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Pyracene-Linked Bis-Imidazolylidene Complexes of Palladium and Some Catalytic Benefits Produced by Bimetallic Catalysts

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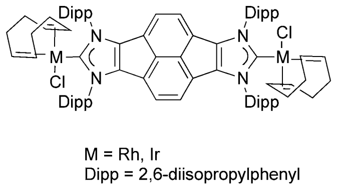
Abstract: Two new palladium complexes with a pyracene-linked bis-imidazolylidene (pyrabim) group have been obtained and fully characterized. The related monometallic analogues were obtained from the coordination of an acetanaphthene-supported N-heterocyclic carbene (NHC). The catalytic properties of all complexes were studied in the acylation of aryl halides with hydrocinnamaldehyde, and in the Suzuki–Miyaura coupling of aryl halides and aryl boronic acids. The results show that the presence of a second metal in the dimetallic complexes induces some benefits in the catalytic behavior of the complexes. This effect is more pronounced in the Suzuki–Miyaura coupling, for which the dimetallic complexes exhibit significantly higher activity than their monometallic counterparts.

Keywords: acylation • carbenes • C−C coupling • homogeneous catalysis • palladium

Introduction

Polytopic N-heterocyclic carbene (NHC) ligands have emerged as promising tools for use in multiple applications.[1] An important class of bis(NHCs) features two facially opposed carbenes that inhibit chelation, thereby facilitating structures in which the ligand is bridging two transition metals that can be comprised in a discrete molecule or in a polymeric system.[2] Some representative examples of this type of bis(NHCs) include triazolylidenes,[3] benzobis(imidazolylidenes),[4] oxanthrobis(imidazolylidenes),[4b] quinobis(imidazolylidenes),[4d,e] bis(imidazolinylidenes),[5] and our recently described pyracenebis(imidazolylidene).[6] Such types of biscarbenes, especially those linked by rigid π-conjugated systems, enable electronic communication between the carbene units, which can allow for interesting applications in molecular electronic devices. The idea of using unsaturated/aromatic ditopic NHCs as linkers in organometallic complexes is based on the possibility of the interaction between metal d_π orbitals and the π-delocalized system of the NHC through M=C π bonding,[7] although we recently proposed that the principal interaction between the metal centers in dimetallic NHC-based complexes is of σ type.[8]

We have recently been interested in the preparation of bis(NHC)-based dimetallic complexes for the preparation of improved homogeneous catalysts. Most of our studies were focused on the preparation of heterobimetallic complexes and their application in tandem catalytic reactions.[3c–e] We recently described a pyracene-linked bis-imidazolylidene (pyrabim) that was coordinated to rhodium and iridium (Scheme 1).[6] In these complexes, the pyracene linker constitutes an interesting polyaromatic connecting system between the two metals. Homogeneous catalysts with polyaromatic-based ligands are an interesting class of complexes because aromatic π stacking between ligands and substrates is known to improve catalytic effects, especially in some asymmetric inductions.[9] We believe that a similar effect might have some consequences in other homogeneously catalyzed reactions that involve aromatic substrates[9a] in which the catalyst–substrate interactions might be facilitated by π stacking. In this regard, we have considered that the pyracene–bis(imidazolylidene) ligand depicted in Scheme 1 might constitute a good starting point for the study of the catalytic properties of their derived complexes. Also, the catalytic activities of dimetallic complexes derived from pyrabim might be influenced by the twofold increase of the local concentration of the metal relative to analogue monometallic catalysts. We wished to examine the reactivity of complexes that combine the stereoelectronic properties of the pyrabim ligand and the activation pathway provided by the NHC-Pd-PEPPSI[10] (PEPPSI = pyridine-enhanced precatalyst preparation stabilization and initiation) and NHC-Pd-allyl-based catalysts.[11] Herein, we report the preparation of two pyrabim-based palladium complexes and the study of their catalytic properties in the acylation of aryl halides as well as the Suzuki–Miyaura coupling of phenyl boronic acid



Scheme 1. Previously reported pyrabim-based Rh and Ir complexes.

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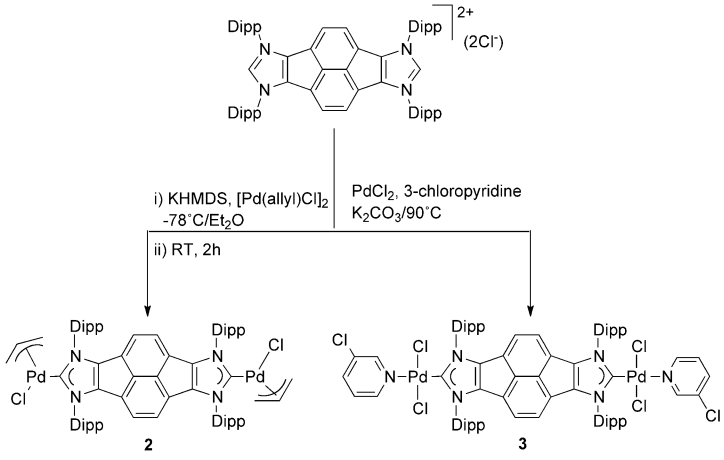
and aryl halides. The catalytic activities have been compared with those shown by the related monometallic complexes.

Results and Discussion

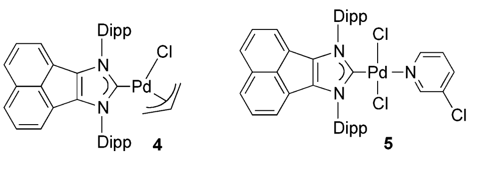
The preparation of [(μ-pyrabim){Pd(allyl)Cl}$_2$] (**2**) was straightforward, starting from the pyracene-linked bis-imidazolium chloride **1** ([pyrabimH$_2$]Cl$_2$). The in situ preparation of the free bis-carbene was performed by deprotonation of **1** with a slight excess amount of potassium bis(trimethylsilyl)amide (KHMDS) in the presence of [{Pd(allyl)Cl}$_2$] at −78 °C in Et$_2$O. This procedure afforded the formation of **2** as a dark green solid in 75 % yield (Scheme 2). The reaction of **1** with PdCl$_2$ and 3-chloropyridine in the presence of K$_2$CO$_3$ at 90 °C allowed the formation of [(μ-pyrabim){PdCl$_2$(3-Clpyr)}$_2$] (**3**), which can be purified by column chromatography to afford a dark green solid in 64 % yield.



Scheme 2. Schematic representation of the preparation of palladium complexes **2** and **3**.

The NMR spectra of both **2** and **3** are consistent with the twofold symmetry of the complexes. The ^{13}C NMR spectra display the resonances due to the metalated carbene carbon atoms at $\delta = 195.8$ and 160.4 ppm for complexes **2** and **3**, respectively.

Because we wanted to compare the structural features and the catalytic properties of both **2** and **3** with their monometallic counterparts, we also obtained the (acetanaphthene)-supported NHC Pd(allyl) and PEPPSI[12] complexes **4** and **5** (Scheme 3) from the adapted synthetic procedures shown in Scheme 2. The (acetanaphthene)-supported-NHC ligand was reported by Cowley and co-workers, who obtained the related complexes of Ag, Au, and Ir.[12] The palladium complex **5** was recently obtained and proved to be an effective catalyst in the amination of aryl chlorides.[13] As relevant spectroscopic features, complex **4** displays its carbene carbon ^{13}C NMR spectroscopic signal at $\delta = 195.8$ ppm.



Scheme 3. Schematic representation of palladium complexes **4** and **5**.

The molecular structures of complexes **2**, **3**, and **4** were confirmed by means of X-ray diffraction studies. Figures 1, 2, and 3 display the corresponding molecular structures of **2**, **3**, and **4**, respectively.

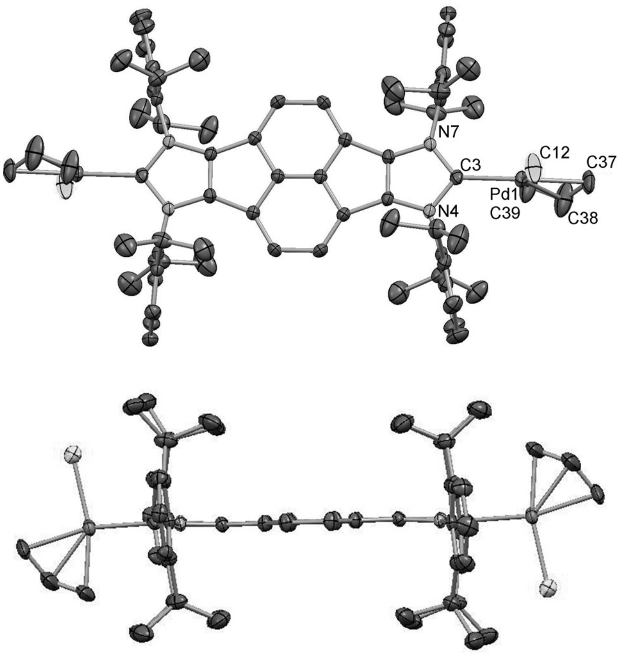


Figure 1. Two perspectives of the molecular structure of **2**. Hydrogen atoms and solvent (C$_6$H$_6$) have been omitted for clarity. Ellipsoids set at 40 % probability. Selected bond lengths [Å] and angles [°]: Pd1−C3 2.035(4), Pd1−Cl2 2.358(13), Pd1−C39 2.100(5), Pd1−C38 2.112(6), Pd1−C39 2.189(4); C3-Pd1-Cl2 98.71(11).

The molecular structure of **2** (Figure 1) consists of a pyrabim ligand bridging two palladium metals, which complete their coordination sphere with chloride and allyl ligands. The relative disposition of the ligands about each metal fragment is *anti*, with the two chloride ligands pointing in opposite directions. The bridging ligand is planar as a consequence of the π delocalization between the two imidazolylidenes. The Pd−C$_{\text{carbene}}$ bond length is 2.036 Å, and the through-space distance between the metals is 13.96 Å. All other distances and angles are unexceptional.

The molecular structure of **3** (Figure 2) consists of a planar pyrabim ligand bridging two palladium metals, which complete their coordination sphere with a 3-chloropyridine and two chloride ligands. The relative disposition of the li-

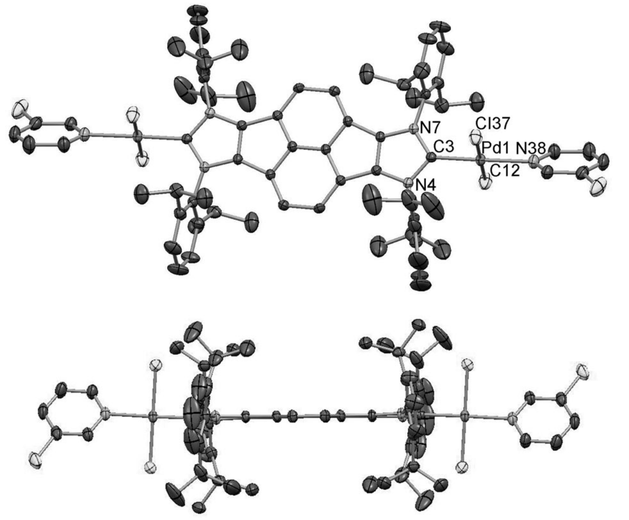


Figure 2. Two perspectives of the molecular structure of **3**. Hydrogen atoms and two molecules of solvent ($CHCl_3$) have been omitted for clarity. Ellipsoids set at 40 % probability. Selected bond lengths [Å] and angles [°]: Pd1−C3 1.966(3), Pd1−Cl2 2.289 (11), Pd1−N38 2.114(3), Pd1−Cl37 2.289(10); C3-Pd1-Cl2 91.47(10).

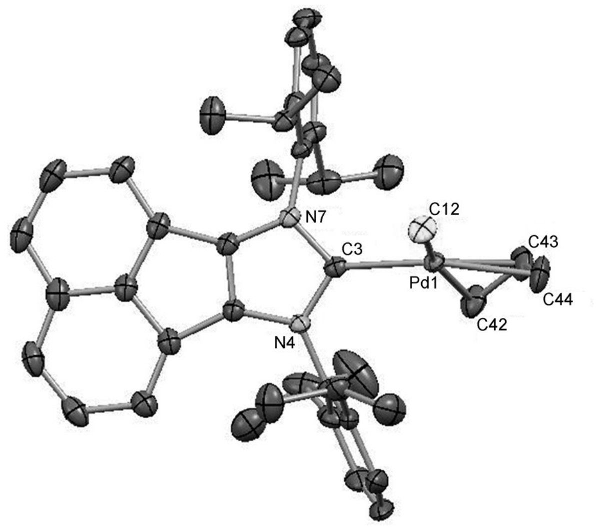


Figure 3. Molecular diagram of **4**. Hydrogen atoms and solvent (dichloromethane) have been omitted for clarity. Ellipsoids set at 40 % probability. Selected bond lengths [Å] and angles [°]: Pd1−C3 2.046(3), Pd1−Cl2 2.373(9), Pd1−C42 2.105(4), Pd1−C43 2.132(4), Pd1−C44 2.177(4); C3-Pd1-Cl2 94.9(8).

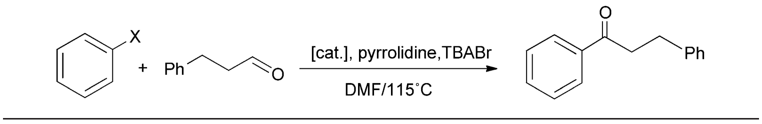
gands about each metal fragment is *anti*, with the chloride atoms of 3-chloropyridine pointing opposite to each other. We believe that in solution there might be free rotation about the Pd−$C_{carbene}$ bond (isomers were not detected from NMR spectroscopic analysis), therefore we think that this structure simply relates to one of the possible stable conformers in the solid state. The Pd−$C_{carbene}$ bond length is 1.966 Å, similar to the related distance in **5** (1.960 Å),[13] and significantly shorter than in **2** and **4**.

The molecular structure of complex **4** (Figure 3) consists of a (acetanaphthene)-supported NHC ligand coordinated to palladium. The metal completes its coordination sphere with a chloride and allyl ligand. The Pd−$C_{carbene}$ bond is 2.048 Å, only slightly longer than in **2**, and significantly longer than in **3** (this work) and **5**.[13] All other structural parameters with regard to the coordination sphere of the metal are similar to those shown by **2**.

To test the catalytic properties of complexes **2**–**5**, we decided to study two model reactions: the acylation of aryl halides with aldehydes, and the Suzuki–Miyaura coupling between aryl halides and phenyl boronic acids. The acylation of aryl halides with aldehydes, first reported by Xiao and co-workers,[14] allows the direct preparation of alkyl aryl ketones by avoiding the traditionally used Friedel–Crafts method, which involves hazardous reagents and does not work when electron-deficient arenes are used. Despite the interest in this reaction, only a small number of examples have been reported to date,[15] and very few of them correspond to intermolecular processes.[14,15c,d]

We tested the catalytic activity of complexes **2**–**5**, when performed at 115 °C in DMF in the presence of pyrrolidine by using an almost equimolecular amount of aryl halide (0.5 mmol) and hydrocinnamaldehyde (0.6 mmol) to simulate the most atom-efficient conditions. In general, the reactions showed excellent conversions, but yields were significantly lower (Table 1), therefore implying that the acylation is competing with the palladium-catalyzed dehalogenation of the aryl halides. Several authors have overcome this difference by increasing the amount of aldehyde used in the process.[15c] From the results shown, it can be seen that our results compare well with previous results obtained by Xiao and co-workers using [Pd(dba)$_2$] (dba = dibenzylideneacetone) and an amount of diphosphane, al-

Table 1. Acylation of aryl halides with hydrocinnamaldehyde.[a]



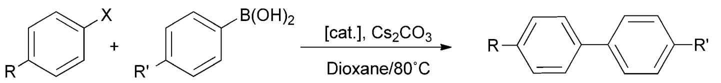
Entry	Catalyst	[Pd] [%]	X	Conv. [%]	Yield [%]
1	**5**	2	I	100	79
2	**4**	2	I	100	67
3	**3**	2	I	100	72
4	**2**	2	I	97	49
5	**5**	1	I	100	48
6	**4**	1	I	100	45
7	**5**	2	Br	70	52
8	**4**	2	Br	61	33
9	**3**	2	Br	64	41
10	**2**	2	Br	65	16
11	**5**	1	Br	84	27
12	**4**	1	Br	44	11

[a] Reactions were carried out with XAr (0.5 mmol), hydrocinnamaldehyde (0.6 mmol), pyrrolidine (1 mmol), 4 Å MS (1 g), and [Pd] (1–2 mol %) in DMF (2 mL) at 115 °C for 16 h. Yields obtained by GC analysis using anisole as internal reference. Conversions refer to the aryl halide.

though in their case the reactions proceeded in shorter reaction times (4–6 h).[14,15c] In our case, the use of our preformed catalysts allowed us to skip the addition of the phosphane.

As can be seen from the data shown in Table 1, the monometallic Pd–PEPPSI catalyst **5** is the one that achieves the best catalytic activity for both reactions performed with aryl iodide and aryl bromide (Table 1, entries 1 and 7). The dimetallic Pd–PEPPSI catalyst **3** also affords good catalytic outcomes, especially when compared to both Pd(allyl) complexes. As a general trend, when using the same amount of catalyst loading (measured as the amount of metal added to the reaction medium), the monometallic catalysts afford a better catalytic outcome than the dimetallic analogues (in Table 1, compare entries 1 with 3, and 7 with 9 to juxtapose the activities of **5** and **3**; entries 2 with 4, and 8 with 10 to juxtapose **4** and **2**). However, if we compare the activities of the monometallic and dimetallic analogue complexes when the same amount of molecular catalyst is used, the results indicate that both dimetallic complexes show a better activity than the monometallic counterparts (in Table 1, compare entries 4 with 6, and also 3 with 5), therefore implying that the presence of the second metal in the molecule has a positive effect on the catalytic activity of the molecule. If we consider that this benefit might not be due to stereoelectronic differences between the NHC ligands present in the monometallic and dimetallic species,[6] we should probably interpret this observation as a result of the simultaneous catalytic activity of the two metals present in the dimetallic complexes.

Table 2. Suzuki–Miyaura coupling between aryl halides and aryl boronic acids.[a]



Entry	Catalyst	X	R	R′	Yield [%]
1	**5**	Br	COMe	Me	95
2	**4**	Br	COMe	Me	92
3	**3**	Br	COMe	Me	98
4	**2**	Br	COMe	Me	98
5	**5**	Br	OMe	Me	48
6	**4**	Br	OMe	Me	37
7	**3**	Br	OMe	Me	56
8	**2**	Br	OMe	Me	59
9	**5**	Br	COMe	H	88
10	**4**	Br	COMe	H	72
11	**3**	Br	COMe	H	88
12	**2**	Br	COMe	H	96
13	**5**	Br	OMe	H	16
14	**4**	Br	OMe	H	39
15	**3**	Br	OMe	H	43
16	**2**	Br	OMe	H	41
17	**5**	Cl	OMe	Me	12
18	**4**	Cl	OMe	Me	15
19	**3**	Cl	OMe	Me	17
20	**2**	Cl	OMe	Me	14
21	**5**	Cl	COMe	Me	14
22	**4**	Cl	COMe	Me	17
23	**3**	Cl	COMe	Me	4
24	**2**	Cl	COMe	Me	28
25[b]	**5**	Br	COMe	Me	53
26[b]	**4**	Br	COMe	Me	95
27[b]	**3**	Br	COMe	Me	67
28[b]	**2**	Br	COMe	Me	98

[a] Reactions were carried out with aryl halide (0.5 mmol), aryl boronic acid (0.5 mmol), Cs_2CO_3 (1 mmol), and [Pd] (2 mol %) in dioxane (2 mL) at 80 °C for 2 h. Yields obtained by GC analysis using anisole as internal reference. [b] Data obtained by adding the substrates after incubating the catalysts over 2 h at 80 °C in dioxane in the presence of Cs_2CO_3 (1 mmol).

The catalytic results in the Suzuki–Miyaura coupling between aryl halides and aryl boronic acids when using catalysts **2**–**5** are summarized in Table 2. The activities of all the complexes are lower than those shown by the best NHC-based catalysts for this reaction,[16] but establish an excellent platform for comparison. The reactions were carried out at 80 °C in dioxane in the presence of Cs_2CO_3 and a catalyst loading of 2 mol % (based on the concentration of the metal). In general, all the catalysts displayed moderate to excellent outcomes in the arylation of aryl bromides, but the arylation of aryl chlorides (*p*-chloroanisole and *p*-chloroacetophenone) afforded very low yields. As can be seen by comparing the catalytic outcomes provided by the different catalysts, the activity of the dimetallic complexes **2** and **3** is significantly superior to that shown by their monometallic analogue complexes (**4** and **5**, respectively). The only exception to this trend is the one shown by catalyst **3** in the arylation of *p*-chloroacetophenone with *p*-tolyl boronic acid, which affords a very low yield, especially when compared to the activity shown by the monometallic complex **5** in the same reaction (compare entries 21 and 23 in Table 1). We still do not have a satisfactory interpretation for this anomalous result.

To discard the possibility that the differences in the catalytic activities are merely due to differences in stability of the complexes, we performed a stability test that consisted of dissolving **3**–**5** in deuterated toluene, and taking the solutions to reflux for three hours in the presence of an internal standard (anisole). The ^{1}H NMR spectra of all four complexes showed that the decomposition under these conditions was negligible for all four complexes. In a parallel experiment, we performed a series of Suzuki–Miyaura couplings of *p*-bromoacetophenone and *p*-tolylboronic acid by adding the substrates after incubating the catalysts for 2 h in dioxane at 80 °C in the presence of Cs_2CO_3. As can be seen from the data shown in entries 25–28 (Table 2), the catalytic outcomes of both allyl-based catalysts (**2** and **4**) remain unchanged compared to the reactions carried out without incubating the catalysts (in Table 2, compare entries 26 and 28 with 2 and 4, respectively). The activities shown by the PEPPSI-based catalysts **3** and **5** show an important reduction after incubation (compare entries 25 and 27 with 1 and 3 in Table 2). These results indicate that the stability of the complexes under these reaction conditions is a matter of whether the catalysts contain the allyl or the pyridine ligand, rather than having the pyrabim or benzimidazolylidene ligand, and therefore discards the possibility that the catalytic benefits provided by the bis-NHC ligand are merely due to an increase in the stability.

Both catalytic reaction patterns that we have shown in this study indicate that the presence of the dimetallic structure in the catalyst introduces some benefits to the catalytic outcomes of the reactions. The results are clearer in the case of the Suzuki–Miyaura coupling, for which both dimetallic complexes unambiguously afford higher yields than their monometallic analogue complexes under exactly the same reaction conditions.

We cannot attribute the reactivity differences to disparities in the stereoelectronic properties of the ligands, which have been proven to be very similar,[6] and also to the catalytic cooperativity between the two metals, which in our dimetallic systems exceed by far the optimum M–M separation that has been proposed for this type of effect (3.6–6 Å).[17] With our results in hand, we believe that the catalytic enhancement shown by our dimetallic catalysts might be either due to the effect of the higher local concentration of the metal in the catalytic reaction (an effect that cannot be replicated by monometallic catalysts), or to the presence of an extended polyaromatic system, which might favor the interaction between the catalyst and the aromatic substrates. Although we are aware that a more detailed study is needed to clarify the mechanisms that lead to this catalytic improvement, we believe that our study introduces an interesting proof of concept that might be worth developing in the near future.

Conclusion

In summary, we have prepared and fully characterized two new Pd-based complexes with our previously reported ligand pyrabim. The molecular structures of both complexes have been determined and compared with the molecular structures of the related monometallic complexes (complexes **4** and **5**). The catalytic activity of all complexes has been tested in the acylation of aryl halides with hydrocinnamaldehyde and in the Suzuki–Miyaura coupling between aryl halides and phenyl boronic acids. The catalytic results show that the presence of a second metal in the catalyst introduces some benefits into the catalytic reaction outcomes, an effect that is clearer in the case of the Suzuki–Miyaura coupling, for which both dimetallic catalysts display higher activity than their monometallic counterparts. Although we believe that the higher local concentration of the metal in the dimetallic architectures might be the origin of this effect, we are carrying out further studies to clarify this point, and to extend the library of NHC-based rigid polytopic ligands for the preparation of novel di- and trimetallic catalysts.

Experimental Section

General procedures: All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents and reagents are commercially available and were used as received from commercial suppliers. Bis(imidazolium)pyracene chloride (**1**),[6] acetanaphtoimidazolium chloride,[12] and complex **5**[13] were prepared according to previously reported methods. NMR spectra were recorded using Varian Innova spectrometers operating at 300 and 500 MHz (^{1}H NMR) and 75 or 125 MHz (^{13}C NMR), respectively, using $CDCl_3$ and CD_2Cl_2 as solvents (Merck and Aldrich). Electrospray mass spectra (ESI-MS) were recorded using a Micromass Quattro LC instrument, and nitrogen was employed as the drying and nebulizing gas.

Synthesis of compound [(μ-pyrabim){Pd(allyl)Cl}$_2$] (2): A 0.5 M solution of KHMDS (1.36 mL, 0. 96 mmol) was added at −78 °C to a flame-dried Schlenk tube that contained a salt precursor (0.30 g, 0.31 mmol), [{Pd(allyl)Cl}$_2$] (0.112 g, 0.31 mmol), and a stirrer bar. After 10 min, diethyl ether (7 mL) was added, the reaction mixture was maintained at −78 °C for 10 min. Then it was allowed to warm to room temperature. After two hours, the solvent was evaporated under vacuum. The crude mixture was washed with a cannula first with hexane (2×10 mL), then diethyl ether (2×10 mL). The product was extracted with a cannula with CH_2Cl_2 (2×10 mL), and the solvent was removed under vacuum to yield a dark green solid. Suitable crystals for X-ray analysis of **2** were obtained after slow evaporation of a benzene solution at room temperature. Yield: 0.2854 g, 75%. ^{1}H NMR (300 MHz, CD_2Cl_2, 303 K): δ=7.36 (t, J=8.4 Hz, 4H), 7.19 (d, J=8.4 Hz, 8H), 5.38 (br, 4H), 4.76 (m, 2H), 3.68 (d, J=7.5 Hz, 2H), 3.19 (br, 4H), 3.11 (br, 4H), 2.65 (d, J=13.5 Hz, 2H), 1.64 (br, 2H), 1.25 (d, J=6.9 Hz, 24H), 1.12 (br, 2H), 1.01 ppm (d, J=6.9 Hz, 24H); ^{13}C{^{1}H} NMR (300 MHz, 303 K): δ=194.3, 146.3, 144.1, 135.9, 134.2, 130.7, 130.6, 124.6, 122.5, 114.9, 72.9, 51.4, 29.0, 25.6, 23.9 ppm; HRMS (ES$^+$, 20 V): m/z calcd: 1227.4325 $[M-Cl]^+$; found: 1227.4326.

Synthesis of compound [(μ-pyrabim){PdCl$_2$(3-Clpyr)}$_2$] (3): 3-Chloropyridine (4 mL) was added to a Schlenk tube that contained $PdCl_2$ (0.109 g, 0.61 mmol), a salt precursor (0.30 g, 0.31 mmol), K_2CO_3 (0.30 g, 0.31 mmol), and a stirring bar. The reaction mixture was heated with vigorous stirring at 90 °C for 24 h to give a brownish mixture. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and passed through a short pad of silica gel covered with a pad of Celite eluting with CH_2Cl_2 until the product was completely recovered. The pure Pd–NHC complex was isolated after precipitation with pentane, decanting off the supernatant, and drying under high vacuum to yield a dark green solid. Crystals suitable for X-ray analysis of **3** were obtained by slow evaporation of a mixture chloroform/pentane. Yield: 0.291 g, 64%. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ=8.57 (s, 2H), 8.49 (d, 2H), 7.46 (ddd, 4H) 7.34 (d, 4H), 7.25 (t, 6H), 7.05 (m, 2H), 5.45 (br, 4H), 3.41 (m, 8H), 1.54 (d, 30H), 1.43 (d, 24H), 1.06 ppm (d, 24H); ^{13}C{^{1}H} NMR (300 MHz, 303 K): δ=160.4, 150.5, 149.4, 148.9, 147.5, 143.8, 137.4, 135.7, 133.0, 132.2, 130.2, 124.6, 124.3, 122.5, 28.8, 25.8, 24.2 ppm; HRMS (ES$^+$, 20 V): m/z calcd: 1443.2959 $[M-Cl]^+$; found: 1443.2957.

Synthesis of [Pd(BIAN)(allyl)Cl] (4): A 0.5 M solution of KHMDS (0.4 mL, 0. 2 mmol) was added at −78 °C to a flame-dried Schlenk tube that contained (imidazolium)acetonaphthene (BIAN) chloride (0.1 g, 0.18 mmol), [{Pd(allyl)Cl}$_2$] (0.033 g, 0.09 mmol), and a stirrer bar. After 10 min, diethyl ether (7 mL) was added. The reaction mixture was maintained at −78 °C for 10 min, and then it was allowed to warm to room temperature. After 2 h, the solvent was evaporated under vacuum. The crude mixture was washed with a cannula with hexane (2×10 mL). The product was extracted with a cannula with diethyl ether (3×10 mL). The solvent was pumped off to yield a yellow solid. Suitable crystals for X-ray analysis were obtained after slow evaporation of a CH_2Cl_2 solution at room temperature. Yield: 0.126 g (92%). ^{1}H NMR (300 MHz, CD_2Cl_2, 303 K): δ=7.69 (d, J=9.3 Hz, 2H), 7.57 (t, J=15.6 Hz, 2H), 7.40 (d, J=8.7 Hz, 4H), 7.32 (t, J=16.2 Hz, 2H), 6.82 (d, J=8.1 Hz, 2H), 4.93 (m, 1H), 3.82 (d, J=7.2 Hz, 1H), 3.30 (br, 2H), 3.09 (br, 2H), 2.82 (d, J=13.5 Hz, 1H), 1.89 (d, J=13.5 Hz, 1H), 1.59 (br, 1H), 1.33 (d, J=6.9 Hz, 12H), 0.94 ppm (d, J=6.9, 12H); ^{13}C{^{1}H} NMR (300 MHz, 303 K): δ=

194.8, 148.4, 142.3, 136.6, 132.1, 131.8, 131.6, 129.7, 129.2, 128.2, 126.3, 123.6, 116.4, 74.4, 30.6, 27.0, 25.4, 24.9 ppm; HRMS (ES$^+$, 20 V): m/z calcd: 659.2632 $[M-\mathrm{Cl}]^+$; found: 659.2639.

General procedure for the acylation of aryl halides: MS (1 g), tetrabutylammonium bromide (16 mg, 0.05 mmol), catalyst (1–2 %), aryl halide (0.5 mmol), hydrocinnamaldehyde (0.080 mg, 0.6 mmol), pyrrolidine (0.071 g, 1 mmol), and DMF (2 mL) were added to a 50 mL high-pressure Schlenk tube. The mixture was stirred and heated at 115 °C for 16 h. The yields of the reaction were calculated by GC and using anisole as internal standard.

General procedure for palladium-catalyzed Suzuki coupling: Under air, a Schlenk tube was charged with catalyst (2 %), aryl halide (0.5 mmol), the corresponding phenyl boronic acid (0.6 mmol), and Cs_2CO_3 (0.326 g, 1 mmol). The Schlenk tube was sealed with a septum and purged with nitrogen three times. Dioxane (2 mL) was added. The mixture was stirred and heated at 80 °C for 2 h. The yields of the reaction were calculated by GC and using anisole as the internal standard.

Crystallographic data: Single crystals were mounted on a glass fiber in a random orientation. Diffraction data were collected using an Agilent SuperNova diffractometer equipped with an Atlas CCD detector $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Absorption corrections based on the multiscan method were applied. By using Olex2,[18] the structure was solved with the olex2.solve[19] structure solution program using Charge Flipping and refined with the olex2.refine[19] refinement package using Gauss–Newton minimization. All non-hydrogen atoms were refined anisotropically.

CCDC-923437 (**2**), 923439 (**3**), and 923438 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*Crystal data and structure refinement for complex **2***: Selected crystal data: $C_{70}H_{78}Cl_2N_4Pd_2$; $M_r=1259.16$ g mol^{-1}; crystal size: $0.12\times0.11\times0.09$ mm; monoclinic, space group $C2/c$ (no. 15); $a=26.812(4)$, $b=15.6254(9)$, $c=19.933(3)$ Å; $\beta=130.42(2)°$; $V=6358(3)$ Å^3; $Z=4$; $T=273.15$ K; $\mu(\mathrm{N/A})=0.693$ mm^{-1}; $\rho_{\mathrm{calcd}}=1.3154$ g mm^3, 35466 reflections measured; independent reflections: 7237 ($R(\mathrm{int})=0.0683$); R_1 ($I\geq2\sigma(I)$) was 0.0527 ($I\geq2\mathrm{u}(I)$) and wR_2 was 0.1322 (all data); min/max residual density: −0.90 and 1.24 e Å^{-3}.

*Crystal data and structure refinement for complex **3***: Selected crystal data: $C_{78}H_{84}Cl_{18}N_6Pd_2$; $M_r=1956.55$ g mol^{-1}; crystal size: $0.472\times0.099\times0.085$ mm; monoclinic, space group, $P2_1/n$; $a=12.7777(11)$, $b=17.8414(14)$, $c=21.33509(15)$ Å; $\alpha=90$, $\beta=92.0631(8)$, $\gamma=90°$; $Z=2$; independent reflections: 9496 [$R(\mathrm{int})=0.0452$]; final R indexes ($I\geq2\sigma(I)$): $R_1=0.0485$, $wR_2=0.1358$; min/max residual density: −1.31 and 1.87 e Å^{-3}.

*Crystal data and structure refinement for complex **4***: Selected crystal data: $C_{41}H_{46}N_2Cl_3Pd$, $M_r=779.61$ g mol^{-1}; crystal size: $0.321\times0.1021\times0.0639$ mm; monoclinic, space group, $P2_1/n$; $a=15.1602(11)$, $b=15.9342(10)$, $c=15.8548(9)$ Å; $\alpha=90$, $\beta=100.884(7)$, $\gamma=90°$; $Z=4$; independent reflections: 9574 [$R(\mathrm{int})=0.0566$]; final R indexes ($I\geq2\sigma(I)$): $R_1=0.0474$, $wR_2=0.1269$; min/max residual density: −1.28 and 1.19 e Å^{-3}.

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