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Hydrophilic Pd^0 Complexes Based on Sugars for Efficient Suzuki–Miyaura Coupling in Aqueous Systems

Giulia Tarantino,[a] Massimiliano Curcio,[a] Andrea Pica,[a] Andrea Carpentieri,[a] Maria E. Cucciolito,[a] Francesco Ruffo,[a] Aldo Vitagliano,[a] and Matteo Lega*[a]

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Two classes of hydrophilic Pd^0 complexes containing P,N and N,N sugar-based ligands were prepared and tested in the Suzuki–Miyaura cross-coupling reaction under environmentally friendly aqueous conditions. The best catalyst was tolerant towards different substrates, and its activity is comparable with the highest values reported so far for reactions in aqueous media [loading 0.0010 %, turnover frequency (TOF) $3.5 \times 104\ h^{-1}$].

Introduction

Over the last few years, carbohydrates have been widely employed as ligand backbones in the field of homogeneous metal-promoted catalysis.[1] This choice is motivated by the high versatility of these natural molecules; the inexpensive natural precursors are easily functionalized to yield chiral ligands with the desired coordinating motifs. Moreover, as the chemistry of carbohydrates is well developed, it is easy to fine tune the chemical–physical properties to make the ligands selectively soluble in desired green solvents, such as water or ionic liquids.[2]

Although sugar-derived ligands have been applied in several catalytic C–C and C–X bond formations (X = O, N, S,

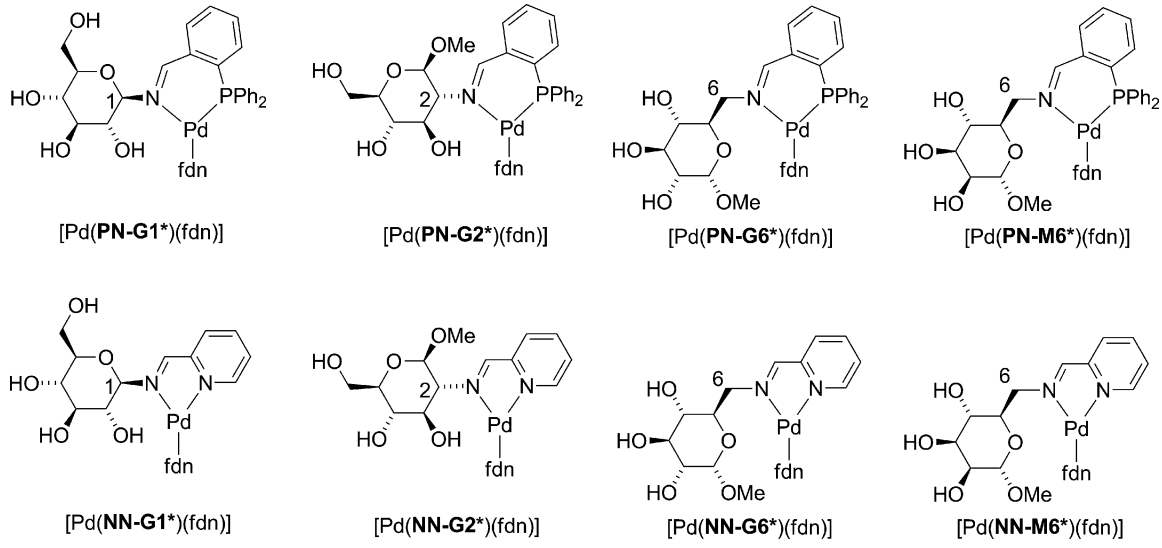

Figure 1. The complexes used in this work. The label of the ligands indicates the donor atoms (PN or NN), the sugar (G = glucose, M = mannose) and the position of the imino function within the sugar ring (1, 2 or 6). The asterisk means that the hydroxy groups are deprotected; fdn = fumarodinitrile.

[a] Dipartimento di Scienze Chimiche, Università di Napoli "Federico II", Complesso Universitario di Monte S. Angelo, Via Cintia, 80126 Napoli, Italy
E-mail: matteo.lega@unina.it
http://scienzechimiche.dip.unina.it/

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P),[1] their scope has not been extended comprehensively to other powerful couplings such as the Suzuki–Miyaura reaction, for which only some sporadic examples have been reported.[3] Nevertheless, in this field, sugar candidates are really attractive building blocks owing to their solubility in

water,[4] which allows the green and sustainable synthesis of biaryls.[5]

On this basis, we report the preparation of diphenylphosphino–imino (PN) and pyridino–imino (NN) sugar-based ligands, along with the syntheses of the corresponding hydrophilic Pd^0 complexes (Figure 1, fdn = fumarodinitrile). Some imino ligands have recently been employed in Suzuki–Miyaura couplings,[6] but in all cases the activities ranged from low to moderate.

The design of both PN and NN ligands was aimed at ensuring their easy, high-yield synthesis.

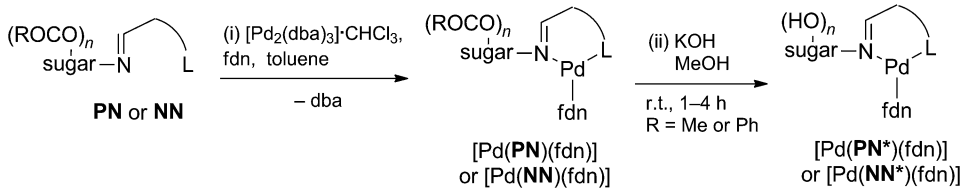
Four imino sugar residues were employed: three of them are derived from glucose functionalized at the 1-, 2- and 6-positions, and the fourth is instead a mannoside derivatized at the 6-position.

As expected, all of the complexes were soluble in aqueous media and could be fruitfully employed in the Suzuki–Miyaura coupling reaction.

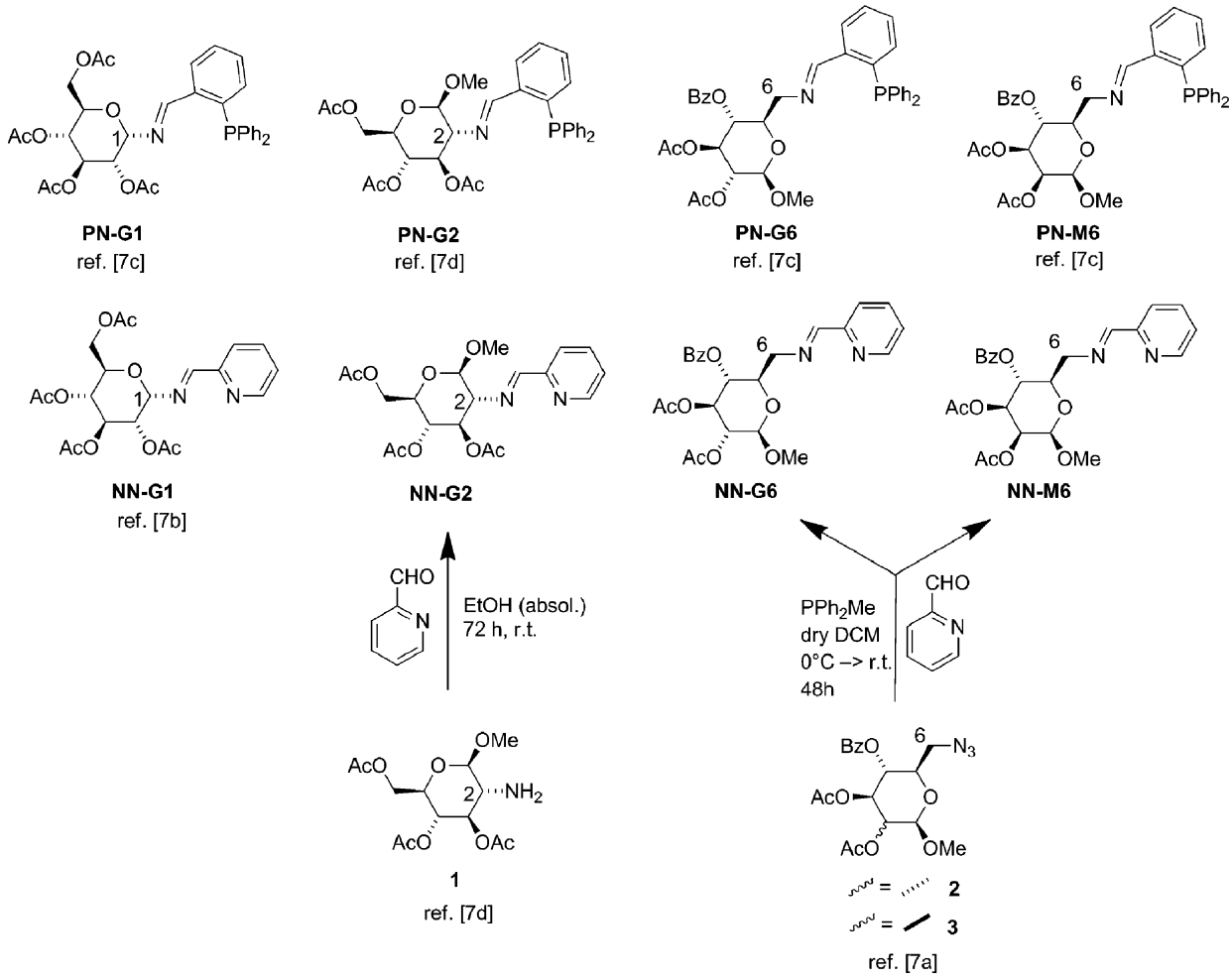
Results and Discussion

Synthesis of the Complexes

The strategy for the synthesis of the complexes involved three major steps. First, protected PN and NN ligands were synthesized from suitable precursors. In a second phase, the corresponding Pd^0 complexes [Pd(PN)(fdn)] or [Pd(NN)(fdn)] were prepared (Scheme 1, Step i) and then transformed into the deprotected hydrophilic species [Pd(PN*)(fdn)] or [Pd(NN*)(fdn)] (Scheme 1, Step ii).



Scheme 1. Synthesis of the complexes.



Scheme 2. Synthesis of the ligands.

Some of the ligands were already known (Scheme 2),[7] and the others were synthesized for the first time. The molecules were prepared from the corresponding amino or azido precursors **1**, **2** and **3** by condensation with the proper aldehyde in the former case and by aza-Wittig reactions in the latter cases. The products were isolated in high yields by column chromatography or precipitation.

The corresponding [Pd(PN)(fdn)] and [Pd(NN)(fdn)] complexes were prepared in good yields from fresh $[Pd_2(dba)_3{\cdot}CHCl_3]$ (dba = dibenzylideneacetone) by an established procedure (Scheme 1, Step i).[7a]

In toluene, the dba molecules were readily displaced by one alkene and one chelating molecule, as revealed by the rapid change of colour of the reaction mixture from brown to orange-yellow. After the removal of the solvent under vacuum, the complexes were obtained as yellow to orange microcrystalline solids by column chromatography over silica. All of the isolated complexes could be handled in air at room temperature and were stored for several weeks at 277 K without appreciable decomposition.

The compounds were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Upon coordination to the Pd centre, the signals of the olefin undergo a large shift to lower frequencies. This behaviour has been reported previously[7a,7c,8,9] and is attributed to the substantial degree of π back-donation in the Pd^0–olefin bond, which stabilizes the low oxidation state of the palladium centre. The consequent partial $sp^2 \rightarrow sp^3$ rehybridization of the alkene carbon atoms shifts the corresponding signals towards the aliphatic region in both the ^1H and the ^{13}C NMR spectra.

It is worth noting that water-soluble Pd^0 compounds are quite rare.[7a,7b,10] The hydrophilic Pd^0 complexes [Pd(PN*)(fdn)] and [Pd(NN*)(fdn)] were obtained by basic hydrolysis of the acetyl and benzoyl groups (Scheme 1, Step ii). The yellow microcrystalline products, which are fairly soluble in water, methanol and ethanol, were isolated in high yields by precipitation with diethyl ether from the reaction mixtures. Also in this case, all of the isolated complexes could be handled in air at room temperature and were stored for several weeks at 277 K without appreciable decomposition. The only exception is [Pd(PN-G1*)(fdn)], which slowly underwent a transformation to another species in solution; this phenomenon is currently under study.

In both the O-acylated and the deprotected species, the coordination of fdn affords two diastereoisomers, because the olefin is prochiral. The diastereoisomers interconvert by an associative mechanism,[9–11] in which an external olefin coordinates to the metal centre with the enantioface opposite to that initially coordinated, which then dissociates.

The isomeric equilibrium is rapidly reached after dissolution of the complexes, and the presence of two resolved patterns for the two isomers indicates that this process is slow at room temp. on the NMR timescale (Figure 2 shows an example).[7c]

The integration of suitably separated peaks allowed us to calculate the diastereomeric ratios, which are reported in Table 1.

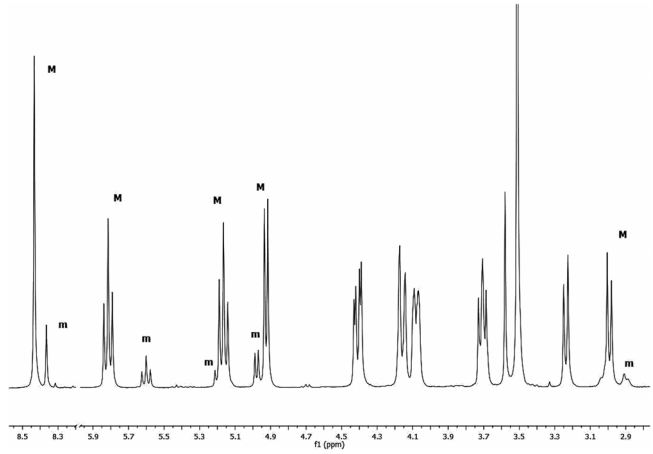


Figure 2. Portion of the ^1H NMR spectrum of [Pd(PN-G2)(fdn)]. The signals of the major (M) diastereoisomer and the corresponding signals for minor (m) one are evidenced.

Table 1. Diastereomeric ratios within the [Pd(PN)(fdn)] and [Pd(NN)(fdn)] complexes.

Entry	Complex	Solvent	Diastereomeric ratio
1[a]	[Pd(PN-G1)(fdn)]	$CDCl_3$	70:30
2	[Pd(PN-G2)(fdn)]	$CDCl_3$	86:14
3[a]	[Pd(PN-G6)(fdn)]	$CDCl_3$	72:28
4[a]	[Pd(PN-M6)(fdn)]	$CDCl_3$	80:20
5[b]	[Pd(NN-G1)(fdn)]	$CDCl_3$	80:20
6	[Pd(NN-G2)(fdn)]	$CDCl_3$	84:16
7	[Pd(NN-G6)(fdn)]	$CDCl_3$	55:45
8	[Pd(NN-M6)(fdn)]	$CDCl_3$	60:40
9	[Pd(PN-G1*)(fdn)]	CD_3OD	50:50
10	[Pd(PN-G2*)(fdn)]	CD_3OD	60:40
11	[Pd(PN-G6*)(fdn)]	CD_3OD	87:13
12	[Pd(PN-M6*)(fdn)]	CD_3OD	73:27
13[b]	[Pd(NN-G1*)(fdn)]	CD_3OD	55:45
14	[Pd(NN-G2*)(fdn)]	CD_3OD	65:35
15	[Pd(NN-G6*)(fdn)]	CD_3OD	50:50
16	[Pd(NN-M6*)(fdn)]	CD_3OD	50:50

[a] From ref.[7c] [b] From ref.[7b]

In almost all cases, a significant discrimination has been found. As a general consideration, the O-acylated complexes have a similar selectivity, and there are only small differences for the two coordinating systems (PN and NN; Table 1, Entry 1 vs. 5 and 2 vs. 6; exceptions are Entry 3 vs. 7 and 4 vs. 8), their position on the sugar backbone (1-, 2- or 6-position; Table 1, Entry 1 vs. 2 vs. 3 and Entry 5 vs. 6 vs. 7; Entry 7 is the only exception) and the epimer used (glucose and mannose; Table 1, Entry 3 vs. 4 and 7 vs. 8).

The differences are larger among the deprotected complexes, for which there is a general drop of selectivity, probably because of the lack of steric hindrance provided by the acyl groups. For these complexes, the presence of the bulky diphenylphosphino group provides a better selectivity compared with that with the pyridyl group (Table 1, Entry 12 vs. 16).

To obtain further evidence of the structures reported, the palladium complex [Pd(NN-G2)(fdn)] was characterized by X-ray crystallography. Crystallization from methanol–

acetonitrile (5:1) yielded single crystals (space group *P*1). Quite surprisingly, the asymmetric unit contains two molecules of the complex, which correspond to the two diastereomers and differ only in the enantioface of the prochiral fumarodinitrile molecule coordinated to the metal centre. The ORTEP drawings of the two molecules are shown in Figure 3. The root-mean-square deviation between the two diastereomers after superposition (calculated excluding fumarodinitrile and hydrogen atoms) is 0.467 Å.

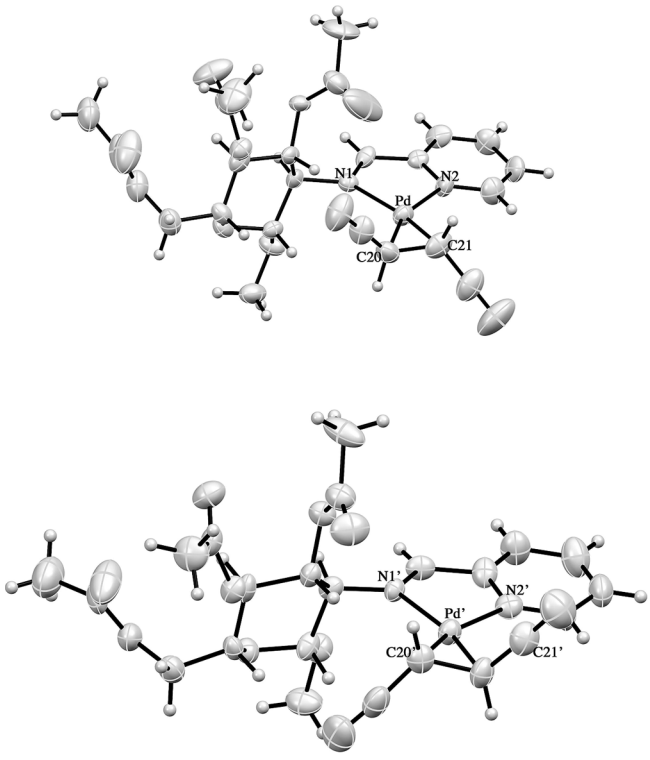


Figure 3. ORTEP drawing of the two diastereomers of [Pd(NN-G2)(fdn)].

All bond lengths and angles are in the normal range. Some interesting bond lengths and angles are reported in Table 2. As expected,[8d] the Pd^0 centre has a trigonal-planar coordination geometry. The coordination plane includes the pyridine ring. The atoms coordinated to the Pd centre are coplanar within 0.09 and 0.10 Å for the two diastereomers. In both molecules, the sugar ring adopts the expected chair conformation, and the mean plane of the sugar ring is almost perpendicular to the coordination plane (ca. 83 and 105° for the two diastereomers).

The coordination bond lengths fall within the expected range for Pd–α-diimine complexes[12,13] and are similar to those found for [Pd(N,N-chelate)(olefin)] complexes.[7a] The length of the olefinic bond is evidence of the substantial rehybridization of the olefinic carbon atoms towards sp^3 upon coordination (1.41 and 1.47 Å for the two diastereomers vs. 1.34 Å for the free alkene). Further evidence is the large out-of-plane displacements of the cyano groups (the torsion angles for the four C atoms of the fdn molecule are 135 and 150°).

Table 2. Selected bond lengths [Å] and angles [°] for the two diastereomers of [Pd(NN-G2)(fdn)].

Bond lengths		
Pd–C20	2.026(8)	2.040(8)
Pd–C21	2.035(10)	2.067(9)
Pd–N1	2.152(7)	2.139(8)
Pd–N2	2.157(6)	2.152(6)
C20–C21	1.411(1)	1.4685(2)
Bond angles		
C20–Pd1–C21	40.7(4)	41.9(3)
C20–Pd1–N1	119.9(3)	118.4(3)
C21–Pd1–N1	160.1(3)	159.1(3)
C20–Pd1–N2	163.4(3)	164.7(3)
C21–Pd1–N2	123.8(3)	122.8(3)
N1–Pd1–N2	75.9(3)	76.8(3)

Suzuki–Miyaura Cross-Coupling Reactions

The Suzuki–Miyaura cross-coupling is an extremely useful tool for C–C bond formation, owing to its versatility and efficiency.[14]

This reaction is usually performed in organic solvents, neat or mixed with water. The drawbacks of aqueous solvents are the low solubility of several substrates and the general lower stability of the metal catalysts in water. On this basis, a large variety of water-compatible protocols has been developed in recent years, which include the use of hydrophilic complexes,[14,15] surfactants[16] and microwave irradiation.[17] However, only a few of them display significant activity.

A good compromise between organic and aqueous solvents is the use of ethanol–water mixtures, as small alcohols are among the greenest solvents in terms of impact on health and the environment and in terms of the energy needed for their manufacture and disposal.[18] Ethanol increases the solubility of the substrate, does not interfere with the separation of the product (as surfactants do) and is bioavailable at a low cost. Hydroalcoholic mixtures are the media of choice[19] to reduce the use of dangerous, environmentally unfriendly organic solvents and to offer easy separation of the product from the reaction system.

For these reasons, the water-soluble complexes [Pd(PN*)(fdn)] and [Pd(NN*)(fdn)] were tested in the Suzuki–Miyaura reaction in ethanol–water mixtures. A protocol should be intended as "truly green" when toxic organic solvent are not involved in any step, including the workup.[5] Our workup procedure involved an extraction with dichloromethane (DCM) and chromatography with hexane–ethyl acetate (Hex/EtOAc) mixtures, but this choice was due to the small scale of our screening reactions and the necessity of reporting isolated yields also for partial conversions. In test experiments with higher scales and complete conversion, we demonstrated that it was possible to isolate the pure hydrophobic products in almost quantitative yields by simple addition of water followed by filtration of the solid products. Analogous protocols have already been reported.[20]

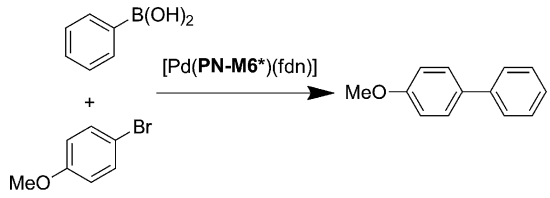
In principle, the parent O-acylated [Pd(PN)(fdn)] and [Pd(NN)(fdn)] species may also function as precatalysts, because the acyl groups are expected to hydrolyze easily under the basic coupling conditions. Nevertheless, the deprotected species were preliminarily isolated to demonstrate their actual existence and, hence, to assess the nature of the catalytic complexes.

Furthermore, their high solubility in ethanol allowed us to prepare concentrated stock solutions for an accurate dosage of the catalyst.

In all cases, glassware and stir bars were washed three times with 37% HCl to avoid artefacts caused by Pd residues.

The first screenings were performed to optimize the reaction conditions in terms of ethanol–water ratio (Table 3, Entries 1–5), concentration (Table 3, Entries 3, 6 and 7) and equivalents of base (Table 3, Entries 8–12).

Table 3. Optimization of reaction conditions with [Pd(PN-M6*)(fdn)].[a]



Entry	EtOH/H_2O (v/v)	Volume [mL]	K_2CO_3 [mmol]	Isolated yield[b] [%]
1	6:0	6	1.5	5
2	2:1	6	1.5	32
3	1:1	6	1.5	47
4	1:2	6	1.5	42
5	0:6	6	1.5	12
6	1:1	4	1.5	69
7	1:1	3	1.5	57
8	1:1	4	without base	0
9	1:1	4	0.50	21
10	1:1	4	1.0	80
11	1:1	4	2.25	61
12	1:1	4	3.0	56

[a] Conditions: 4-bromoanisole (0.50 mmol), phenylboronic acid (0.55 mmol), [Pd(PN-M6*)(fdn)], (5.0×10^{-3} mmol, 1.0 mol-%), 1 h, hotplate temperature 120 °C. [b] Average of two runs.

Phenylboronic acid, 4-bromoanisole and potassium carbonate were used as benchmark substrates and base, and [Pd(PN-M6*)(fdn)] was selected as the catalyst.

The reactions in neat ethanol or water (Table 3, Entries 1 and 5) resulted in poor yields. This was expected, because the former is not able to dissolve the base, whereas the latter does not dissolve the substrate properly. The best water–ethanol ratio was 1:1 (Table 3, Entry 3).

This solvent ratio at total volumes of 6, 4 and 3 mL was used to adjust the concentration (Table 3, Entries 3, 6 and 7). Unexpectedly, the highest concentration resulted in a drop of activity, probably because the higher concentration of complex favours the formation of metallic Pd. Similar behaviour has been reported for the formation of Pd_2Te_3 nanoparticles.[21]

The volume that resulted in the best yield (4 mL, Table 3, Entry 6, ca. 0.13 M in coupling partners) was used for the screening of the equivalents of base. As reported, its presence is fundamental for this reaction (as confirmed by Table 3, Entry 8). The highest yield was obtained with 2 equiv. of base with respect to the aryl bromide (Table 3, Entry 10).

These optimized conditions were used in the next screening, in which lower amounts of catalyst were used (Table 4).

Table 4. Screening of catalyst loading with [Pd(PN-M6*)(fdn)].[a]

Entry	Catalyst loading [mol-%][b]	Isolated yield [%][c]	TOF [h^{-1}]
1	1.0	80	80
2	0.10	95	950
3	0.010	75	7500
4	0.0050	83	16600
5	0.0010	0	0

[a] Conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.55 mmol), [Pd(PN-M6*)(fdn)], K_2CO_3 (1.0 mmol), water (2 mL), ethanol (2 mL), 1 h, hotplate temperature 120 °C. [b] Catalyst loading with respect to 4-bromoanisole. [c] Average of two runs.

Interestingly, catalyst loadings of less than 1.0 mol-% resulted in higher yields, most likely because of the abovementioned faster deactivation of the catalyst with formation of metallic Pd at higher complex concentration. The catalyst had no activity at a concentration of 0.0010 mol-% (Table 4, Entry 5).

On the basis of these results, the other complexes were tested with a loading of 0.010 mol-% or lower to find the most-active catalyst (Table 5). We purposely chose catalyst loadings and reaction times to maintain conversions far from completeness so that the performances of the different complexes could be effectively compared. In almost all cases, it is possible to achieve complete conversion just by extending the reaction time.

Table 5. Screening of complexes at different catalyst loadings.[a]

Entry	Complex	Catalyst loading [mol-%][b]	Isolated yield [c] [%]	TOF [h^{-1}]
1	[Pd(PN-G1*)(fdn)]	0.010	87	8700
2	[Pd(PN-G2*)(fdn)]	0.010	56	5600
3	[Pd(PN-G6*)(fdn)]	0.010	72	7200
4	[Pd(NN-M6*)(fdn)]	0.010	68	6800
5	[Pd(PN-G1*)(fdn)]	0.0050	58	11660
6	[Pd(NN-M6*)(fdn)]	0.0050	97	19400
7	[Pd(PN-G1*)(fdn)]	0.0020	0–15	–
8	[Pd(NN-M6*)(fdn)]	0.0020	65	32500

[a] Conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.55 mmol), K_2CO_3 (1.0 mmol), water (2 mL), ethanol (2 mL), 1 h, hotplate temperature 120 °C. [b] Catalyst loading with respect to 4-bromoanisole. [c] Average of two runs.

All of the PN complexes and one NN complex were tested at a catalyst loading of 0.010% and produced good results (Table 5, Entries 1–4). The best-performing PN species and the NN complex, namely, [Pd(PN-G1*)(fdn)] and [Pd(NN-M6*)(fdn)], were then examined at lower catalyst loadings of 0.0050 and 0.0020 mol-% (Table 5, Entries 5–8). In the latter case, the PN catalyst showed a lack of reproducibility, and the isolated yields ranged from 0 to 15%.

Owing to the satisfying results achieved with [Pd(NN-M6*)(fdn)], the whole NN family was tested under the same conditions and provided good yields; they are more active than the corresponding PN species (Table 6).

Table 6. Screening of complexes at different catalyst loadings.[a]

Entry	Complex	Catalyst loading [mol-%][b]	Isolated yield[c] [%]	TOF [h^{-1}]
1	[Pd(NN-G6*)(fdn)]	0.0020	65	32500
2	[Pd(NN-G1*)(fdn)]	0.0020	4	2000
3	[Pd(NN-G2*)(fdn)]	0.0020	70	35000
4	[Pd(NN-G6*)(fdn)]	0.0010	12	12000
5	[Pd(NN-G2*)(fdn)]	0.0010	12	12000
6[d]	[Pd(NN-G6*)(fdn)]	0.0010	37	9250
7[d]	[Pd(NN-G2*)(fdn)]	0.0010	38	9500

[a] Conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.55 mmol), K_2CO_3 (1.0 mmol), water (2 mL), ethanol (2 mL), 1 h, hotplate temperature 120 °C. [b] Catalyst loading with respect to 4-bromoanisole. [c] Average of two runs. [d] Reaction time: 4 h.

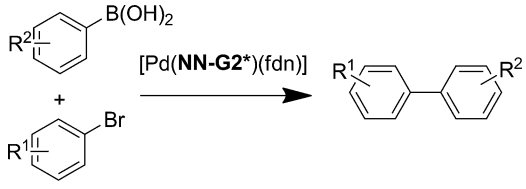
Only [Pd(NN-G1*)(fdn)] was almost ineffective, probably because of the higher sensitivity of the sugar functionalized at the 1-position.

The complexes [Pd(NN-G2*)(fdn)] and [Pd(NN-G6*)(fdn)] were further employed at 0.0010 mol-% loading (Table 6, Entries 4 and 5), at which they still presented appreciable yields after 1 h, whereas [Pd(NN-M6*)(fdn)] was ineffective and, hence, it is not reported in the table.

When the reaction was prolonged to 4 h, the yield increased to 38% (Table 6, Entries 6 and 7); therefore, the complexes are still active after the first hour of reaction. The activities of the two complexes were almost the same.

Owing to its easier synthesis, [Pd(NN-G2*)(fdn)] was tested as the catalyst of choice for the entire set of substrates (Table 7).

Table 7. Screening of substrates with [Pd(NN-G2*)(fdn)].[a]



Entry	R^1	R^2	Isolated yield [%][b]
1	4-OMe	4-Me	74
2	4-OMe	3-Me	63
3	4-OMe	2-Me	48
4	4-OMe	4-NO_2	<5
5	4-OMe	4-CHO	25
6	4-OMe	4-OH	<5
7	4-OMe	4-OMe	33
8	2-OMe	H	30
9	3-OMe	H	76
10	4-NO_2	H	85
11	4-OH	H	15
12	4-CHO	H	85
13	H	H	50

[a] Conditions: aryl bromide (0.50 mmol), arylboronic acid (0.55 mmol), [Pd(NN-G2*)(fdn)], (5×10^{-5} mmol, 0.010 mol-%), 1 h, hotplate temperature 120 °C. [b] Average of two runs.

The catalyst was also effective with sterically demanding substrates (Table 7, Entries 2, 3, 8, 9), although with slightly lower activity, and towards substrates with electron-releasing or -withdrawing groups. Disappointingly, aryl chlorides resulted in very poor conversions; hence, they are not reported in the table.

Conclusions

In this work, two classes of water-soluble Pd^0 complexes (PN and NN) were prepared and tested in the Suzuki–Miyaura cross-coupling reaction under environmentally friendly aqueous conditions. The best catalyst, namely, [Pd(NN-G2*)(fdn)], was active at really low loading (0.0010 mol-%), tolerant towards different substrates and very efficient in comparison to previously reported systems; the TOFs are up to 3.5×10^4 h^{-1}, which is close to the best results[22] for reactions in aqueous media. Future studies will focus on the expansion of the library to achieve reactivity towards aryl chlorides and eventually catalyst recycling, which, as observed in preliminary studies, is compromised by leaching during the extraction of the product.

Experimental Section

General Considerations: NMR spectra were recorded with samples in $CDCl_3$ ($CHCl_3$ δ = 7.26 ppm and $^{13}CDCl_3$ δ = 77 ppm as internal standards), C_6D_6 [tetramethylsilane (TMS) δ = 0 ppm and $^{13}C_6D_6$ δ = 128.6 ppm as internal standards] and CD_3OD (CHD_2OD δ = 3.34 ppm and $^{13}CD_3OD$ δ = 49.9 ppm as internal standards) with 200 (Varian Model Gemini) and 400 MHz (Bruker DRX-400) spectrometers. ^{31}P NMR experiments were performed with aqueous 85% phosphoric acid as an external reference (δ = 0 ppm). The following abbreviations are used to describe the NMR multiplicities: s singlet, d doublet, dd double doublet, t triplet, dt double triplet, m multiplet, app apparent, br broad. Compounds PN-G1, PN-G2, PN-G6, PN-M6, NN-G1, [Pd(PN-G1)(fdn)], [Pd(PN-G6)(fdn)], [Pd(PN-M6)(fdn)], [Pd(NN-G1)(fdn)] and [Pd(NN-G1*)(fdn)] were prepared according to literature methods.[7d,7b,7c] Tetrahydrofuran (THF) was distilled from $LiAlH_4$, and dichloromethane was distilled from CaH_2.

NN-G2: The amino intermediate **1** (640 mg, 2.0 mmol) was suspended in absolute EtOH (25 mL), and then 2-pyridincarboxyaldehyde (240 mg, 2.20 mmol) was added. After 72 h, hexane (80 mL) was added, and the precipitated product was collected by filtration and washed three times with hexane (yield: 560 mg, 69%) to afford a white powder. $C_{19}H_{24}N_2O_8$ (408.4): calcd. C 55.88, H 5.92, N 6.86; found C 55.64, H 5.85, N 7.01. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.64 (d, $^3J_{H,H}$ = 4.6 Hz, 1 H, aromatic), 8.31 (s, 1 H, N=CH), 7.97 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, aromatic), 7.73 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, aromatic), 7.33 (dd, $^3J_{H,H}$ = 5.4 Hz, $^3J_{H,H}$ = 6.7 Hz, 1 H, aromatic), 5.43 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.6 Hz, 1 H, 3-H), 5.14 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{4\text{-}H,5\text{-}H}$, 1 H, 4-H), 4.69 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.8 Hz, 1 H, 1-H), 4.36 (dd, $^3J_{6\text{-}H,5\text{-}H}$ = 4.6, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 12.2 Hz, 1 H, 6-H), 4.18 (dd, $^3J_{6'\text{-}H,5\text{-}H}$ = 1.8 Hz, 1 H, 6′-H), 3.84 (m, 1 H, 5-H), 3.49 (s, 3 H, OMe), 3.42 (t, 1 H, 2-H), 2.10 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 1.88 (s, 3 H, OAc) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 171.2, 170.3, 170.2, 166.2, 154.3, 149.9, 137.1, 125.6, 122.2, 102.9, 74.4, 73.5, 72.3, 69.0, 62.6, 57.6, 21.2, 21.1, 21.0 ppm.

NN-G6 and NN-M6: A known procedure was adapted.[7a] The desired azide (810 mg, 2.0 mmol) was dissolved in dry dichloromethane (10 mL) under argon. Then, 2-pyridincarboxyaldehyde (235 mg, 2.2 mmol, 210 μL) and PPh_2Me (440 mg, 410 μL, 2.2 mmol) were added in this order at 0 °C. The reaction mixture was left to warm to room temp., and after 72 h the solvent was removed under vacuum. The crude product was purified by column chromatography on florisil (eluent Hex/EtOAc = 1:1), yields: NN-G6 480 mg, 51%; NN-M6 510 mg, 54%. **NN-G6**: $C_{24}H_{26}N_2O_8$ (470.47): calcd. C 61.27, H 5.57, N 5.95; found C 61.49, H 5.68, N 5.83. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.48 (s, 1 H, N=CH), 8.44 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, aromatic), 8.13 (m, 2 H, aromatic), 8.06 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, aromatic), 7.16–6.97 (m, 4 H, aromatic), 6.60 (m, 1 H, aromatic), 6.19 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.9 Hz, 1 H, 3-H), 5.73 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$, 1 H, 4-H), 5.14 (dd, $^3J_{1\text{-}H,2\text{-}H}$ = 3.7 Hz, 1 H, 2-H), 4.91 (d, 1 H, 1-H), 4.38 (m, 1 H, 5-H), 3.78 (dd, $^3J_{5\text{-}H,6\text{-}H}$ = 3.1, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 13.0 Hz, 1 H, 6-H), 3.58 (dd, $^3J_{5\text{-}H,6'\text{-}H}$ = 6.7 Hz, 1 H, 6′-H), 3.01 (s, 3 H, OMe), 1.60 (s, 3 H, OAc), 1.58 (s, 3 H, OAc) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 169.8, 165.7, 165.0, 155.6, 149.7, 136.1, 133.4, 130.4 (2 C), 130.2, 128.8 (2 C), 124.6, 97.1, 72.0, 71.9, 70.8, 69.0, 61.5, 54.9, 32.1, 23.1, 20.3, 14.5 ppm. **NN-M6**: $C_{24}H_{26}N_2O_8$ (470.5): calcd. C 61.27, H 5.57, N 5.95; found C 61.10, H 5.54, N 6.03, ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.46 (s, 1 H, N=CH), 8.42 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, aromatic), 8.07 (m, 3 H, aromatic), 7.16–6.97 (m, 4 H, aromatic), 6.60 (m, 1 H, aromatic), 6.09 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$ = 9.6 Hz, 1 H, 4-H), 6.02 (dd, $^3J_{3\text{-}H,2\text{-}H}$ = 3.3 Hz, 1 H, 3-H), 5.63 (dd, $^3J_{1\text{-}H,2\text{-}H}$ = 1.7 Hz, 1 H, 2-H), 4.54 (d, 1 H, 1-H), 4.45 (m, 1 H, 5-H), 3.90 (dd, $^3J_{5\text{-}H,6\text{-}H}$ = 1.4 Hz, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 11.3 Hz, 1 H, 6-H), 3.70 (dd, $^3J_{5\text{-}H,6'\text{-}H}$ = 7.3 Hz, 1 H, 6′-H), 2.98 (s, 3 H, OMe), 1.67 (s, 3 H, OAc), 1.56 (s, 3 H, OAc) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 169.8, 165.8, 164.8, 155.6, 149.6, 136.0, 133.4, 130.3 (2 C), 130.2, 128.9, 128.8, 128.7, 124.6, 120.9, 98.9, 70.6, 70.4, 70.0, 69.4, 62.0, 54.8, 20.4, 20.3 ppm.

General Procedure for the Preparation of the [Pd(ligand)(fdn)] Complexes: A known procedure was adapted:[7d] $[Pd_2(dba)_3{\cdot}CHCl_3]$ (215 mg, 0.21 mmol) was added to a solution of the desired ligand (0.50 mmol) and fdn (39 mg, 0.50 mmol) in toluene (5 mL). After 1 h, the solution was filtered through Celite, and the solvent was evaporated; the crude product was purified by column chromatography over silica (eluent Hex/EtOAc 1:1 for PN family, neat EtOAc for NN family), and the pure product was isolated as a yellow microcrystalline solid (yields 68–85%).

[Pd(PN-G2)(fdn)]: $C_{36}H_{36}N_3O_8PPd$ (776.1): calcd. C 55.71, H 4.68, N 5.41; found C 55.87, H 4.56, N 5.55. Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.29 (d, $^4J_{H,P}$ = 1.5 Hz, 1 H, N=CH), 7.65–7.05 (m, 14 H, aromatic), 6.08 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.6 Hz, 1 H, 3-H), 5.12 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$, 1 H, 4-H), 5.04 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.8 Hz, 1 H, 1-H), 4.36 (dd, $^3J_{5\text{-}H,6\text{-}H}$ = 4.0 Hz, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 12.3 Hz, 1 H, 6-H), 4.24 (m, 1 H, 5-H), 4.14 (dd, $^3J_{5\text{-}H,6'\text{-}H}$ = 1.8 Hz, 1 H, 6′-H), 3.44 (t, 1 H, 2-H), 3.20 (s, 3 H, OMe), 3.14 (dd, $^3J_{H,H}$ = 9.6 Hz, $^{cis}J_{H,P}$ = 3.0 Hz, 1 H, fdn), 2.99 (t, $^3J_{H,H}$ = $^{trans}J_{H,P}$, 1 H, fdn), 2.07 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 1.67 (s, 3 H, OAc) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.7, 170.2, 170.1, 169.1, 137.7, 137.6, 137.3, 137.1, 135.2, 134.1, 133.9, 133.8, 132.9, 132.7, 132.7, 132.6, 131.7, 131.4, 130.8, 130.6, 129.5, 129.4, 129.2, 129.1, 101.1, 80.9, 73.8, 72.2, 69.3, 62.0, 57.2, 27.1, 25.4 ($J_{C,P}$ = 44 Hz), 20.5, 20.5, 20.0 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 16.15 ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.36 (d, $^4J_{H,P}$ = 1.5 Hz, 1 H, N=CH), 5.78 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.6 Hz, 1 H, 3-H), 5.19 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.8 Hz, 1 H, 1-H), 3.39 (s, 3 H, OMe), 2.61 (t, $^3J_{H,H}$ = $^{trans}J_{H,P}$ = 9.6 Hz, 1 H, fdn) ppm.

[Pd(NN-G2)(fdn)]: $C_{23}H_{26}N_4O_8Pd$ (592.9): calcd. C 46.59, H 4.42, N 9.45; found C 46.73, H 4.52, N 9.30. Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.92 (d, $^3J_{H,H}$ = 4.6 Hz, 1 H, aromatic), 8.43 (s, 1 H, N=CH), 8.05 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, aromatic), 7.76 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, aromatic), 7.67 (dd, $^3J_{H,H}$ = 5.5 Hz, $^3J_{H,H}$ = 6.8 Hz, 1 H, aromatic), 5.82 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.6 Hz, 1 H, 3-H), 5.17 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$, 1 H, 4-H), 4.93 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.6 Hz, 1 H, 1-H), 4.41 (dd, $^3J_{5\text{-}H,6\text{-}H}$ = 4.1 Hz, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 12.4 Hz, 1 H, 6-H), 4.16 (dd, $^3J_{5\text{-}H,6'\text{-}H}$ = 1.2 Hz, 1 H, 6′-H), 4.08 (m, 1 H, 5-H), 3.71 (t, 1 H, 2-H), 3.51 (s, 3 H, OMe), 3.24 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, fdn), 2.99 (d, 1 H, fdn), 2.09 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 1.93 (s, 3 H, OAc) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 171.1, 170.6, 169.6, 166.9, 153.7, 152.4, 139.4, 129.7, 127.6, 124.3, 122.9, 101.4, 74.9, 74.8, 72.1, 68.8, 62.2, 58.1, 21.2, 21.1, 21.1, 20.1, 19.8 ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.37 (s, 1 H, N=CH), 5.60 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.6 Hz, 1 H, 3-H), 5.19 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$, 1 H, 4-H), 4.98 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.6 Hz, 1 H, 1-H), 3.58 (s, 3 H, OMe), 3.00 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, fdn), 2.91 (d, 1 H, fdn) ppm.

[Pd(NN-G6)(fdn)]: $C_{28}H_{28}N_4O_8Pd$ (655.0): calcd. C 51.35, H 4.31, N 8.55; found C 51.65, H 4.44, N 8.86. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.84 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H, aromatic), 8.40 (s, 1 H, N=CH), 8.08 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, aromatic), 5.79 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.6 Hz, 1 H, 3-H), 5.27 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$, 1 H, 4-H), 4.94 (m, 2 H, 1-H, 2-H), 4.81 (m, 1 H, 5-H), 3.55 (s, 3 H, OMe), 2.97 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, fdn), 2.91 (s, 1 H, fdn), 2.09 (s, 3 H, OAc), 1.92 (s, 3 H, OAc) ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.58 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H, aromatic), 8.28 (s, 1 H, N=CH), 3.53 (s, 3 H, OMe) ppm. The other signals are in the following regions: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.06–7.02 (15 H, aromatic), 4.21–4.00 (m), 3.83 (m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.9, 170.9, 170.1, 169.9, 166.4, 166.1, 165.2, 164.9, 153.7, 153.4, 152.6, 152.4, 143.8, 139.4, 139.0, 135.1, 134.3, 134.1, 131.0, 130.6, 130.4, 129.4, 129.2, 129.1, 128.8 (2 C), 128.6, 128.4, 127.0, 126.8, 125.8, 123.2, 123.0, 122.7, 97.2, 97.0, 72.3, 71.5 (2 C), 71.1, 70.2, 70.0, 69.1, 68.2, 65.3, 63.7, 57.1, 56.4, 21.2 (2 C), 21.0 (2 C), 19.3, 18.9, 18.8, 18.7 ppm.

[Pd(NN-M6)(fdn)]: $C_{28}H_{28}N_4O_8Pd$ (655.0): calcd. C 51.35, H 4.31, N 8.55; found C 51.61, H 4.14, N 8.77. Major diastereoisomer: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.46 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, aromatic), 8.05 (d, $^3J_{H,H}$ = 4.7 Hz, 1 H, N=CH), 7.26–6.86 (m, 4 H, aromatic), 6.70 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, aromatic), 6.30 (m, 2 H, aromatic), 6.06 (dd, $^3J_{3\text{-}H,4\text{-}H}$ = 10.1 Hz, $^3J_{3\text{-}H,2\text{-}H}$ = 3.3 Hz, 1 H, 3-H), 5.94 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$, 1 H, 4-H), 5.68 (dd, $^3J_{1\text{-}H,2\text{-}H}$ = 1.6 Hz, $^3J_{3\text{-}H,2\text{-}H}$ = 3.3 Hz, 1 H, 2-H), 4.97 (m, 1 H, 5-H), 4.39 (m, 1 H, 1-H), 3.95 (d, $^3J_{6\text{-}H,6'\text{-}H}$ = 12.4 Hz, 1 H, 6-H), 3.40 (dd, $^3J_{5\text{-}H,6'\text{-}H}$ = 9.6 Hz, 1 H, 6′-H), 3.33 (s, 3 H, OMe), 2.82 (s, 2 H, fdn), 1.73 (s, 3 H, OAc), 1.59 (s, 3 H, OAc) ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.13 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, aromatic), 7.92 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, N=CH), 7.26–6.86 (m, 4 H, aromatic), 6.64 (t, $^3J_{H,H}$ = 7.0 Hz, 1 H, aromatic), 6.34 (m, 2 H, aromatic), 6.10 (dd, $^3J_{3\text{-}H,4\text{-}H}$ = 10.0 Hz, $^3J_{3\text{-}H,2\text{-}H}$ = 3.3 Hz, 1 H, 3-H), 5.88 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$, 1 H, 4-H), 5.72 (dd, $^3J_{1\text{-}H,2\text{-}H}$ = 1.5 Hz, $^3J_{3\text{-}H,2\text{-}H}$ = 3.0 Hz, 1 H, 2-H), 4.94 (m, 1 H, 5-H), 4.55 (m, 1 H, 1-H), 3.90 (d, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 12.1 Hz, 1 H, 6-H), 3.82 (dd, $^3J_{5\text{-}H,6'\text{-}H}$ = 9.6 Hz, 1 H, 6′-H), 3.35 (s, 3 H, OMe), 2.82 (s, 2 H, fdn), 1.73 (s, 3 H, OAc), 1.53 (s, 3 H, OAc) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C) for the two diastereoisomers: δ = 169.7, 169.6, 169.5, 169.4, 166.7, 166.3, 164.1 (2 C), 163.9, 153.0 (2 C), 152.6, 152.2, 152.1, 137.8 (2 C),

137.5, 135.5, 134.2, 133.8, 130.9, 130.4, 129.4, 129.3, 129.2, 129.0, 128.7, 125.6, 122.9, 122.7 (2 C), 122.6 (2 C), 104.0, 99.3, 99.0, 70.8, 70.3, 70.2, 70.0, 69.9, 69.8, 69.6, 68.5, 65.6, 63.4, 56.5, 55.7, 20.5 (2 C), 20.3 (2 C), 20.2, 20.1, 19.3, 19.2 ppm.

General Procedure for the Preparation of the [Pd(ligand*)(fdn)] Complexes: The desired [Pd(ligand)(fdn)] complex (0.50 mmol) was suspended in methanol (5 mL), and KOH was added (2.8 mg, 0.050 mmol). The reaction was monitored by NMR spectroscopy; small samples of the solution were taken, the solvent was evaporated, and the residue was dissolved in CD_3OD. After completion of the reaction, the solution was concentrated to a volume of 0.5 mL, and the product was precipitated by the addition of diethyl ether (10 mL). The yellow, microcrystalline product was washed three times with diethyl ether and dried under vacuum (yields 80–95%).

[Pd(PN-G1*)(fdn)]: $C_{29}H_{28}N_3O_5PPd$ (635.94): calcd. C 54.77, H 4.44, N 6.61; found C 54.39, H 4.28, N 6.32. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.69 (d, $^4J_{H,P}$ = 2.5 Hz, 1 H, N=CH), 7.80–7.10 (m, 28 H, aromatic), 4.55 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 8.3 Hz, 1 H, 1-H), 2.81 (t, 1 H, 2-H) ppm. ^{31}P NMR (162 MHz, CD_3OD, 25 °C): δ = 22.9 ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.61 (d, $^4J_{H,P}$ = 2.8 Hz, 1 H, N=CH), 4.43 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 8.3 Hz, 1 H, 1-H) ppm. ^{31}P NMR (162 MHz, CD_3OD, 25 °C): δ = 21.9 ppm. The other signals are in the following regions: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 3.98–3.90 (m, 3 H), 3.85–3.75 (m, 2 H), 3.69–3.53 (m, 4 H), 3.52–3.42 (m, 4 H), 3.16–3.00 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 172.79, 171.56, 164.0–130.0 (aromatic), 128.7, 128.5, 126.4 (2 C), 105.6, 104.4, 83.5, 83.0, 81.9, 81.8, 76.8, 76.7, 74.8, 73.9, 66.4, 65.7, 27.3 (d, $J_{P,C}$ = 44 Hz), 26.9 (d, $J_{P,C}$ = 59 Hz, 2 C), 26.4 (d, $J_{P,C}$ = 46 Hz) ppm.

[Pd(PN-G2*)(fdn)]: $C_{30}H_{30}N_3O_5PPd$ (650.0): calcd. C 55.44, H 4.65, N 6.46; found C 55.81, H 4.50, N 6.39. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.46 (d, $^4J_{H,P}$ = 2.9 Hz, 1 H, N=CH), 5.12 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.9 Hz, 1 H, 1-H), 4.36 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.2 Hz, 1 H, 3-H), 3.93 (dd, $^3J_{6\text{-}H,6'\text{-}H}$ = 11.4 Hz, $^3J_{5\text{-}H,6\text{-}H}$ = 1.4 Hz, 1 H, 6-H), 3.21 (s, 3 H, OMe), 3.16 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, fdn), 2.86 (t, $^3J_{H,H}$ = $J_{H,P}$, 1 H, fdn) ppm. ^{31}P NMR (162 MHz, CD_3OD, 25 °C): δ = 18.9 ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.45 (d, $^4J_{H,P}$ = 2.7 Hz, 1 H, N=CH), 5.04 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.9 Hz, 1 H, 1-H), 4.22 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.2 Hz, 1 H, 3-H), 3.89 (dd, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 11.4 Hz, $^3J_{5\text{-}H,6\text{-}H}$ = 1.4 Hz, 1 H, 6-H), 3.10 (s, 3 H, OMe), 3.09 (dd, $^3J_{H,H}$ = 8.0 Hz, $J_{H,P}$ = 3.5 Hz, 1 H, fdn), 2.84 (t, $^3J_{H,H}$ = $J_{H,P}$ = 8.0 Hz, 1 H, fdn) ppm. ^{31}P NMR (162 MHz, CD_3OD, 25 °C): δ = 18.5 ppm. The other signals are in the following regions: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 7.75 (m, 2 H, aromatic), 7.66 (m, 2 H, aromatic), 7.60–7.30 (m, 22 H, aromatic), 7.08 (m, 2 H), 3.78–3.66 (m, 3 H), 3.55–3.45 (m, 3 H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 170.5, 170.0, 137.8–129.0 (aromatic), 122.2, 103.9, 101.4, 82.2, 81.0, 76.8, 76.4, 73.5, 72.9, 70.8, 70.5, 61.6, 61.4, 56.6, 56.2, 23.6, 22.5, 22.3 (d, $J_{P,C}$ = 46 Hz), 21.8 (d, $J_{P,C}$ = 46 Hz) ppm.

[Pd(PN-G6*)(fdn)]: $C_{30}H_{30}N_3O_5PPd$ (650.0): calcd. C 55.44, H 4.65, N 6.46; found C 55.11, H 4.88, N 6.62. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.51 (d, $^4J_{H,P}$ = 2.0 Hz, 1 H, N=CH), 8.01 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, aromatic), 7.84 (m, 1 H, aromatic), 7.72 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, aromatic), 7.59 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, aromatic), 7.50–7.15 (m, 10 H, aromatic), 4.77 (d, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 11.4 Hz, 1 H, 6-H), 4.35 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 3.6 Hz, 1 H, 1-H), 4.12 (t, $^3J_{5\text{-}H,6\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$ = 9.3 Hz, 1 H, 5-H), 3.90 (t, 1 H, 6′-H), 3.62 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{3\text{-}H,2\text{-}H}$ = 9.1 Hz, 1 H, 3-H), 3.30 (dd, covered by the signal of the solvent, 2-H), 3.16 (m, 2 H, 4-H, fdn), 2.94 (t, $^3J_{H,H}$ = $^{trans}J_{H,P}$ = 9.7 Hz, 1 H, fdn), 2.50 (s, 3 H, OMe) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 171.4, 140.9, 140.5, 138.5, 136.2, 136.1, 135.6, 135.5, 135.3, 134.3, 133.3, 132.9, 131.8, 131.5, 131.4, 131.0, 125.0, 102.0, 89.4, 76.4, 75.0, 74.9, 73.5, 59.7, 56.2, 32.1, 26.5, 25.7, 25.3, 19.7 ppm. ^{31}P NMR (162 MHz, CD_3OD, 25 °C): δ = 20.2 ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.42 (d, $^4J_{H,P}$ = 2.0 Hz, 1 H, N=CH), 4.57 (d, $^{gem}J_{6\text{-}H,6'\text{-}H}$ = 10.6 Hz, 1 H, 6-H), 4.47 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 4.5 Hz, 1 H, 1-H) ppm. ^{31}P NMR (162 MHz, CD_3OD, 25 °C): δ = 19.7 ppm.

[Pd(PN-M6*)(fdn)]: $C_{30}H_{30}N_3O_5PPd$ (650.0): calcd. C 55.44, H 4.65, N 6.46; found C 55.76, H 4.87, N 6.48. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.37 (br s, 1 H, N=CH), 4.79 (d, $^3J_{6\text{-}H,6'\text{-}H}$ = 11.0 Hz, 1 H, 6-H), 4.47 (s, 1 H, 1-H), 3.68 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$ = 9.5 Hz, 1 H, 3-H), 3.20 (dd, $^3J_{H,H}$ = 9.6, $^{cis}J_{H,P}$ = 2.9 Hz, 1 H, fdn), 2.89 (t, $^3J_{H,H}$ = $^{trans}J_{H,P}$, 1 H, fdn), 2.61 (s, 3 H, OMe) ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.37 (br s, 1 H, N=CH), 4.71 (d, $^3J_{6\text{-}H,6'\text{-}H}$ = 11.3 Hz, 1 H, 6-H), 4.48 (s, 1 H, 1-H), 3.65 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$ = 9.5 Hz, 1 H, 3-H), 3.11 (dd, $^3J_{H,H}$ = 9.6, $^{cis}J_{H,P}$ = 3.0 Hz, 1 H, fdn), 2.74 (t, $^3J_{H,H}$ = $^{trans}J_{H,P}$, 1 H, fdn), 2.53 (s, 3 H, OMe) ppm. The other signals are in the following regions: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65–7.10 (m, aromatic), 4.20–3.55 (m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 169.3, 168.5, 137.9–129.3 (aromatic), 125.1, 123.0, 100.8, 100.7, 73.2, 72.4, 72.2, 70.9 (2 C), 70.4, 70.0, 69.7, 54.4, 54.2, 25.2, 24.7, 23.8 ($J_{P,C}$ = 43 Hz), 22.6 ($J_{P,C}$ = 44 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 17.8 ppm.

[Pd(NN-G2*)(fdn)]: $C_{17}H_{20}N_4O_5Pd$ (466.8): calcd. C 43.74, H 4.32, N 12.00; found C 43.59, H 4.32, N 11.67. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.63 (s, 1 H, N=CH), 4.92 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.7 Hz, 1 H, 1-H), 3.50 (s, 3 H, OMe), 3.02 (AB q, 2 H, fdn) ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.60 (s, 1 H, N=CH), 4.90 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 7.7 Hz, 1 H, 1-H), 3.57 (s, 3 H, OMe), 2.97 (s, 2 H, fdn) ppm. The other signals are in the following regions: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.87 (m, aromatic), 8.16 (m, aromatic), 7.95 (m, aromatic), 7.64 (m, aromatic), 4.11 (t, $J_{H,H}$ = 8.7 Hz), 3.97–3.85 (m), 3.60–3.32 (m), 3.07–2.94 (m) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 171.32, 171.06, 157.2, 157.1 (2 C), 157.0, 143.8 (2 C), 133.1, 131.5, 127.7, 126.8, 108.2, 106.1, 81.1, 80.7, 80.1, 79.6, 77.7, 74.7, 74.1, 69.8, 65.6, 65.4, 60.5, 60.3, 21.2, 20.9, 18.4 ppm.

[Pd(NN-G6*)(fdn)]: $C_{17}H_{20}N_4O_5Pd$ (466.8): calcd. C 43.74, H 4.32, N 12.00; found C 44.01, H 4.36, N 11.66. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.62 (s, 1 H, N=CH), 4.59 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 2.0 Hz, 1 H, 1-H), 4.27 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$ = 9.0 Hz, 1 H, 4-H), 3.76 (t, $^3J_{5\text{-}H,6\text{-}H}$ = $^3J_{6\text{-}H,6'\text{-}H}$ = 10.0 Hz, 1 H, 6-H), 3.42 (s, 3 H, OMe), 2.94 (AB q, 2 H, fdn) ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.59 (s, 1 H, N=CH), 4.57 (d, $^3J_{1\text{-}H,2\text{-}H}$ = 2.0 Hz, 1 H, 1-H), 4.24 (t, $^3J_{3\text{-}H,4\text{-}H}$ = $^3J_{5\text{-}H,4\text{-}H}$ = 9.0 Hz, 1 H, 4-H), 3.86 (t, $^3J_{5\text{-}H,6\text{-}H}$ = $^3J_{6\text{-}H,6'\text{-}H}$ = 10.0 Hz, 1 H, 6-H), 3.30 (s, 3 H, OMe), 2.91 (s, 2 H, s, fdn) ppm. The other signals are in the following regions: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.85 (m, 2 H, aromatic), 8.15 (m, 2 H, aromatic), 7.92 (m, 2 H, aromatic), 7.62 (m, 2 H, aromatic), 4.48 (m, 2 H), 3.70–3.65 (m, 2 H), 3.50–3.25 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 166.1, 165.7, 152.8 (2 C), 152.5, 152.3, 139.0 (2 C), 128.1 (2 C),

126.3 (2 C), 122.4 (2 C), 122.0 (2 C), 99.4, 99.03, 73.4 (2 C), 72.0 (2 C), 71.8 (2 C), 70.3, 69.2, 64.0, 63.0, 54.5, 53.8, 16.5 (2 C), 15.3 (2 C) ppm.

[Pd(NN-M6*)(fdn)]: $C_{17}H_{20}N_4O_5Pd$ (466.8): calcd. C 43.74, H 4.32, N 12.00; found C 43.39, H 4.18, N 12.36. Relevant signals for the major diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.63 (s, 1 H, N=CH), 3.30 (s, 3 H, OMe) ppm. Relevant signals for the minor diastereoisomer: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.61 (s, 1 H, N=CH), 3.29 (s, 3 H, OMe) ppm. The other signals are in the following regions: ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 8.85 (m, aromatic), 8.14 (m, aromatic), 7.92 (m, aromatic), 7.70 (m, aromatic), 4.50 (m), 4.20 (m), 3.78 (m), 3.63 (m), 2.91 (m, fdn) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 170.8, 170.4, 157.6 (2 C), 157.3 (2 C), 143.8 (2 C), 132.8 (2 C), 131.0 (2 C), 127.1, 126.8, 105.7, 105.4, 75.9, 75.4 (2 C), 75.1, 74.9 (2 C), 73.3, 73.1, 68.8, 67.7, 58.9, 58.2, 21.3 (2 C), 19.9 (2 C) ppm.

X-ray Crystal-Structure Determination of [Pd(NN-G2)(fdn)]: Crystals suitable for X-ray diffraction were grown by slow evaporation of a methanol–acetonitrile (1:5) solution at room temperature. A dark yellow crystal (0.22 × 0.17 × 0.11 mm) was mounted at room temperature, and the data were collected with a Bruker-Nonius Kappa CCD diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å, CCD rotation images). Semi-empirical absorption correction (SADABS) was applied. The structure was solved by direct methods (SHELXS)[23] and refined by the full-matrix least-squares method on F^2 against all independent measured reflections (SHELXL).[23] All non-hydrogen atoms were refined anisotropically. The final refinement converged to an R value of 0.0474 for 7323 reflections with $I > 2\sigma(I)$ and 0.0796 for all 9727 reflections (Table 8).

Table 8. Crystallographic data.

Empirical formula	$C_{23}H_{26}N_4O_8Pd$
Mr	592.88
Crystal system, space group	triclinic, $P1$
Temperature /K	293
a, b, c /Å	9.3980(9), 11.8020 (12), 12.8400 (9)
α, β, γ /°	69.362 (8), 84.886 (10), 70.297 (8)
V /Å^3	1254.0 (2)
Z	2
F(000)	604
Radiation type	Mo-K_α
μ /mm^{-1}	0.79
Crystal size /mm	0.22 × 0.17 × 0.11
$D_{calcd.}$ /Mg m^{-3}	1.57
Diffractometer	Bruker-Nonius KappaCCD
Radiation source	normal-focus sealed X-ray tube
Measured reflections	17102
Independent reflections	9727
Observed reflections [$I > 2\sigma(I)$]	7323
Rint	0.055
θ_{max}, θ_{min} /°	27.5, 3.3
Range of h, k, l	h = –12, 11 k = –15, 15 l = –16, 16
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$, S	0.047, 0.093, 1.02
$(\Delta/\sigma)_{max}$	0.002
$\Delta\rho_{max}$ /e Å^{-3}	0.54
$\Delta\rho_{min}$ /e Å^{-3}	–0.55
Flack parameter	0.02(3)
Parameters	651
Number of restraints	3

CCDC-995160 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical Procedure for the Suzuki–Miyaura Coupling: To a solution of phenylboronic acid (0.55 mmol, 67 mg) and 4-bromanisole (0.50 mmol, 63 μL) in absolute ethanol (1 mL) were added a solution of potassium carbonate (1.00 mmol, 138 mg) in water (2 mL) and a solution of the catalyst in absolute ethanol. The system was heated to reflux by setting the hotplate temperature to 120 °C. After 1 h, the product was extracted with dichloromethane (3 × 10 mL), dried with anhydrous sodium sulfate, filtered and concentrated under vacuum. The solution was filtered through a short pad of silica and then chromatographed over silica gel (eluent: hexane → hexane/ethyl acetate 4:1). The structure of the pure product was confirmed by MS and by comparison of the NMR spectra with previously reported data.

Supporting Information (see footnote on the first page of this article): ^{1}H, ^{13}C and ^{31}P NMR spectra of new compounds.

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