzene and 1-bromo-3-(chloromethyl)benzene within only a few minutes.

Table 2. Suzuki–Miyaura cross-coupling reactions between benzyl bromides and phenylboronic acid catalyzed by **3**.[a]

Entry	Aryl halide	Conv. [%][b,c]	*t* [min]
1	(bromomethyl)benzene	100 (93)	15
2	methyl 4-(bromomethyl)benzoate	98 (92)	10
3	1-(bromomethyl)-4-methoxybenzene	96 (88)	15
4	1-(bromomethyl)-2-methylbenzene	100 (94)	10
5	1,3-bis(bromomethyl)benzene	99 (94)	20
6	1-bromo-3-(bromomethyl)benzene	94 (85)	15
7	1-(bromomethyl)-3-chlorobenzene	97 (92)	15
8	1-bromo-3-(chloromethyl)benzene	96 (87)	5

[a] Reaction conditions: 2.0 mmol aryl bromide, 1.1–1.2 equiv phenylboronic acid (rel. bromide), 1.1 equiv K_3PO_4 (rel. bromide), 2.5 mL of toluene, catalyst (0.2 mol%) added in solution, 80°C, air. [b] Determined by GC–MS, based on aryl halide. [c] Isolated yields are given in parentheses.

Although 2-naphthylboronic acid performed similarly (Table 3, entries 1–14), a slightly reduced activity was noticed with (2-methylphenyl)boronic acid (Table 3, entries 15–21) and (2-methoxyphenyl)boronic acid (Table 3, entries 22–28).[21]

In almost all the reactions examined, catalyst **3** is more efficient than the reference systems of $[(C_7H_7)Pd(Cl)_2(PPh_3)]$,[22] $[(\{C_6H_2(tBu)_2O\}P(OR)_2)(Cl)Pd]_2$,[13f,g] and $Pd(OAc)_2/PCy_2Ar$,[2i] among others. Similar activities were obtained with the aminophosphine-based pincer complex $[(C_6H_3\{NHP(piperidinyl)_2\}_2)Pd(Cl)]$.[15a] Comparisons with

Table 3. Suzuki–Miyaura cross-coupling reactions between aryl bromides and different arylboronic acids catalyzed by **3**.[a,b]

Entry	Aryl halide	Conv. [%][c,d]	*t* [min]
1	4-bromobenzonitrile	96 (92)	5
2	3-bromobenzaldehyde	98 (92)	5
3	methyl 2-bromobenzoate	90 (85)	15
4	phenyl bromide	97 (93)	15
5	1-bromo-4-ethenylbenzene	89 (81)	30
6	2-bromobenzonitrile	99 (95)	15
7	1-bromo-2-methoxybenzene	90 (84)	15
8	2-bromo-1,3,5-trimethylbenzene	75 (64)	30
9	1-bromo-3-chlorobenzene	100 (93)	15
10	2,6-dibromopyridine	100 (91)	15
11	2-bromothiophene	92 (86)	20
12	3-bromothiophene	94 (89)	20
13	2-bromo-5-chlorothiophene	87 (80)	20
14	(bromomethyl)benzene	89 (74)	60
15	1-bromo-4-nitrobenzene	93 (89)	75
16	phenyl bromide	92 (83)	15
17	4-bromoaniline	75 (62)	30
18	4-bromo-*N*,*N*-dimethylaniline	88 (81)	60
19	1-bromo-3-chlorobenzene	92 (86)	15
20	2,6-dibromopyridine	76 (64)	240
21	1-(bromomethyl)-2-methylbenzene	95 (87)	60
22	1-(4-bromophenyl)ethanone	95 (88)	60
23	methyl 3-bromobenzoate	89 (81)	60
24	phenyl bromide	94 (86)	120
25	1-bromo-4-methoxybenzene	80 (68)	120
26	4-bromoaniline	76 (66)	120
27	1-bromo-2,6-dichlorobenzene	86 (73)	120
28	5-bromothiophene-2-carbaldehyde	92 (85)	30

[a] 2-Naphthylboronic acid (entries 1–14), (2-methylphenyl)boronic acid (entries 15–21), and (2-methoxyphenyl)boronic acid (entries 22–28). [b] Reaction conditions: 2.0 mmol aryl bromide, 1.1–1.2 equiv arylboronic acid (rel. bromide), 1.1 equiv K_3PO_4 (rel. bromide), 2.5 mL of toluene, catalyst (0.2 mol%) added in solution, 80°C, air. [c] Determined by GC–MS, based on aryl halide. [d] Isolated yields are given in parentheses.

the highly active but air-sensitive $[Pd_2(dba)_3]/P(t\text{Bu})_3$[23] and the extremely active air- and moisture-stable NHC-bearing [Pd(Cl)(R-allyl)][14k] (NHC = N-heterocyclic carbene) complexes are difficult because the Suzuki reactions were often performed at lower temperatures.[24] However, the situation is similar for benzylic halides: The reference systems of $[Pd(PPh_3)_4]$ and $[Pd(C_3H_5)(Cl)]_2$/DPEphos are less efficient.[25,26] $[Pd(C_3H_5)(Cl)]_2$/tedicyp, another catalyst, allows the coupling reactions to be performed with very low catalyst loadings, but requires temperatures of 130°C and reaction times of ~20 h to achieve high conversions.[27] A remarkably high catalytic activity (high yields within a few hours at 100°C with 0.1 mol% of catalyst) was found for the asymmetric pincer complex $[\{C_6H_3(NHPh_2)(C_3H_3N_2)\}Pd(Cl)]$ in water.[28] Comparisons with the oxime-derived palladacycle $[\{C_6H_3(OH)C(CH_3)NOH\}Pd(Cl)]_2$ are not appropriate because these reactions were performed with benzyl chlorides at 25°C and typically require 1–4 days for high conversions.[29] Overall, **3** is one of the most active, convenient, and versatile Suzuki catalysts to have been reported,[24] enabling a wide variety of aryl and benzyl bromides to be coupled with arylboronic acids in very high yields within only a few minutes (and most important) using one reaction protocol in all the reactions examined.

The steric bulk and σ-donor strengths of 1,1′,1″-(phosphanetriyl)tripiperidine, 1,1′-(cyclohexylphosphanediyl)dipiperidine, 1-(dicyclohexylphosphanyl)piperidine, and tricyclohexylphosphine are almost identical (as indicated by the CO stretching frequency of complexes of the type *trans*-$[(PR_3)_2Rh(CO)(Cl)]$)[30] and hence this cannot explain the dramatic difference in the activities of the aminophosphine-based systems compared with their phosphine analogue.[31] However, aminophosphines, which degrade in the presence of water and air (and thus under catalytic reaction conditions), promote (in contrast to phosphines) the formation of palladium nanoparticles and hence provide a simple and plausible explanation for their strikingly improved catalytic activity.[32] Decomposition products are dicyclohexyl phosphinate, cyclohexyl phosphonate, and phosphate[33] with weak ligating properties, which can easily be separated from the coupling products, another great advantage compared with phosphine-based systems.[34] The following observations indicate palladium nanoparticle formation: Sigmoidal-shaped kinetics curves, with induction periods of between 1 and 2 min generally observed with **3,** the catalyst with the most stable aminophosphine (Figure 1). Increased induction

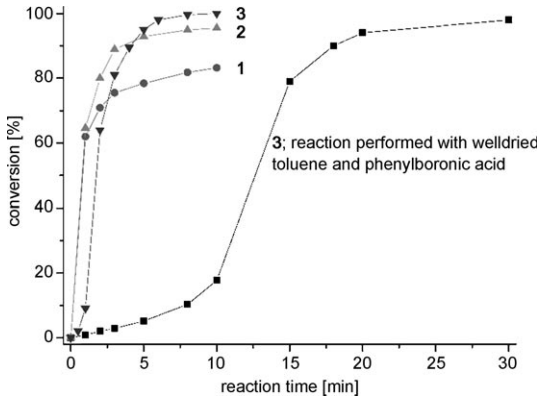


Figure 1. Kinetics of the coupling reactions of 2-bromo-1,3-dimethylbenzene with phenylboronic acid catalyzed by 0.2 mol% of catalyst under different reaction conditions.

periods were noticed when the coupling reactions were performed with well-dried toluene and phenylboronic acid. The addition of water to these reaction mixtures significantly reduced the induction periods again, clear evidence that **3** is a precatalyst and transforms into palladium nanoparticles.[35–37]

Conclusion

Dichlorobis[1-(dicyclohexylphosphanyl)piperidine]palladium (**3**) is an excellent and reliable Suzuki catalyst with outstanding functional group tolerance, which allows quantitative coupling of a wide variety of activated, nonactivated, and deactivated and/or sterically hindered and functionalized aryl and benzyl bromides with arylboronic acids at 80°C within only a few minutes. The reaction protocol pre-

sented herein is extremely simple, highly convenient, and, most important, universally applicable. The reactions are extremely clean (side-products have only rarely been detected).[38] As a consequence, the isolated yields of the coupling products are typically only between 5 and 10% (sometimes up to 15%) lower than the conversions reported. The catalytic activities of the aminophosphine-based systems were found to be dramatically improved compared with their phosphine analogue due to significantly faster palladium nanoparticle formation. Decomposition products are dicyclophosphinate, cyclohexylphosphonate, and phosphate, which can easily be separated from the coupling products, a great advantage when compared to non-water-soluble phosphine-based systems.

Experimental Section

General procedures: All synthetic operations for the catalyst preparation were carried out in oven-dried glassware using a combination of glovebox (M. Braun 150B-G-II) and Schlenk techniques under a dinitrogen atmosphere. Solvents were reagent grade or better and freshly distilled under a N_2 atmosphere by standard procedures. Deuteriated solvents were purchased from Armar, dried by standard procedures, and degassed by freeze–thaw cycles before use. All chemicals were purchased from Aldrich Chemical Co., Acros Organics, or Fluka and used without further purification.

Analysis: ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data were recorded at 500.13, 125.76, and 202.46 MHz, respectively, on a Bruker DRX-500 spectrometer or at 300.1, 121.5, and 75.4 MHz, respectively, on a Varian Gemini spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants (J) are given in Hz. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane; the resonance of the residual protons of the solvent was used as the internal standard for ^{1}H ($\delta = 7.15$ ppm benzene) and all deuterium solvent peaks for ^{13}C ($\delta = 128.0$ ppm benzene). All measurements were carried out at 298 K. Abbreviations used in the description of NMR data are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed on a Leco CHNS-932 analyzer at the University of Zurich, Switzerland.

Preparation of $P(NC_5H_{10})_3$: Phosphorus trichloride (5 mL, 57.31 mmol) was dissolved in diethyl ether (200 mL) and cooled in an ice bath to 0°C. Piperidine (42.5 mL, 429.8 mmol, 7.5 equiv) was slowly added dropwise, during which the formation of a white precipitate ($C_5H_{10}N{\cdot}HCl$) was observed. After complete addition, the suspension was allowed to warm up to room temperature and was then stirred for an additional hour. The reaction mixture was filtered and the solid was washed with additional diethyl ether (100 mL). The pale-yellow filtrate was dried in vacuo to give 12.36 g (43.61 mmol, 76%) of an off-white solid. ^{1}H NMR (C_6D_6): $\delta =$ 2.95 (t, $^3J_{HH} = 5.0$ Hz, 12H), 1.45 ppm (brs, 18H); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 47.3$ (d, $^2J_{PC} = 64.4$ Hz), 27.5 (d, $^3J_{PC} = 19.6$ Hz), 26.1 ppm (s); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 117.3$ ppm (s, $P(NC_5H_{10})_3$).

Preparation of $P(NC_5H_{10})_2(C_6H_{11})$: Phosphorus trichloride (5 mL, 57.31 mmol) was dissolved in diethyl ether (400 mL) and cooled to −78°C. Cyclohexyl Grignard reagent $C_6H_{11}MgBr$ (1 equiv, 1 M, 57.3 mL) was slowly added. After complete addition (monitored by ^{31}P{^{1}H} NMR spectroscopy), an excess of piperidine (34 mL, ~6 equiv) was added and then the reaction mixture was warmed up to room temperature and stirred for an additional hour before filtering it. The solid was washed with diethyl ether (100 mL). The combined pale-yellow filtrates were dried in vacuo and extracted with pentane to give 84% of the pure phosphine as a colorless solid. Colorless crystals were obtained by recrystallization in pentane. ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 2.92$ (t, $^3J_{HH} = 4.8$ Hz, 8H), 1.80–1.62 (m, 5H) 1.40–1.14 ppm (m, 18H); ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): $\delta = 50.6$ (overlapping signals), 33.5 (brs), 30.5 (d, $J = 28.5$ Hz), 29.0 (brs), 27.9 (d, $J = 22.2$ Hz), 27.3 (brs), 25.7 ppm (s); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): $\delta = 99.3$ ppm (s); elemental analysis calcd (%) for $C_{16}H_{31}N_2P$: C 68.05, H 11.06, N 9.92; found: C 68.22, H 11.14, N 9.81.

Preparation of $P(NC_5H_{10})(C_6H_{11})_2$: Phosphorus trichloride (5 mL, 57.31 mmol) was dissolved in diethyl ether (400 mL) and cooled to −78°C. Cyclohexyl Grignard reagent $C_6H_{11}MgBr$ (2 equiv, 1 M, 114.6 mL) was slowly added. After complete addition (monitored by ^{31}P{^{1}H} NMR spectroscopy), the reaction mixture was warmed up to room temperature and stirred for an hour and then an excess of piperidine (17 mL, ~3 equiv) was added. After stirring for an additional hour at room temperature, the reaction mixture was filtered. The solid was washed with diethyl ether (100 mL). The combined pale-yellow filtrates were dried in vacuo and extracted with pentane to give 81% of the pure phosphine as a colorless oil that solidified upon standing. ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 2.94$ (brs, 4H), 1.89–1.65 (m, 6H), 1.39–1.13 ppm (m, 22H); ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): $\delta = 52.4$ (brs), 36.6 (d, $J = 65.1$ Hz), 30.5 (d, $J =$ 33.6 Hz), 29.9 (brs), 27.5 (overlapping signals), 25.4 ppm (s); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): $\delta = 76.5$ (s); elemental analysis calcd (%) for $C_{17}H_{32}NP$: C 72.56, H 11.46, N 4.98; found: C 72.71, H 11.69, N 4.80.

General procedure for the synthesis of $[(P((NC_5H_{10})_{3-n}(C_6H_{11})_n)_2Pd(Cl)_2]$ (1–4): $[Pd(cod)(Cl)_2]$ (100 mg, 0.35 mmol) was suspended in toluene (10 mL). After the addition of solutions of toluene (10 mL) containing 2 equiv of the appropriate ligand, the reaction mixture was stirred for 10 min. Removal of the volatiles under reduced pressure and the addition of pentane, followed by filtration afforded the yellow, analytically pure palladium complexes **1–4** in almost quantitative yields.

Data for catalyst 1: ^{1}H NMR (C_6D_6): $\delta = 3.35$ (s, 24H; NCH_2), 1.50 (s, 24H; NCH_2CH_2), 1.46 ppm (s, 12H; CH_2); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 48.5$ (s, NCH_2), 27.0 (s, NCH_2CH_2), 25.7 ppm (s, $NCH_2CH_2CH_2$); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 92.5$ ppm (s, $P(NC_5H_{10})_3$); elemental analysis calcd (%) for $C_{30}H_{60}Cl_2N_6P_2Pd$: C 48.43, H 8.13, N 11.29; found: C 48.71, H 8.29, N 11.36.

Data for catalyst 2: ^{1}H NMR (C_6D_6): $\delta = 3.31$ (brs, 8H), 3.21 (brs, 8H), 2.24 (m, 4H), 1.82–1.21 ppm (m, 42H); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 49.0$ (brs), 38.6 (t, $J = 71.5$ Hz), 28.6 (brs), 27.5 (overlapping signals), 27.0 (overlapping signals), 25.5 ppm (s); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 102.7$ ppm (s, $P(NC_5H_{10})_2(C_6H_{11})$); elemental analysis calcd (%) for $C_{32}H_{62}Cl_2N_4P_2Pd$: C 51.79, H 8.42, N 7.55; found: C 51.78, H 8.31, N 7.46.

Data for catalyst 3: ^{1}H NMR (C_6D_6): $\delta = 3.21$ (brs, 8H), 3.62 (brs, 4H), 3.32–2.28 (m, 4H), 1.95–1.16 ppm (m, 48H); ^{13}C{^{1}H} NMR (C_6D_6): $\delta =$ 51.8 (t, $J = 49.5$ Hz), 35.9 (t, $J = 50.3$ Hz), 30.4 (s), 28.6 (s), 27.5–27.2 (overlapping signals), 25.0 ppm (s); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 80.0$ ppm (s, $P(NC_5H_{10})(C_6H_{11})_2$); elemental analysis calcd (%) for $C_{34}H_{64}Cl_2N_2P_2Pd$: C 55.17, H 8.72, N 3.78; found: C 55.24, H 8.80, N 3.77.

General procedure for Suzuki cross-coupling reactions of aryl and benzyl bromides with arylboronic acids: All catalytic reactions were carried out in reaction vessels open to the air. A round-bottomed flask was charged with the newly purchased or freshly recrystallized arylboronic acid (2.0 mmol), the aryl halide, powdered K_3PO_4 (2.2 mmol), and toluene (2.5 mL) of technical quality. The mixture was vigorously stirred and heated to 80°C. Then the correct amount of catalyst was added by syringe as a toluene solution. Samples were periodically taken from the reaction mixture, quenched with water, extracted with ethyl acetate, and analyzed by GC–MS. At the end of catalytic reaction, the reaction mixtures were allowed to cool to room temperature, quenched with water (adjusted to an appropriate pH when biaryls with acidic or basic groups had to be extracted), and extracted with ethyl acetate (3×40 mL). The combined extracts were dried ($MgSO_4$) and evaporated to dryness. The crude material was purified by flash chromatography on silica gel, as necessary. Isolated yields of the coupling products were typically between 5 and 10% (sometimes up to 15%) lower than the conversions reported in the tables.

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[16] For details, see the Experimental Section.
[17] The higher catalytic activities of the dichloro-bis(aminophosphine) complexes compared with their phosphine analogue was attributed to significantly slower nanoparticle formation (see below). The generally improved catalytic activity of **3** compared with **2** (and **1**), however, was attributed to its higher stability towards water, which results in a retarded release of the palladium nanoparticles. Although this can lead to significant induction periods, the palladium nanoparticles are more active because their growth is slower and therefore the size of the nanoparticles will be smaller, which makes the ratio between palladium on the outer rim and palladium on the inside of the particles more favorable. Thus, whereas essentially the same activity was noted for **2** and **3** with electronically activated and nonactivated substrates, improved conversion rates and yields were generally observed with **3** with substrates that require "prolonged" reaction times (compare Tables 1–3).
[18] For the results obtained with **1**, **2**, and **4**, see Tables T1–T3 in the Supporting Information.
[19] Selective conversion of tetrabromothiophene into 3,4-dibromo-2,5-diphenylthiophene (90%) was achieved at 70°C within 4 h with 2 equiv of phenylboronic acid.
[20] A conversion of 86% of 4,5-dibromothiophene-2-carbaldehyde into 3-bromo-2-phenylthiophene (91%) was achieved within 5 min at 80°C with 1 equiv of phenylboronic acid.
[21] Note that homocoupling and protodeboration (up to 10%) was sometimes detected in reactions performed with sterically hindered arylboronic acids.
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[24] Importantly, even though other highly active Suzuki catalysts have been reported to enable the efficient coupling of aryl chlorides with arylboronic acids (by molecular mechanisms), this does not imply that they show a significant increase in activity with aryl bromides as coupling partners. Moreover, many of these systems have been prepared by (multistep) syntheses using expensive starting materials and require inconvenient air- and water-free reaction conditions, additives, and/or expensive bases such as Cs_2CO_3 for their successful use. In addition, modified reaction conditions are often reported for

different substrates, which strongly limit their application in industrial processes for example.

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[31] In the "classical" mechanism with dichloro-bis(phosphine) complexes, coordinatively unsaturated $14e^-$ Pd^0 complexes of the type $[Pd(PR_3)_2]$ are assumed to be the catalytically active species. Phosphine dissociation and oxidative addition of an aryl halide to yield the tricoordinated Pd^{II} intermediates $[Pd(Ar)(X)(PR_3)]$ are subsequent reaction steps. Thus, the efficiency of bulky and electron-rich phosphines in Suzuki reactions (and others) seems to be a result of their ability to generate monophosphine-Pd^0 and -Pd^{II} complexes in the catalytic cycle, which implies that steric factors are probably more important than electronic effects. However, nanoparticles are assumed to be involved with **4** (under the chosen reaction conditions), as indicated by the sigmoidal-shaped kinetics curves observed in all the reactions examined.[32]

[32] The improved catalytic activity of **1**–**3** in Suzuki–Miyaura cross-coupling reactions compared with other precatalysts (depot forms of palladium nanoparticles) was attributed to the ideal stability (sensitivity towards water) of dichloro-bis(aminophosphine) complexes, which results in an optimal rate of release of palladium and thus the formation of small and consequently highly active palladium nanoparticles (the ratio between palladium on the outer rim and palladium on the inside of the particles is more favorable the smaller the particle size). Apart from the ideal rate of release of palladium, the presence of phosphinates, phosphonates, and phosphate,[33] may additionally stabilize the nanoparticles formed and thus retard their growth and consequently prevent the formation of inactive palladium black. Finally, different precatalysts may lead to palladium nanoparticles with different morphologies, which most probably also has a large impact on their activities.

[33] The addition of water to THF solutions of **1**–**3** in air (in the presence of K_3PO_4) resulted in their decomposition and the formation of dicyclohexylphosphinate, cyclohexylphosphonate, and phosphate, respectively, after thermal treatment (as shown by $^{31}P\{^1H\}$ NMR spectroscopy), in accord with the expected trend; the more P–N bonds the aminophosphines contain the faster the decomposition occurs. Catalyst degradation was also observed under the catalytic reaction conditions.

[34] The use of catalysts containing water-soluble phoshanes offers similar advantages, see, for example: a) C. J. Li, *Chem. Rev.* **2005**, *105*, 3095; b) N. Pinault, D. W. Bruce, *Coord. Chem. Rev.* **2003**, 241; c) F. Alonso, I. P. M. Yus, *Tetrahedron* **2005**, *61*, 11711.

[35] Induction periods were only observed for the more stable catalysts **3** and **4**. Thus, sigmoidal-shaped kinetics curves with very short induction periods (less than 30 s) are highly probable for **1** and **2**.

[36] For the kinetics of catalyst **4** see Graph S1 in the Supporting Information.

[37] Even though palladium nanoparticles are expected to be the catalytically active form of **1**–**3**, the addition of metallic mercury to reaction mixtures of aryl bromides, phenylboronic acid, and the catalyst had an effect on neither the conversion rate nor the product yield and demonstrates that the mercury drop test is not applicable here. The following reasons might provide an explanation for this behavior: The coupling reactions are too fast (and/or the amalgamation of the palladium nanoparticles too slow) to affect the coupling reaction and/or the rate of liberation of palladium from the dichloro-bis(aminophosphine) complexes is too high, thereby affording a constant amount of palladium in solution.

[38] See the gas chromatograms of exemplary Suzuki–Miyaura cross-coupling reactions in the Supporting Information.

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