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N-Heterocyclic-Carbene Complexes Readily Prepared from Di-μ-hydroxopalladacycles Catalyze the Suzuki Arylation of 9-Bromophenanthrene

J. Luis Serrano,*[,†] José Pérez,[†] Luis García,[†] Gregorio Sánchez,[‡] Joaquín García,[‡] Pedro Lozano,[§] Vidya Zende,[∥] and Anant Kapdi*[,∥]

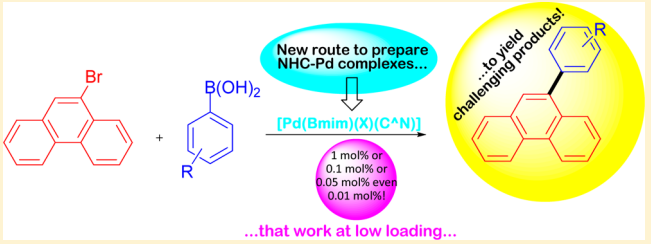
[†]Departamento de Ingeniería Minera, Geológica y Cartográfica, Regional Campus of International Excellence "Campus Mare Nostrum", Universidad Politécnica de Cartagena, Área de Química Inorgánica, 30203 Cartagena, Spain

[‡]Departamento de Química Inorgánica and [§]Departamento de Bioquímica y Biología Molecular B e Inmunología, Facultad de Química, Regional Campus of International Excellence "Campus Mare Nostrum", Universidad de Murcia, 30071 Murcia, Spain

[∥]Department of Chemistry, Institute of Chemical Technology, Mumbai, Nathalal Road, Matunga, Mumbai 400019, India

Supporting Information

ABSTRACT: New cyclometalated palladium complexes of general formula [Pd(Bmim)(X)(C^N)] have been synthesized by a novel reaction route involving di-μ-hydroxo-palladacycles [{Pd(μ-OH)(C^N)}$_2$] (C^N = 2-benzoylpyridine (Bzpy), **I**, previously unreported, or C^N = 2-phenylpyridine (Phpy), **II**)] and 1,3-butylmethylimidazolium salts [HBmim]X (X: Cl, Br, I, or saccharinate (Sacc); **a**, **b**, **c**, or **d** complexes, respectively). This simple acid−base reaction could not be achieved under identical conditions when corresponding di-μ-acetate complexes were used as starting materials. An alternative pathway to NHC/imidate complexes has also been explored by reacting **IIb** with [Ag(Phthal)(SMe$_2$)]$_2$ (Phthal = phthalimidate, **e**) to obtain [Pd(Bmim)(Phthal)(Phpy)], **IIe**. Structural characterization by X-ray diffraction of complexes **Id**, **IIb**, **IId**, and **IIe** has confirmed the proposed formulas. The mononuclear complexes have shown to catalyze the scalable Suzuki−Miyaura cross-coupling of 9-bromophenanthrene with a wide scope of aryl boronic acids, irrespective of their electronic properties and at a very low catalyst concentration of 0.01%.



INTRODUCTION

The synthesis of carbene complexes has been developed since 1968,[1] when deprotonation of imidazolium salts was achieved using appropriate coordinatively unsaturated metal complexes that provided both a ligand acting as a base and a metal center able to stabilize the imidazolin-2-ylidene thus formed. Together with this original method, the treatment of electron-rich enetetraamines[2] with suitable transition metals or the use of free and stable N-heterocyclic carbene ligands (NHCs available from 1991)[3] for direct preparation of complexes make up the main synthetic routes to these interesting compounds. Other approaches, such as carbene transfer from silver NHC complexes, have been profusely reported, as shown in the excellent review of Hahn and Jahnke.[4] However, the first described *in situ* deprotonation of azolium salts with suitable metal complexes, such as Pd(AcO)$_2$, or its modification by adding an external base remains at present a very convenient method.

Regarding the synthesis of monocarbene cyclopalladated complexes, it was assumed that acetate-bridged precursors [{Pd(μ-AcO)(C^D)}$_2$] would have a similar reactivity. In fact they have been successfully employed to prepare a diverse library of NHC-palladacycles with D = N, P, S, or O.[5] Although this reaction has a wide scope, it still has noticeable drawbacks: it does not work with some palladacycles, the use of hard to remove dimethysulfoxide as solvent, and additional base is required, in other examples, for azolium salt deprotonation with subsequent extra workup steps.[6] Other routes to synthesize NHC-palladacycles use air-sensitive free carbenes[7] or suggest a one-pot reaction of imidazolium salts, PdCl$_2$, *N*,*N*-dimethylbenzylamine, and excess K$_2$CO$_3$ in refluxing acetonitrile.[8] Given the enhanced catalytic activity of monocarbene palladium complexes that combine the desirable electronic/sterical properties of NHCs with the robustness of a palladacycle backbone,[9] we envisaged the interest of designing a new route to prepare them using cyclometalated binuclear hydroxo complexes.[10] Indeed, we have recently explored the usefulness of such [{Pd(μ-OH)(C^N)}$_2$] complexes in the preparation of a wide variety of new derivatives by means of a simple acid−base reaction,[11] proving its superior performance against specific ligands when compared to analogous di-μ-AcO precursors.[11b,g]

On the other hand, during the last 10 years we have studied the applications of palladacycles in Stille,[12] Suzuki,[11a,13] and Sonogashira reactions in the frame of wider research on

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complexes containing imidate ligands (a variety of pseudohalides showing mixed σ-donating and π-accepting properties).[14] In our hands they have shown incredible potential for cross-coupling reactions, far from just mimicking halide ligands.[15] That is the case of still scarce saccharinate-palladium complexes,[16] in which the expanded coordinative possibilities of saccharinate confer to this ligand additional interest in several fields if compared with simple cyclic imides such as succinimide or phthalimide, which still considerably differ from halides. The possibility of including imidate ligands in the coordination sphere of a palladacyclic complex that also contains NHCs has not been explored to date, although an interesting potential in catalysis for such species can be anticipated, given the fact that subtle changes in the imidate ligand structure have been claimed to have a pronounced effect on the catalytic activity of related [Au(N-imidate)(NHC)] complexes.[17]

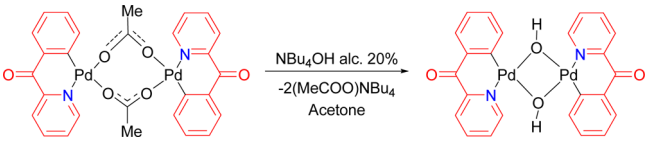
The unquestionable performance of NHC-palladacyclic complexes in Suzuki couplings using benchmark aryl bromide and chloride substrates[5b,8,9] encourages the study of reactions targeting more specific and challenging compounds, such as the 9-arylphenanthrene derivatives that we (aim for/work towards) in this study. Since the initial isolation of phenanthrene from coal tar,[18] several synthetic procedures have been developed over the years[19] to address the growing need for phenanthrene-based derivatives in a variety of fields. For example, some phenanthrene derivatives have shown biological activity,[20] and others displayed promising photo- and electroluminescence properties brought about by the subtle variation in the electronic properties of the phenanthrene backbone, which has resulted in their employment as potential organic light-emitting diodes (OLEDs).[21] Specifically, 9-arylphenanthrenes are important phenanthrene-based derivatives that are commonly employed as intermediates toward the synthesis of OLEDs or bioactive phenanthrenes.[20,21] Metal-mediated coupling reactions have played a major role in accessing these molecules, with palladium and nickel leading the way as the metals of choice. Suzuki–Miyaura[22] cross-coupling reactions, Hiyama[23] coupling, and several other processes have been routinely employed, although most of these processes suffer from poor yields, high catalyst loadings, and harsh conditions. C–H bond functionalization[24] has also been recently employed[25] for the purpose of making the process environmentally useful. However, the protocol produced low yields of the desired products with the catalyst (Fe in this case) concentration particularly higher than desired. A low-catalyst-loading protocol for the Suzuki–Miyaura cross-coupling of 9-bromophenanthrene with phenylboronic acid at 0.5 mol % Pd concentration has been reported to give good yields of the cross-coupled product.[26] However, the use of a phosphine ligand in this case makes the protocol less attractive due to the involvement of phosphine-related byproducts, as does the employment of higher temperatures.

In this article we report a highly efficient, phosphine-free Suzuki protocol to obtain 9-arylphenanthrene derivatives in very good yields at low catalyst loading (0.01 mol %). We also describe the synthesis of a new dinuclear hydroxo complex, $[Pd(\mu\text{-}OH)(C^{\wedge}N)\}_2]$ ($C^{\wedge}N$ = 2-benzoylpyridine, **I**), that together with its analogue with 2-phenylpyridine, **II**, have proved to be convenient precursors in a novel route to prepare the NHC-palladacyclic catalysts employed, [Pd(Bmim)(X)-($C^{\wedge}N$)]. Halide/imidate substitution in the latter has also been explored as a synthetic alternative to obtain the carbene/imidate/palladacyclic complexes that are the subject of our study.

RESULTS

Synthesis and Characterization. Since the first description of 2-benzoylpyridine cyclopalladation in 1982[27] to form dinuclear complexes with bridging chloride or acetate ligands, only two articles about its reactivity can be found,[28] one of them displaying the only X-ray crystal structure reported to date containing such a palladacyclic unit (refcode WOSYEI as searched in the CSD version 5.35 updated Feb 2014). We have moved one step beyond, and the hydroxo-complex $[\{Pd(\mu\text{-}OH)(Bzpy)\}_2]$ has been prepared by reaction of the related di-μ-AcO precursor with NBu_4OH (Scheme 1) in the specific conditions detailed in the Experimental Section.

Scheme 1. Synthesis of Dimeric $[\{Pd(\mu\text{-}OH)(Bzpy)\}_2]$



The formation of **I** is evident through its IR spectra, characterized by the appearance of a typical –OH stretching absorption at 3433 cm^{-1} and considerable changes in the carbonyl region due to the absence of the bridging acetate groups. The ^1H NMR spectrum displayed a high-field resonance (–1.60 ppm) characteristic of palladium hydroxo complexes.[11b,29] Mass spectrometry (HPLC/MS TOF) also contributed to the characterization of the new complex, displaying a fragment assigned to M^+.

The use of **I** and **II** as suitable basic precursors has been explored making them react with 1,3-butylmethyl-imidazolium salts in the mild conditions displayed in Scheme 2a. Interestingly, our attempts to reproduce the same reactions using the corresponding $[Pd(\mu\text{-}AcO)(C^{\wedge}N)\}_2]$ complexes failed and the starting material was recovered, confirming the superior performance of **I** and **II** and their specific usefulness in the preparation of NHC-palladacycles. Again, noticeable

Scheme 2. (a) Preparation of Monocarbene Palladium Complexes [Pd(Bmim)(X)($C^{\wedge}N$)]; (b) Halide/Imidate Exchange Using Labile Silver Complexes

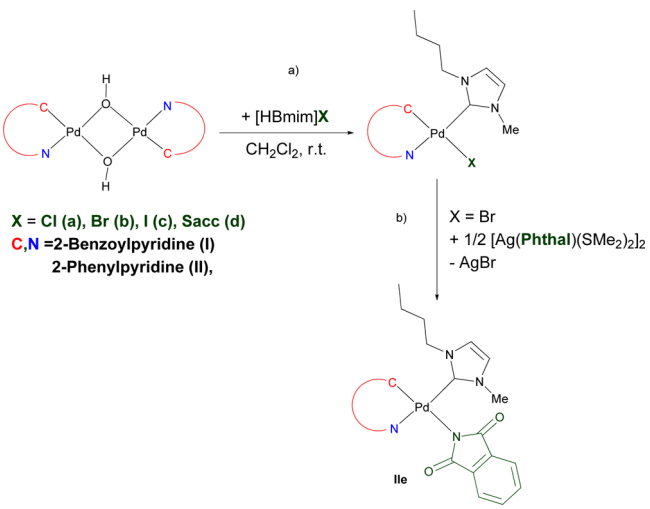


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Table 1. Selected Bond Lenghts (Å) and Angles (deg) Ib, IIb, IId, and IIe

bond/angle	Id	IIb[b]	IId	IIe
Pd(1)−C(7)				1.9936(18)
Pd(1)−C(8)	1.9851(15)			
Pd(1)−C(11)		2.012(10)	2.0024(16)	
Pd(1)−C(12)		1.966(10)	2.0049(16)	
Pd(1)−C(20)	1.9854(15)			1.9788(17)
Pd(1)−N(1)	2.0772(13)	2.080(7)	2.0912(13)	2.0696(15)
Pd(1)−N(2)	2.1335(12)			2.0899(16)
Pd(1)−N(4)			2.1263(14)	
Pd(1)−Br(1)		2.5367(13)		
C(11)−Pd(1)−C(12)		90.0(4)	93.44(7)	
C(11)−Pd(1)−N(1)		82.0(3)	80.54(6)	
C(11)−Pd(1)−Br(1)		178.4(3)		
C(12)−Pd(1)−N(1)		171.3(4)	173.69(6)	
C(12)−Pd(1)−Br(1)		91.5(3)		
N(1)−Pd(1)−Br(1)		96.5(2)		
C(11)−Pd(1)−N(4)			173.62(6)	
C(12)−Pd(1)−N(4)			91.44(6)	
N(1)−Pd(1)−N(4)			94.69(5)	
C(7)[a]−Pd(1)−C(20)	88.58(6)			93.01(7)
C(7)[a]−Pd(1)−N(1)	90.05(6)			81.44(7)
C(7)[a]−Pd(1)−N(2)	171.44(6)			174.43(7)
C(20)−Pd(1)−N(1)	176.78(6)			173.82(7)
C(20)−Pd(1)−N(2)	92.73(5)			91.96(7)
N(1)−Pd(1)−N(2)	88.20(5)			93.70(6)

[a]C(8) in compound **Id**. [b]Compound **IIb** presents four molecules in the asymmetric unit.

changes that were observed in the IR spectra as the −OH stretching absorbances have now disappeared. Spectroscopic characterization was completed by ^{1}H and ^{13}C NMR data, which displayed typical carbene resonances, and HPLC/MS TOF, where a common fragment at $M^{+}-X$ was detected.

Another alternative route to the novel NHC/imidate palladium complexes has been explored by reacting the silver complex $[Ag(Phthal)(SMe_2)]_2$ with [Pd(Bmim)(Br)(Phpy)], **IIb**, to yield [Pd(Bmim)(Phthal)(Phpy)], **IIe** in Scheme 2b, fully characterized as can be found in the Experimental Section. This is an interesting possibility that expands the scope beyond the limitations imposed by the availability of [HBmim](Imidate) salts.

X-ray crystal structures of complexes **Id**, **IIb**, **IId**, and **IIe** confirmed the proposed formulas of the new complexes. It is worth highlighting that these are the first crystal structures reported to date of palladacycles containing the Bmim carbene ligand (CSD version 5.35 updated Feb 2014). Selected bond distances and angles are listed in Table 1, and molecular structures together with the atom-numbering scheme are displayed in Figures 1, 2, 3, and 4, respectively.

In complex **Id** the arrangement of the Pd atom can be described as planar; its deviation from the planar coordination geometry has been quantified by the measurement of improper torsion angles[30] $w_1 = 2.19°$ and $w_2 = -6.05°$ for Pd1. These values correspond to a moderate square pyramidal distortion from the ideal square planar geometry. The N−Pd−C bond angle, 90.05(6)°, in the ortho-metalated moiety is slightly higher than that found in the only previously reported structure, WOSYEI (87.4(3)°),[28b] while the distances Pd(1)−C(8), Pd(1)−N(1), and carbonylic C(6)−O(1) are very similar despite the different coligands involved. The conformation of the six-membered ring Pd(1)−C(8)−C(7)−C(6)−C(5)−N(1) is *boat* deformed 19° (B = 0.7312; SB = 0.2684).[31]

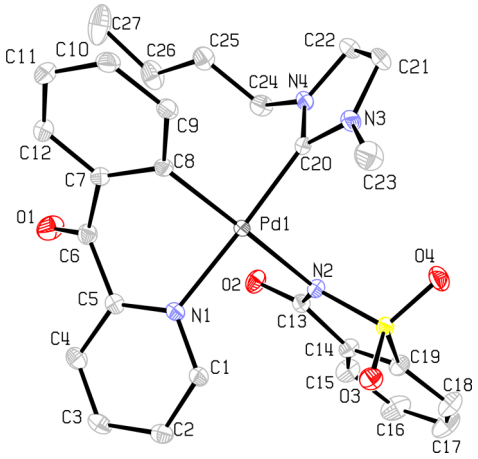

Figure 1. Thermal ellipsoid plot of **Id**, drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity.

The arrangement of the Pd atoms in **IIb**, **IId**, and **IIe** can be described as planar. For complex **IIb** $w_1 = -0.54°$ and $w_2 = 2.13°$ in Pd1, $w_1 = -2.80°$ and $w_2 = -0.98°$ for **IId**, and for **IIe** $w_1 = 1.68°$ and $w_2 = 1.72°$. These values correspond to a moderate square pyramidal (**IIb**) or tehtrahedral (**IId** and **IIe**) distortion from the ideal square planar geometry. In these complexes bite angles Pd−C−N are very similar and close to 81°. Complex **IIb** displays four molecules in the asymmetric unit and exhibits very close structural parameters compared to the analogous complex [Pd(Bzmim)(Br)(Phpy)] (Bzmim = 1-methyl-3-(2,3,4,5,6- pentamethylbenzyl)-2,3-dihydro-1*H*-imidazole, with refcode IGUVOW).[32]

Supramolecular Description. We have recently reported that phthalimidate and saccharinate ligands tend to adopt a perpendicular conformation about the coordination plane in

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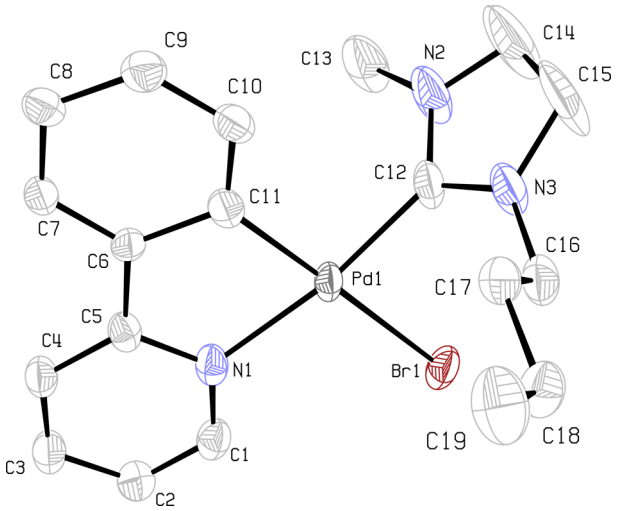

Figure 2. Thermal ellipsoid plot of **IIb** drawn at the 50% probability level. The hydrogen atoms have been omitted.

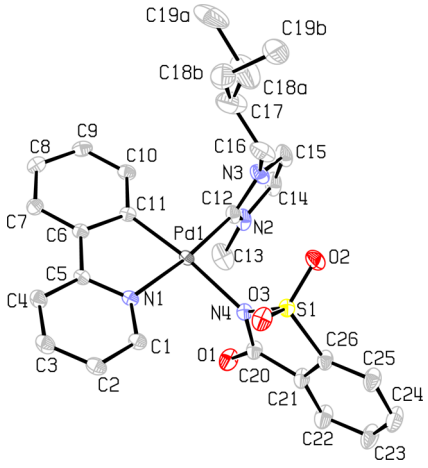

Figure 3. Thermal ellipsoid plot of **IId**, drawn at the 50% probability level. The hydrogen atoms have been omitted.

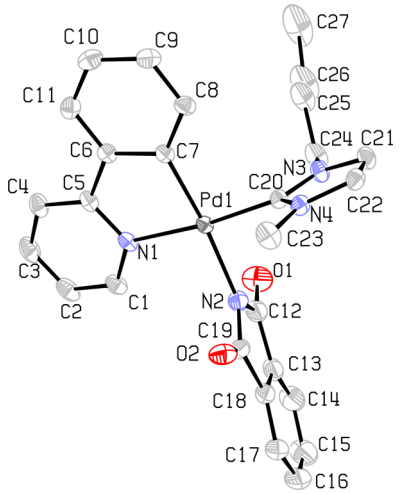

Figure 4. Thermal ellipsoid plot of **IIe**, drawn at the 50% probability level. The hydrogen atoms have been omitted.

their palladium complexes.[33] The Bmim ligand also appears perpendicular to the coordination plane, as can be seen in Table 2. Probably a less steric impediment due to the lack of

Table 2. Relevant Conformational Features

	Id	IIb	IId	IIe
Bmim^C plane angle (deg)	86.23	73.39[a]	85.72	88.55
imidate^C plane angle (deg)	70.00		87.60	83.86

[a]Mean value for the four molecules in the asymmetric unit.

imidate results in **IIb** being the complex under study in which Bmim is less perpendicular. In complexes **Id** and **IId** saccharinate and Bmim can adopt two different relative configurations, and each complex displays one of them.

Each molecule in complex **Id** interacts with the other 10 around it, but the most significant links take place with two of them: (i) a C−H···O═C and a C−H···O═S hydrogen bond and (ii) C−H···π by Bzpy ligands (omitted in Figure 5 for clarity).

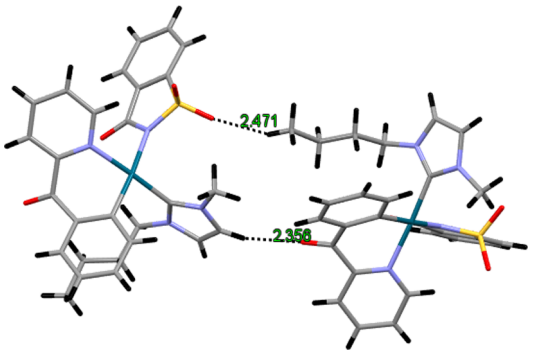

Figure 5. Crystal packing in **Id**, displaying main interactions.

Complex **IIb** in the solid state can be described as a "tetramer" linked by C−H···π interactions between Phpy ligands as shown in Figure 6. This fact could explain the four

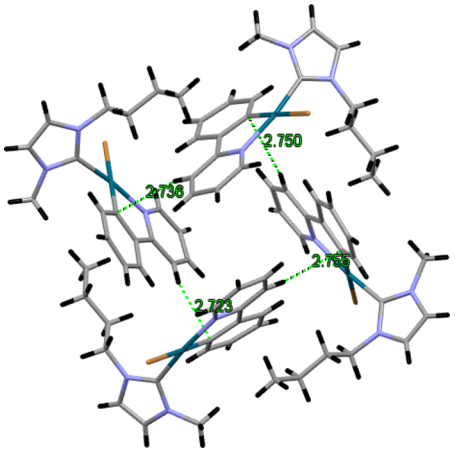

Figure 6. Crystal packing in **IIb**.

molecules in the asymmetric unit. Each Phpy ligand is nearly perpendicular to the adjacent Phpy ligands (angles between consecutive PhPy's 83.68°, 85.26°, 82.09°, and 83.85°, respectively). In spite of the fact that hydrogen atoms have been added in calculated positions, the short H···C distances inside the "tetramers" (Table 3, Figure 6) allow concluding that they are strong C−H···π interactions.[34] The most significant interactions between "tetramers" are C−H···Br contacts.

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Table 3. Relevant Supramolecular Interactions Found in the New Crystal Structures

complex	interaction type	geometrical parameters		
Id	hydrogen bonds	D···A (Å)	H···A (Å)	D−H···A (deg)
	C−H···O=C	3.280	2.356	164.2
	C−H···O=S	3.382	2.471	154.4
	C−H···π	shortest H···C distances (Å)		
		2.888, 2.891		
IIb	C−H···π	shortest H···C distances (Å)		
		2.750, 2.736, 2.723, 2.755		
IId	π···π	plane−plane distance (Å)	centroid−centroid distance (Å)	
		3.384	3.604	
	hydrogen bonds	D···A (Å)	H···A (Å)	D−H···A (deg)
	C−H···O=C	3.630	2.714	162.29
	C−H···O=S	3.453	2.664	140.86
	C−H···O=C	3.282	2.337	172.35
	C−H···O=S	3.375	2.691	129.45
	anagostic interaction	Pd···H distance (Å)		
		2.661		
IIe	π···π	plane−plane distance (Å)	centroid−centroid distance (Å)	
		3.489	3.626	
	anagostic interaction	Pd···H distance (Å)		
		2.750		
	hydrogen bonds	D···A (Å)	H···A (Å)	D−H···A (deg)
	C−H···O=C	3.508	2.564	172.83
	C−H···O=C	3.302	2.355	173.77

The most relevant supramolecular interactions in **IId** take place with three molecules as displayed in Figure 7. With one of

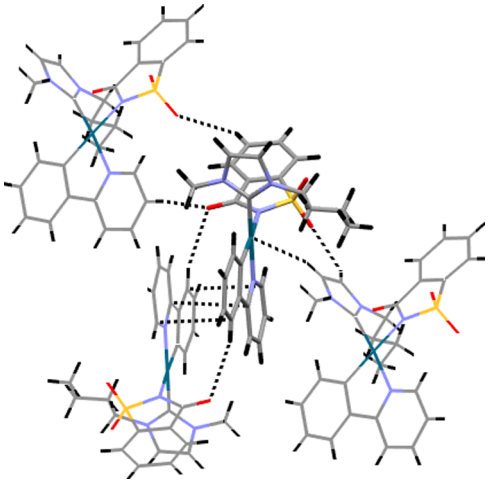

Figure 7. Crystal packing in **IId**.

the molecules relevant links are established by π···π and C−H···O=C interactions. Phpy ligands define parallel planes (plane−plane distance of 3.384 Å). Both molecules are related by a center of symmetry, so the py ring stacks over the Ph ring but in a offset π-stacked geometry (centroid−centroid distance of 3.604 Å, longer than the distance between planes). Two weak C−H···O=C hydrogen bonds strengthen the link between both molecules. With the second one there are anagostic Pd···H and C−H···O=S interactions. With the third one there are hydrogen bonds of the type C−H···O=S and C−H···O=C (this is the strongest hydrogen bond in this structure; the O=C has been reported as the group producing the shortest supramolecular interactions in the saccharinate ligand).[33]

The more relevant interactions in compound **IIe** (Figure 8) are (i) π···π interactions by Phpy ligands that define parallel

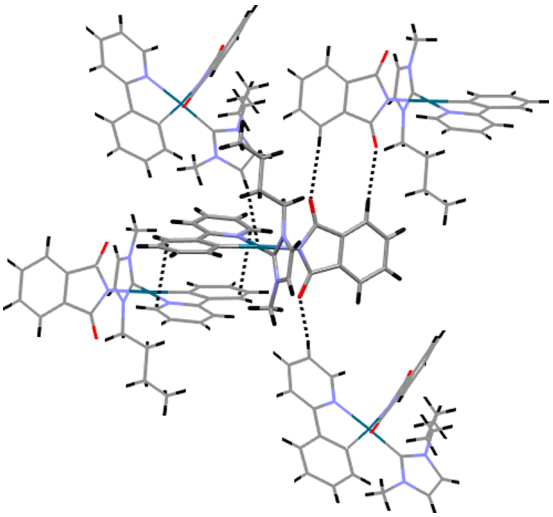

Figure 8. Crystal packing in **IIe**.

planes (plane−plane distance of 3.489 Å). Again, like in **IId**, both molecules are related by a center of symmetry (centroid−centroid distance of 3.626 Å). The distance between planes in **IIe** and **IId** is short according to the values reported in the literature for π···π interactions;[35] (ii) anagostic Pd···H interactions; this kind of interaction in **IIe** and **IId** is strong according to metal···H distances reported;[36] (iii) two phthalimide ligands linked by two hydrogen bonds forming a planar centrosymmetric ring, $R_2^2(10)$; (iv) phthalimide also interacting with a Phpy ligand by a hydrogen bond that can be classified as moderate.[37]

Catalytic Studies: Suzuki−Miyaura Cross-Coupling of 9-Bromophenanthrene with Different Aryl Boronic Acids. At the outset of our studies we first subjected the Pd complexes **Ia,b** and **IIa,b** to the Suzuki−Miyaura cross-coupling of 9-bromophenanthrene **III** with phenylboronic acid **IVa** in a PhMe/H_2O system at 80 °C with Na_2CO_3 as the base with a Pd concentration kept at 1.0 mol % (much lower than most examples reported in the literature;[22−25] once the superior performance of phenylpyridine complexes was checked, the whole series was tested, entries 1−6, Table 4).

It was observed that out of the six catalysts tested, complex **IId** (entry 6, Table 4) gave an almost quantitative yield of the cross-coupled product, although other catalysts were also found to furnish the product in relatively similar yields with smaller differences in reactivity.

Optimum results for better product formation were obtained at 80 °C, although at room temperature the reaction still proceeded in good yield (entries 7 and 8, Table 4, respectively). Catalyst loading experiments were also performed to reveal the extent of catalytic activity of the Pd-NHC complexes (entries 9−13, Table 4). On reducing the catalyst loading from 1.0 mol % to 0.1 mol %, it was still able to provide the cross-coupled product in competitive yield (entries 9 and 10, Table 4,

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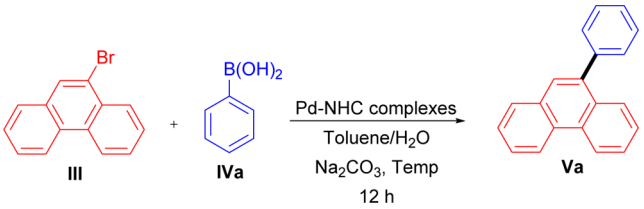
Table 4. Catalyst Screening Studies for Suzuki–Miyaura Cross-Coupling of 9-Bromophenanthrene with Phenyl Boronic Acid



no.	complex	temp (°C)	catalyst conc (mol %)	% yield	TON
			Complex Screening		
1.	**Ia**	80	1.0	81	
2.	**Ib**	80	1.0	87	
3.	**IIa**	80	1.0	88	
4.	**IIb**	80	1.0	95	
5.	**IIc**	80	1.0	92	
6.	**Id**	80	1.0	96	
Temperature Study					
7.	**IId**	80	1.0	96	
8.	**IId**	r.t.	1.0	87	
Catalyst Loading					
9.	**IId**	80	1.0	96	96
10.	**IId**	80	0.1	92	920
11.	**IId**	80	0.01	92	9200
12.	**IId**	80	0.005	80	40,000
13.	**IId**	80	0.001	70	70,000

respectively). Interestingly, at 0.01 mol % catalyst loading the product could be obtained in very good yield, while any further reduction resulted in slightly lower yields of the product (0.005 mol % gave 80% with a TON of 40 000, while reaction at 0.001 mol % gave 70% having a TON of 70 000).

Catalyst Comparison Study. To investigate the findings of Table 4 regarding the difference in reactivity of the various Pd-NHC complexes, gas chromatographic profiles were obtained for all the complexes by injecting small aliquots of reaction mixtures (in the conditions of entry 11 for the whole series) quenched before injection and after regular time intervals. Analysis was carried out on a Shimadzu Parvum 2 gas chromatograph mass spectrometer using hexadecane as the internal standard (with autosampler). The injections were done at intervals of 0, 1, 2, 3, 6, 9, and 12 h to get enough data points.

The GC plot to a larger extent confirmed our initial findings about the active nature of the Pd-NHC catalyst **IId** in comparison to others (Figure 9). Depending on the type of backbone, a marked difference in reactivity could be observed between the complexes. Phenylpyridine-backbone-containing Pd-NHC complexes converted at a faster rate than their benzoylpyridine counterparts. Commercial NHC-based palladium complexes [Pd(SIPr)(allyl)Cl] (**A**) and Pd-PEPPSI-SIPr (**B**) got initiated at a much slower rate than **IId** (comparably better performing among the whole lot). With standard phosphinated Pd complexes, namely, $Pd(PPh_3)_4$ (**C**) and $PdCl_2(PPh_3)_2$ (**D**), an induction period is observed extending up to 2 h, after which these catalysts were found to convert, although at a much slower rate than the others.

Scope Study. Next we turned our attention toward exploring the scope of the catalytic reaction. A variety of arylboronic acids were cross-coupled with 9-bromophenanthrene using a 0.01 mol % catalyst concentration of Pd-NHC complex **IId** at 80 °C in a $PhMe/H_2O$ system (Scheme 3). Electronic properties of the arylboronic acid were found to show less effect on the activity of the catalytic system. Although lower product formation was observed in the case of 3-nitrophenylboronic acid, overall in most cases the arylated products were obtained in good to excellent yields. It therefore highlights the activity of the Pd-NHC complex **IId** to catalyze the transformation of such synthetically important substrates at a very low catalyst loading of 0.01 mol %.

Following the scope investigation, scale-up studies were performed. The catalytic reaction was performed between 9-bromoanthracene and phenylboronic acid on a 5.0 mmol scale. It was observed that rather than performing the catalytic reaction at 0.01 mol %, further reduction in the catalyst concentration to 0.005 mol % also furnished the cross-coupled product in excellent quantity (Scheme 4). Given the ease of synthesis of the complexes as well as the mildness of the protocol, such a synthetic route becomes highly attractive and could be used successfully in obtaining good to excellent yields of 9-arylated products on a larger scale for further applications.

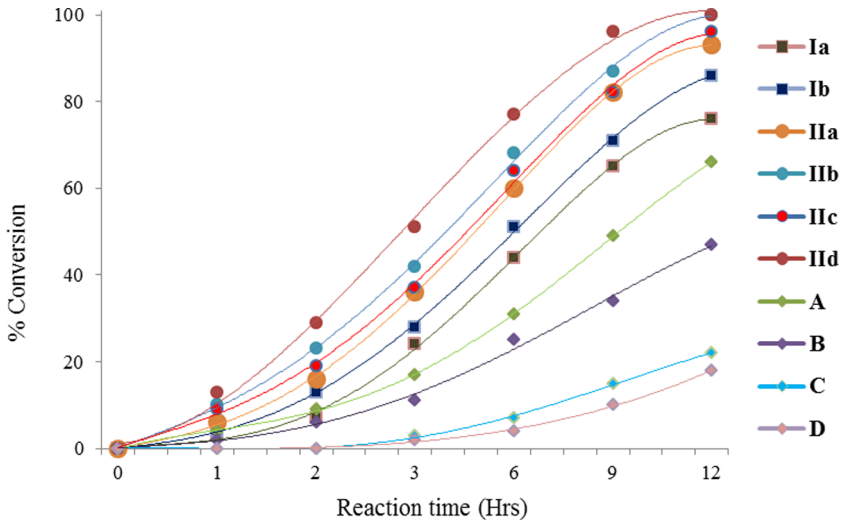


Figure 9. GC profiles for the catalytic reaction of 9-bromophenanthrene **III** with phenylboronic acid **IVa** using different palladium catalysts. **A** = [Pd(SIPr)(allyl)Cl]; **B** = Pd-PEPPSI-SIPr; **C** = $Pd(PPh_3)_4$; **D** = $PdCl_2(PPh_3)_2$. Hexadecane was used as an internal standard.

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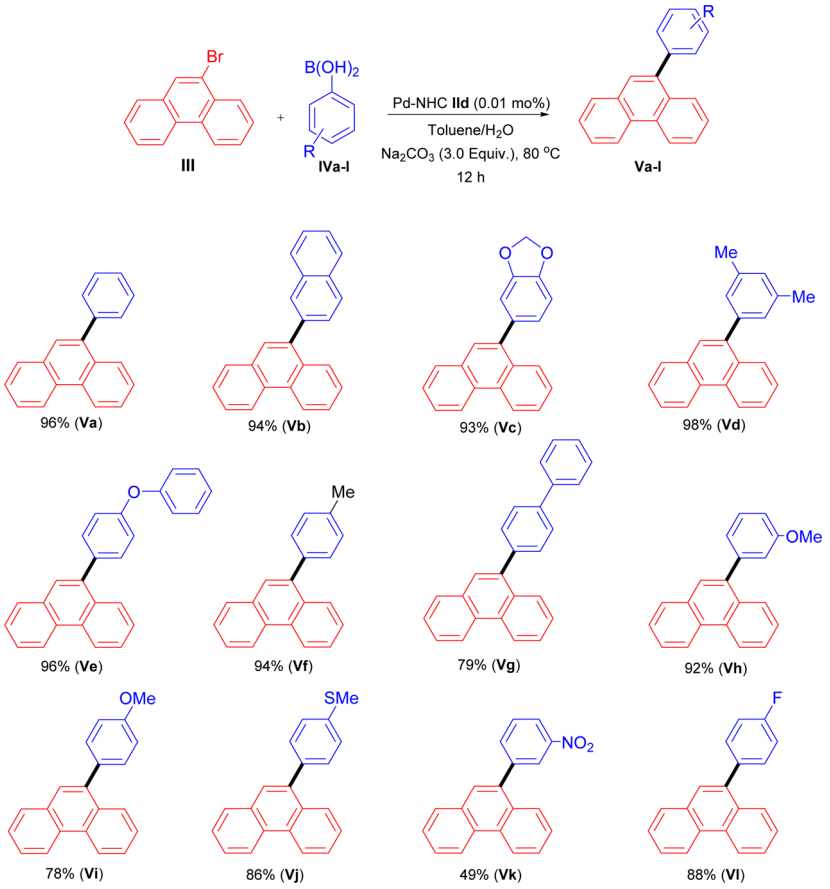
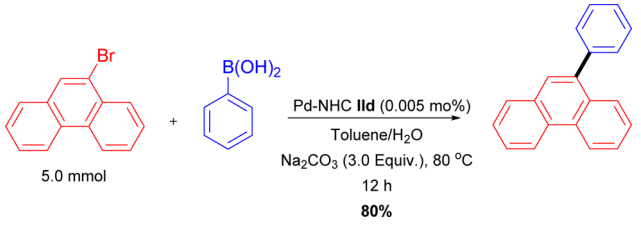
Scheme 3. Pd-Catalyzed Arylation of 9-Bromophenanthrene Using Pd-NHC Complex IId[a]



[a]Typically the reaction was performed on a 1.0 mmol scale of the 9-bromophenanthrene with 1.2 mmol of phenylboronic acid and 3.0 mmol of Na_2CO_3 in a PhMe/H_2O mixture (1:2) containing Pd-NHC complex **IId** in 0.01 mol % concentration. Isolated yields obtained after purification by column chromatography.

Scheme 4. Scale-up Study for the Arylation of 9-Bromophenanthrene



Study for Possible Cationic Pd Intermediates. The noticeable activity of Pd-NHC complex **IId** was further investigated toward the possible presence of cationic Pd species. In the literature several studies have highlighted the rate-enhancing effect of cationic Pd species formed either via oxidative addition of the electrophilic partner to the Pd center[38] or via ligand displacement by a coordinating solvent.[39] Our initial assumption was based on the mass spectral analysis results for the Pd-NHC complexes described here, which showed the presence of the cationic Pd species as the base peak. The presence of such species via ligand displacement has also been shown to exist in the reactions using electrospray ionization mass spectrometry.[39b]

To verify this extent, we performed an experiment involving the addition of silver salt[40] ($AgNO_3$) in an equimolar amount to that of the Pd-NHC complex **IId** with the intention of generating a cationic Pd species *in situ*. It should typically catalyze the Suzuki–Miyaura cross-coupling reaction at a much faster rate than the complex **IId** itself. A kinetic profile was obtained for the catalytic reaction with the added $AgNO_3$ and was compared with the one obtained for complex **IId** (Figure 10).

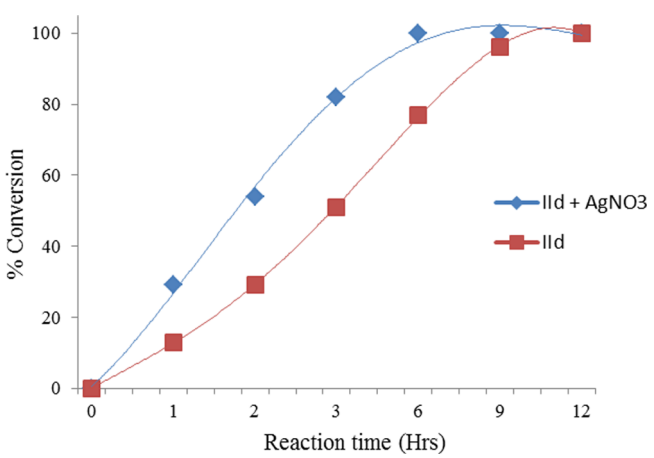


Figure 10. Effect of Ag salt addition on the reactivity of the catalytic reaction.

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It seems that indeed the addition of silver salt helps to accelerate the formation of the cationic Pd species, leading to the faster conversion of the substrate to the product (complete conversion was observed in around 3−6 h). In the case of **IId** alone, the formation of cationic Pd species might take place at a slower rate, which could explain the difference in reactivity. Nevertheless, further ongoing studies to get better insight into the possible mechanism acting in these types of coupling reactions, including isolation and characterization of cationic complexes, are needed and will be reported in due course.

CONCLUSION

A new and convenient route to obtain palladacyclic complexes containing NHC ligands [Pd(Bmim)(X)(C^N)] has been explored, exploiting the enhanced reactivity of di-μ-hydroxo precursors. Novel NHC/imidate palladium complexes can also be prepared by removing halide X in the former using a silver/imidate source. Structural characterization by X-ray diffraction of four complexes confirmed the proposed formula. In addition, catalytic activity of the new complexes in Suzuki−Miyaura cross-coupling of 9-bromoanthracene with aryl boronic acids at very low catalyst loading has been disclosed. Faster conversion of the substrate in the presence of $AgNO_3$ suggests a key role of intermediate cationic species.

EXPERIMENTAL SECTION

General Procedures. All catalytic reactions were conducted under an inert atmosphere of N_2 on a Schlenk line. Melting points were recorded on an electrothermal digital melting point apparatus and are uncorrected. TLC analysis was performed on aluminum-backed silica gel plates, and compounds were visualized by ultraviolet light (254 nm), phosphomolybdic acid solution (5% in EtOH), or 1% ninhydrin in EtOH. NMR data (^{1}H) were recorded on 200, 300, or 400 spectrometers. ESI-MS analyses were performed on a mass spectrometer. Chemical shifts are reported in parts per million downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in hertz (Hz). IR spectra were recorded on an FT-IR spectrophotometer, using Nujol mulls between polyethylene sheets.

GC Parameters. GC analysis for the kinetic profile was done on a Shimadzu GC-MS Parvum 2 equipped with an autosampler. Separation was achieved using a Zebron ZB-1 capillary column (i.d. 0.25 mm, length 30 m) with a temperature ramp from 50 to 250 °C at 10 °C min^{-1}. The injection volume was 1 μL with a split ratio of 50.

Materials and Methods. The cyclometalated precursor [{Pd(μ-OH)(C^N)}$_2$] (C^N = 2-phenylpyridine (Phpy), **II**) was prepared as described previously.[29b] The 1,3-butylmethylimidazolium salts [HBmim]X (X: Cl, Br, I) were obtained from IoLiTec GmbH (Germany). [HBmim](Sacc) was prepared adapting a method previously described.[41] Other commercially available chemicals such as arylboronic acids, 9-bromophenanthrene, and $AgNO_3$ were purchased from Aldrich Chemical Co. and were used without further purification, and all the solvents were dried by standard methods before use.

*Preparation of Complex [{Pd(μ-OH)(C^N)}$_2$] (C^N = 2-benzoylpyridine (Bzpy), **I**).* To a solution of [{Pd(Bzpy)(μ-AcO)}$_2$] (348 mg, 0.5 mmol) in 10 mL of acetone was added 20% NBu_4OH(aq) (1.45 mL, 1.1 mmol). After 1 h stirring at room temperature the solvent was partially evaporated under reduced pressure. Addition of water followed by vigorous stirring and filtration afforded a yellow solid, which was air-dried. The complex was recrystallized from acetone/diethyl ether.

*[{Pd(μ-OH)(Bzpy)}$_2$], **I:*** 0.275g, 90%. IR (cm^{-1}): ν(OH) 3434, ν(Bzpy) 1660, 1596, 1550, 766. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.07 (d, J = 5.0 Hz, 2H^2 Bzpy), 8.17 (d, J = 8.0 Hz, 2H^5 Bzpy), 7.97 (m, 2H^4 Bzpy), 7.75 (d, J = 7.6 Hz, 2H^6 Bzpy), 7.46 (m, 2H^3 Bzpy), 7.19−7.15 (m, 4H Bzpy); 6.93 (m, 2H$^\alpha$ Bzpy), −1.60 (s, 2H, OH). ^{13}C NMR (200 MHz, $CDCl_3$): δ 124.63, 125.45, 126.66, 128.15, 130.42, 130.93, 137.09, 138.58, 148.53, 150.43, 151.77, 192.35 C═O. HPLC-MS (positive mode) m/z: 610.17 (M$^+$). Anal. Calcd for $C_{24}H_{18}N_2O_4Pd_2$: C, 47.16; H, 2.97; N, 4.58. Found: C, 47.35; H, 3.23; N, 4.63.

*Preparation of the Complexes [Pd(Bmim)(X)(C^N)] (X = Cl **a**, Br **b**, I **c**, or saccharinate (sacc) **d** (C^N = 2-benzoylpyridine (Bzpy) **I** series; C^N = 2-phenylpyridine (Phpy) **II** series).* The new complexes were obtained by treating a CH_2Cl_2 suspension (20 mL) of the appropriate precursor [{Pd(μ-OH)(C^N)}$_2$] (0.2 g) with the corresponding 1,3-butylmethylimidazolium salt (molar ratio 1:2) in dichloromethane (15 mL). The pale yellow solution thus formed was stirred at room temperature for 1 h, passed through a short silica gel column, and then concentrated under reduced pressure until ca. one-fifth of the initial volume. Slow addition of hexane/diethyl ether (1:1) caused the precipitation of the title complexes, which were filtered off and air-dried.

*[Pd(Bzpy)(Bmim)Cl], **Ia:*** 0.16 g, 53%;. IR (cm^{-1}): ν(Bzpy) 1660 vs, 1603 vs, 772 vs. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (d, J = 5.6 Hz, 1H^2 Bzpy), 8.13 (d, J = 8.0 Hz, 1H^5 Bzpy), 7.97 (m, 1H^4 Bzpy), 7.73 (d, J = 7.6 Hz, 1H^6 Bzpy), 7.52 (m, 1H^3 Bzpy); 7.07 (m, 1H^7 Bzpy); 6.95 (m, 1H^8 Bzpy); 6.90 (d, J = 1.6 Hz, 1H carbene), 6.87 (d, J = 1.6 Hz, 1H carbene), 6.55 (d, J = 7.6 Hz, 1H$^\alpha$ Bzpy), 4.29 (m, 1H N−C$\underline{H}_2$−), 4.03 (m, 1H N−C$\underline{H}_2$−), 3.96 (s, 3H N−CH_3), 1.76 (m, 1H N−CH_2−C$\underline{H}_2$−), 1.51 (m, 1H N−CH_2−C$\underline{H}_2$−), 1.26 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.86 (t, J = 7.2 Hz, 3H N−CH_2−CH_2−CH_2−CH_3). ^{13}C NMR (400 MHz, $CDCl_3$): δ: 13.61 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19.84 (N−CH_2−CH_2−$\underline{C}H_2$−), 32.27 (N−CH_2−$\underline{C}H_2$−), 38.20 (N−$\underline{C}H_3$), 50.99 (N−$\underline{C}H_2$−CH_2−CH_2−), 120.62 carbene, 122.01 carbene, 124.46, 124.57, 126.40, 129.19, 130.43, 137.03, 138.37, 138.88, 148.77, 151.87, 152.53, 170.44 [Pd−C$_{carbene}$], 192.92 C═O. HPLC-MS (positive mode) m/z: 426.08 (M$^+$ − Cl). Anal. Calcd for $C_{20}H_{22}ClN_3OPd$: C, 51.96; H, 4.80; N, 9.09. Found: C, 52.09; H, 5.06; N, 9.12.

*[Pd(Bzpy)(Bmim)Br], **Ib:*** 0.23 g, 71%. IR (cm^{-1}): ν(Bzpy) 1663 vs, 1590 vs, 772 vs. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (d, J = 5.2 Hz, 1H^2 Bzpy), 8.12 (d, J = 7.6 Hz, 1H^5 Bzpy), 7.97 (m, 1H^4 Bzpy), 7.73 (d, J = 7.6 Hz, 1H^6 Bzpy), 7.49 (m, 1H^3 Bzpy), 7.08 (m, 1H^7 Bzpy), 6.96 (m, 1H^8 Bzpy), 6.91 (s, 1H^{10} carbene), 6.86 (s, 1H^{11} carbene), 6.56 (d, J = 7.6 Hz, 1H$^\alpha$ Bzpy), 4.25 (m, 1H N−C$\underline{H}_2$), 4.03 (m, 1H N−C$\underline{H}_2$), 3.97 (s, 3H N−CH_3), 1.86 (m, 1H N−CH_2−C$\underline{H}_2$−),1.44 (m, 1H N−CH_2−C$\underline{H}_2$−), 1.24 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.84 (t, J = 7.6 Hz, 3H N−CH_2−CH_2−CH_2−CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.62 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19.84 (N−CH_2−CH_2−$\underline{C}H_2$−), 32.27 (N−CH_2−$\underline{C}H_2$−), 38.41 (N−$\underline{C}H_3$), 51.06 (N−$\underline{C}H_2$−CH_2−CH_2−), 120.61, carbene, 122.06 carbene, 124.55, 124.60, 126.29, 129.16, 130.41, 137.94, 138.38, 138.86, 150.17, 152.13, 153.89, 170.20 [Pd−C$_{carbene}$], 192.85 C═O. HPLC-MS (positive mode) m/z: 426.08 (M$^+$ − Br). Anal. Calcd for $C_{20}H_{22}BrN_3OPd$: C, 47.40; H, 4.38; N, 8.29. Found: C, 47.50; H, 4.61; N, 8.31.

*[Pd(Bzpy)(Bmim)I], **Ic:*** 0.20 g, 55%. IR (cm^{-1}): ν(Bzpy) 1665 vs, 1603 vs, 772 vs. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.10 (d, J = 4.4 Hz, 1H^2 Bzpy), 8.70 (d, J = 7.0 Hz, 1H^5 Bzpy), 8.02 (m, 2H Bzpy), 7.56 (m, 3H Bzpy), 6.86 (m, 3H carbene+H$^\alpha$), 4.32 (m, 1H N−C$\underline{H}_2$−), 4.10 (m, 1H N−C$\underline{H}_2$−), 3.94 (s, 3H N−CH_3), 1.94 (m, 2H N−CH_2−C$\underline{H}_2$−), 1.37 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.98 (t, J = 7.0 Hz, 3H N−CH_2−CH_2−CH_2−CH_3,). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.71 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 20.03 (N−CH_2−CH_2−$\underline{C}H_2$−), 32.09 (N−CH_2−$\underline{C}H_2$−), 38.44 (N−$\underline{C}H_3$), 50.87 (N−$\underline{C}H_2$−CH_2−CH_2−), 120.98, carbene, 122.27 carbene, 124.50, 124.61, 126.17, 128.14, 130.92, 137.06, 138.41, 138.92, 150.27, 152.63, 153.99, 170.15 [Pd−C$_{carbene}$], 192.82 C═O. HPLC-MS (positive mode) m/z: 426.08 (M$^+$ − I). Anal. Calcd for $C_{20}H_{22}IN_3OPd$: C, 43.38; H, 4.00; N, 7.59. Found: C, 43.51; H, 4.20; N, 7.67.

*Pd(Bzpy)(Bmim)(Sacc)], **Id:*** 0.23 g, 58%. IR (cm^{-1}): ν(Bzpy) 1666 vs, 1594 vs, 782 vs ν(Sacc) 1660 vs, 1285s, 1168s, 968vs, 679s. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (d, J = 5.2 Hz, 1H^2 Bzpy), 8.19 (d, J = 7.6 Hz, 1H^5 Bzpy), 7.92 (m, 1H^4 Bzpy), 7.65 (d, J = 7.6 Hz, 1H^6 Bzpy), 7.54 (m, 2H Sacc), 7.38 (m, 1H^3 Bzpy), 7.10 (m, 1H^7 Bzpy), 6.99 (m, 1H^8 Bzpy), 6.90 (s, 1H^{10} carbene), 6.81 (s, 1H^{11} carbene),

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6.75 (d, J = 7.6 Hz, 1H$^{\alpha}$ Bzpy), 4.55 (m, 1H N−C$\underline{H}_2$), 4.18 (s, 3H N−CH_3), 4.04 (m, 1H N−C$\underline{H}_2$), 1.44 (m, 2H N−CH_2−C$\underline{H}_2$−), 1.18 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.78 (t, J = 7.6 Hz, 3H N−CH_2−CH_2−CH_2−CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.66 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19,68 (N−CH_2−CH_2−$\underline{C}H_2$−), 31.99 (N−CH_2−$\underline{C}H_2$−), 38.38 (N−$\underline{C}H_3$), 51.05 (N−$\underline{C}H_2$−CH_2−CH_2−), 119.81 Sacc, 120.37 carbene, 122.09 carbene, 123.37 Sacc, 124.61, 124.76, 126.66, 129.35, 130.23, 131.98 Sacc, 132.67 Sacc, 137.13, 138.03, 138.92, 142.64 Sacc, 148.18 Sacc, 151.83, 152.48, 153.86, 167.35 Sacc, 169.41 [Pd−$C_{carbene}$], 192.30 C═O. HPLC-MS (positive mode) m/z: 426.08 (M^+ − Sacc). Anal. Calcd for $C_{28}H_{32}N_4O_4PdS$: C, 53.63; H, 5.14; N, 8.93; S, 5.11. Found: C, 53.65; H, 5.40; N, 9.12; S, 5.23.

[Pd(Phpy)(Bmim)Cl], ***IIa:*** 0.21 g, 66%. IR (cm^{-1}): ν(Phpy) 1604 vs, 752 vs. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (d, J = 1.6 Hz, 1H^2 Phpy), 7.79 (m, 1H^4 Phpy), 7.69 (d, J = 7.9 Hz, 1H^5 Phpy), 7.53 (d, J = 7.9 Hz, 1H^6 Phpy), 7.21 (m, 1H^3 Phpy), 7.05 (m, 1H^8 Phpy), 7.00 (s, 2H carbene), 6.87 (m, 1H^7 Phpy), 6.10 (d, J = 7.2 Hz, 1H$^{\alpha}$ Phpy), 4.37 (m, 1H N−C$\underline{H}_2$−), 4.31 (m, 1H N−C$\underline{H}_2$−), 3.96 (s, 3H N−CH_3), 1.89 (m, 2H N−CH_2−C$\underline{H}_2$−, 1.31 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.84 (t, J = 7.3 Hz, 3H N−CH_2−CH_2−CH_2−C$\underline{H}_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.59 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19.75 (N−CH_2−CH_2−$\underline{C}H_2$−), 32.44 (N−CH_2−$\underline{C}H_2$−), 38.46 (N−$\underline{C}H_3$), 51.05 (N−$\underline{C}H_2$−CH_2−CH_2−), 117.87 carbene, 120.90 carbene, 122.06, 122.02, 123.55, 123.92, 129.56, 136.51, 138.42, 146.49, 149.60, 154.66, 164.09, 173.15 [Pd−$C_{carbene}$]. HPLC-MS (positive mode) m/z: 398.08 (M^+ − Cl). Anal. Calcd for $C_{19}H_{22}ClN_3Pd$: C, 52.55; H, 5.11; N, 9.68. Found: C, 52.76; H, 5.36; N, 9.69.

[Pd(Phpy)(Bmim)Br], ***IIb:*** 0.23 g, 71%. IR (cm^{-1}): ν(Phpy) 1605 vs, 752 vs. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.49 (d, J = 5.6 Hz, 1H^2 Phpy), 7.79 (m, 2H Phpy), 7.53 (d, J = 7.8 Hz, 1H^6 Phpy), 7.23 (m, 1H^3 Phpy), 7.06 (m, 1H^8 Phpy), 7.00 (s, 2H carbene), 6.90 (m, 1H^7 Phpy), 6.08 (d,, J = 7.6 Hz, 1H$^{\alpha}$ Phpy), 4.37 (m, 2H N−C$\underline{H}_2$−), 3.95 (s, 3H N−CH_3), 1.87 (m, 2H N−CH_2−C$\underline{H}_2$−), 1.28 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.82 (t, J = 7.3 Hz, 3H, N−CH_2−CH_2−CH_2−C$\underline{H}_3$). ^{13}C NMR (200 MHz, $CDCl_3$): δ 13.61 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19.80 (N−CH_2−CH_2−$\underline{C}H_2$−), 32.24 (N−CH_2−$\underline{C}H_2$−), 38.54 (N−$\underline{C}H_3$), 51.13 (N−$\underline{C}H_2$−CH_2−CH_2−), 117.99 carbene, 120.92 carbene, 122.07, 122.34, 123.63, 124.03, 129.63, 136.18, 138.29, 146.54, 151.14, 155.62, 164.11, 172.83 [Pd−$C_{carbene}$]. HPLC-MS (positive mode) m/z: 398.08 (M^+ − Br). Anal. Calcd for $C_{19}H_{22}BrN_3Pd$: C, 47.67; H, 4.63; N, 8.78. Found: C, 47.95; H, 4.76; N, 8.91.

[Pd(Phpy)(Bmim)I], ***IIc:*** 0.20 g, 55%. IR (cm^{-1}): ν(Phpy) 1603 vs, 752 vs. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.70 (d, J = 5.0 Hz, 1H^2, Phpy), 7.75 (m, 2H Phpy), 7.53 (d, J = 7.9 Hz, 1H^6 Phpy), 7.26−6.86 (m, 5H 3H Phpy + 2H carbene), 5.98 (d, J = 7.4 Hz, 1H$^{\alpha}$ Phpy), 4.34 (m, 2H N−C$\underline{H}_2$−), 3.95 (s, 3H N−CH_3), 1.85 (m, 2H N−CH_2−C$\underline{H}_2$−), 1.31 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−); 0.87 (t, J = 7.4 Hz, 3H N−CH_2−CH_2−CH_2−C$\underline{H}_3$,). ^{13}C NMR (200 MHz, $CDCl_3$): δ 13.56 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19.80 (N−CH_2−CH_2−$\underline{C}H_2$-), 31.98 (N−CH_2−$\underline{C}H_2$-), 38.59 (N-$\underline{C}H_3$), 51.12 (N-$\underline{C}H_2$−CH_2−CH_2−), 118.19 carbene, 120.95 carbene, 122.21, 122.68, 123.68, 124.16, 129.68, 135.41, 138.05, 146.59, 153.89, 157.15, 164.06, 171.92 [Pd−$C_{carbene}$]. HPLC-MS (positive mode) m/z: 398.08 (M^+ − I). Anal. Calcd for $C_{19}H_{22}IN_3Pd$: C, 43.41; H, 4.22; N, 7.99. Found: C, 43.54; H, 4.37; N, 8.01.

[Pd(Phpy)(Bmim)(Sacc)], ***IId:*** 0.23 g, 58%. IR (cm^{-1}): ν(Phpy) 1602 vs, 1567 vs, 752 vs ν(Sacc) 1661 vs, 1288s, 1151s, 964vs. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 5.2 Hz, 1H^2 Phpy), 7.87 (m, 1H^5 Phpy), 7.77 (m, 2H Sacc), 7.61 (m, 1H^6 Phpy), 7.54 (m, 2H Sacc), 7.46 (m, 1H^3 Phpy), 7.12 (m, 2H Phpy), 6.99 (d, J = 2.0 Hz, 1H carbene); 6.97 (d, J = 2.0 Hz, 1H carbene), 6.89 (m, 1H^7 Phpy), 6.07 (d, J = 7.2 Hz, 1H$^{\alpha}$ Phpy), 4.74 (m, 1H N−C$\underline{H}_2$−), 4.21 (m, 1H N−C$\underline{H}_2$−), 4.06 (s, 3H N−CH_3), 1.77 (m, 2H N−CH_2−C$\underline{H}_2$−), 1.33 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.82 (t, J = 7.3 Hz, 3H, N−CH_2−CH_2−CH_2−C$\underline{H}_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.64 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19.79 (N−CH_2−CH_2−$\underline{C}H_2$−), 32.26 (N−CH_2−$\underline{C}H_2$−), 38.63 (N−$\underline{C}H_3$), 51.00 (N−$\underline{C}H_2$−CH_2−CH_2−), 118.20 carbene, 119.90 carbene, 120.59, 122.18, 122.51, 123.57, 124.28, 127.88 Sacc, 128.33 Sacc, 129.42, 131.98, 132.38 Sacc, 132.93 Sacc, 136.67, 138.51, 147.02, 149.88 Sacc, 154.16, 164.18, 167.40 Sacc, 171.93 [Pd−$C_{carbene}$]. HPLC-MS (positive mode) m/z: 398.08 (M^+ − Sacc). Anal. Calcd for $C_{26}H_{26}N_4O_3PdS$: C, 53.75; H, 4.51; N, 9.64; S, 5.52. Found: C, 53.92; H, 4.65; N, 9.84; S, 5.75.

Preparation of Complex [Ag(Phthal)(SMe$_2$)]$_2$. To a 20 mL solution of Ag(CH_3COO) (500 mg, 3.0 mmol) in CH_2Cl_2 were added phthalimide (440 mg, 3 mmol) and 0.222 mL (3.0 mmol) of SMe_2. After 1 h of stirring at room temperature the solvent was partially evaporated under reduced pressure. Addition of diethyl ether afforded a white solid, which was filtered, air-dried, and recrystallized from acetone/hexane.

[Ag(Phthal)(SMe$_2$)]$_2$: 0.743g, 79%. IR (cm^{-1}): ν(Phthal) 1702, 1644, 3434, ν(SMe_2) 1052, 1034. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.86 (m, 4H Phthal); 7.75 (m, 4H Phthal); 2.18 (s, 12H SMe_2). Anal. Calcd for $C_{20}H_{20}Ag_2N_2O_4S_2$: C, 37.99; H, 3.19; N, 4.43. Found: C, 38.18; H, 3.22; N, 4.53.

Preparation of Complex [Pd(Phpy)(Bmim)(Phthal)], ***IIe.*** To a 20 mL CH_2Cl_2 solution of [Pd(Phpy)(Bmim)Br] (250 mg, 0.521 mmol) was added 165 mg (0.521 mmol) of complex [Ag(phthal)(SMe_2)]. After 1 h of stirring at room temperature a yellow solid was obtained. The solvent was then partially evaporated under reduced pressure, and slow addition of diethyl ether caused complete precipitation of a white solid, which was filtered, air-dried, and recrystallized from CH_2Cl_2/ether.

[Pd(Phpy)(Bmim)(Phthal)], ***IIe:*** 0.15 g, 52%. IR (cm^{-1}): ν(Phpy) 1605 vs, 1570 vs, 755 vs ν(Phthal) 1721s, 1643 vs, 1298s, 1127s, 849s. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 5.2 Hz, 1H^2 Phpy), 7.74 (m, 1H^5 Phpy), 7.65 (m, 2H Phthal), 7.56 (m, 1H^6 Phpy), 7.49 (m, 2H, Phthal), 7.05 (m, 1H^3 Phpy), 6.95 (d, J = 2.1 Hz, 1H carbene), 6.91 (d, J = 2.1 Hz, 1H carbene), 6.88 (m, 1H^7 Phpy), 6.11 (d, J = 7.0 Hz 1H$^{\alpha}$ Phpy), 4.67 (m, 1H N−C$\underline{H}_2$-), 4.21 (m, 1H N−C$\underline{H}_2$-), 4.10 (s, 3H N−CH_3), 1.71 (m, 2H, N−CH_2−C$\underline{H}_2$), 1.32 (m, 2H N−CH_2−CH_2−C$\underline{H}_2$−), 0.80 (t, J = 7.5 Hz, 3H, N−CH_2−CH_2−CH_2−C$\underline{H}_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.66 (N−CH_2−CH_2−CH_2−$\underline{C}H_3$), 19.80 (N−CH_2−CH_2−$\underline{C}H_2$−), 32.41 (N−CH_2−$\underline{C}H_2$−), 38.65 (N−$\underline{C}H_3$), 50.88 (N−$\underline{C}H_2$−CH_2−CH_2−), 118.21 carbene, 120.25 carbene, 120.93, 122.06, 122.19, 123.40, 123.57, 123.83 Phthal, 129.33, 131.35, 136.95, 137.55 Phthal, 138.43, 147.10, 149.59 Phthal, 164.92, 173.45 [Pd−$C_{carbene}$], 181.41 C═O. HPLC-MS (positive mode) m/z: 398.08 (M^+ − Phthal). Anal. Calcd for $C_{27}H_{26}N_4O_2Pd$: C, 59.51; H, 4.81; N, 10.28. Found: C, 59.72; H, 4.65; N, 10.36.

General Procedure for Suzuki−Miyaura Cross-Coupling of 9-Bromophenanthrene with Aryl Boronic Acids Using Pd-NHC Complex II. In a dry Schlenk tube, Pd-NHC complex **IId** solution in PhMe was taken via syringe (to obtain a 0.01 mol % catalyst concentration a stock solution of 1.0 mol % **IId** was prepared in PhMe as solvent by dissolving 5.8 mg of **IId** in 100 mL of PhMe under nitrogen in a Schlenk tube from which 1.0 mL of the solution was taken out to provide the catalyst in the desired concentration for the reaction) and was stirred under a N_2 atmosphere. To this was added 9-bromophenanthrene **III** (1.0 mmol, 0.255 g), and the resultant solution was stirred at 80 °C for 5 min. The reaction mixture was cooled, and to this was added phenylboronic acid **IVa** (1.2 mmol, 0.145 g) as well as Na_2CO_3 (3.0 mmol, 0.318 g). Finally H_2O (2 mL) was added, and the resultant mixture was stirred at 80 °C for 12 h. At the end of the reaction, solvent was removed *in vacuo*, and the resultant crude product was purified using column chromatography (hexane) to give the product **Va** in 96% yield.

*Phenylphenanthrene (**Va**):* 96%, 0.243 g. Mp: 100−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, J = 8.2 Hz, 1H), 8.77 (d, J = 8.2 Hz, 1H), 7.99−7.94 (m, 2H), 7.74−7.70 (m, 3H), 7.68−7.65 (m, 1H), 7.62−7.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 138.9, 131.7, 131.3, 130.8, 130.2, 130.1, 128.8, 128.4, 127.6, 127.5, 127.1, 127.0, 126.7, 126.6, 126.5, 123.0, 122.7. MS (EI, m/z): 254 (100). Anal. Calcd (%) for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.32; H, 5.41.

*9-(2-Naphthyl)phenanthrene (**Vb**):* 94%, 0.285 g. Mp: 141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, J = 8.2 Hz, 1H), 8.78 (d, J = 8.2 Hz, 1H), 8.06 (s, 1H), 8.01−7.93 (m, 5H), 7.82 (s, 1H), 7.72−

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7.65 (m, 4H), 7.60−7.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.5, 133.6, 132.8, 131.7, 131.4, 130.8, 130.2, 128.8, 128.6, 128.2, 128.0, 127.9, 127.8, 127.1, 127.0, 126.8, 126.7, 126.6, 126.5, 126.2, 123.1, 122.7. MS (EI, *m*/*z*): 304 (100). Anal. Calcd (%) for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.63; H, 5.26.

*5-(Phenanthren-9-yl)benzo[d][1,3]dioxole (**Vc**):* 93%, 0.277 g. Mp: 97−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.2 Hz, 1H), 8.75 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.73−7.64 (m, 4H), 7.62−7.59 (m, 1H), 7.11−7.01 (m, 3H), 6.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 147.1, 138.4, 134.7, 131.6, 131.3, 130.7, 130.0, 128.7, 127.6, 127.0, 126.9, 126.7, 126.6, 126.5, 123.5, 123.0, 122.6, 110.8, 108.4. MS (EI, *m*/*z*): 298 (100). Anal. Calcd (%) for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.37; H, 4.59.

*9-(3,5-Dimethylphenyl)phenanthrene (**Vd**):* 98%, 0.276 g. Mp: 154−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.3 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 8.04−8.01 (m, 2H), 7.94−7.92 (m, 1H), 7.74−7.57 (m, 5H), 7.24 (d, *J* = 5.0 Hz, 2H), 7.16 (s, 1H), 2.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 139.2, 137.9, 131.7, 131.4, 130.7, 130.0, 129.1, 128.7, 128.0, 127.4, 127.2, 126.9, 126.6, 126.5, 123.0, 122.6, 21.5. MS (EI, *m*/*z*): 282 (100). Anal. Calcd (%) for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.47; H, 6.48.

*9-(4-Phenoxyphenyl)phenanthrene (**Ve**):* 96%, 0.332 g. Mp: 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.2 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.73−7.53 (m, 7H), 7.45−7.42 (m, 1H), 7.21−7.15 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0. 156.7, 138.0, 135.5, 131.5, 131.3, 131.1, 130.6, 129.8, 129.7, 128.5, 127.5, 126.7, 126.5, 126.4, 126.3, 123.4, 122.9, 122.4, 119.1, 118.4. MS (EI, *m*/*z*): 346 (100). Anal. Calcd (%) for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.21; H, 5.28.

*9-(4-Methylphenyl)phenanthrene (**Vf**):* 94%, 0.251 g. Mp: 90−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 7.7 Hz, 1H), 8.75 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.92 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.70−7.68 (m, 3H), 7.66−7.66 (m, 1H), 7.58−7.55 (m, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 137.8, 137.0, 131.6, 131.2, 130.6, 129.8, 128.9, 128.5, 127.3, 126.9, 126.7, 126.4, 126.3, 122.8, 122.4, 21.2. MS (EI, *m*/*z*): 268 (100). Anal. Calcd (%) for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.84; H, 5.83.

*9-(4-Biphenyl)phenanthrene (**Vg**):* 79%, 0.260 g. Mp: 215−218 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.3 Hz, 1H), 8.76 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.3 Hz, 1H), 7.93 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.78−7.63 (m, 10H), 7.61−7.57 (m, 1H), 7.54−7.50 (m, 2H), 7.43−7.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 140.4, 139.9, 138.5, 131.7, 131.2, 130.8, 130.6, 130.1, 129.0, 128.8, 127.7, 127.5, 127.3, 127.2, 127.1, 127.0, 126.8, 126.7, 126.6, 123.1, 122.7. MS (EI, *m*/*z*): 330 (100). Anal. Calcd (%) for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.39; H, 5.33.

*9-(3-Methoxyphenyl)phenanthrene (**Vh**):* 92%, 0.269 g. Mp: 92−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.71−7.67 (m, 3H), 7.65−7.61 (m, 1H), 7.57−7.54 (m, 1H), 7.46−7.43 (m, 1H), 7.16−7.11 (m, 2H), 7.04−7.01 (m, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 142.3, 138.8, 131.6, 131.2, 130.7, 130.1, 129.4, 128.8, 127.5, 127.1, 127.0, 126.8, 126.7, 126.6, 123.0, 122.7, 122.6, 115.7, 113.1, 55.5. MS (EI, *m*/*z*): 284 (100). Anal. Calcd (%) for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.61; H, 5.49.

*9-(4-Methoxyphenyl)phenanthrene (**Vi**):* 78%, 0.221 g. Mp: 157−159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.3 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.70−7.62 (m, 4H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.52−7.50 (m, 2H), 7.10−7.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 138.5, 133.3, 131.8, 131.5, 131.3, 130.8, 130.0, 128.7, 127.6, 127.1, 126.9, 126.6, 126.5, 123.0, 122.7, 113.9, 55.5. MS (EI, *m*/*z*): 284 (100). Anal. Calcd (%) for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.53; H, 5.46.

*9-(4-Thiomethylphenyl)phenanthrene (**Vj**):* 86%, 0.257 g. Mp: 154−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.92−7.90 (m, 1H), 7.70−7.67 (m, 3H), 7.64−7.62 (m, 1H), 7.57−7.54 (m, 1H), 7.51−7.49 (m, 2H), 7.42−7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 137.8, 137.7, 131.7, 131.2, 130.8, 130.6, 130.1, 128.8, 127.6, 127.0, 126.9, 126.8, 126.7, 126.6, 126.5, 123.1, 122.7, 16.0. MS (EI, *m*/*z*): 300 (100). Anal. Calcd (%) for $C_{21}H_{16}S$: C, 83.96; H, 5.37; S, 10.67. Found: C, 83.74; H, 5.23.

*9-(3-Nitrophenyl)phenanthrene (**Vk**):* 49%, 0.146 g. Mp: 122−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.4 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 8.44 (s, 1H), 8.34−8.32 (m, 1H), 7.93−7.91 (m, 1H), 7.89−7.87 (m, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.74−7.64 (m, 5H), 7.59−7.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 142.6, 136.3, 136.2, 131.3, 130.9, 130.4, 129.4, 129.0, 128.4, 127.4, 127.3, 127.1, 127.0, 126.2, 125.0, 123.3, 122.8, 122.6. MS (EI, *m*/*z*): 299 (100). Anal. Calcd (%) for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.02; H, 4.43; N, 4.75.

*9-(4-Fluorophenyl)phenanthrene (**Vl**):* 88%, 0.238 g. Mp: 148−150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.2 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H), 7.93−7.91 (m, 1H), 7.74−7.65 (m, 4H), 7.61−7.53 (m, 3H), 7.28−7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 161.5, 137.8, 136.8, 131.8, 131.7, 131.6, 131.2, 130.8, 130.1, 128.8, 127.8, 127.1, 126.9, 126.8, 126.7, 126.6, 123.1, 122.7, 115.5, 115.3. MS (EI, *m*/*z*): 272 (100). Anal. Calcd (%) for $C_{20}H_{13}F$: C, 88.21; H, 4.81. Found: C, 88.04; H, 4.65.

Scale-up Studies for Suzuki−Miyaura Cross-Coupling of 9-Bromophenanthrene with Aryl Boronic Acids Using Pd-NHC Complex IId. In a dry 50 mL Schlenk tube, a Pd-NHC complex **IId** solution in PhMe was taken via syringe (to obtain a 0.005 mol % catalyst concentration, a stock solution of 5.0 mol % **IId** was prepared in PhMe as solvent by dissolving 29 mg of **IId** in 100 mL of PhMe under nitrogen in a Schlenk tube, from which 5.0 mL of the solution was taken out and further diluted to 50 mL using dry PhMe under a nitrogen atmosphere; 5.0 mL of this stock solution provides the catalyst in the desired concentration for the 5.0 mmol reaction) and was stirred under a N_2 atmosphere. To this was added 9-bromophenanthrene **III** (5.0 mmol, 0.1.275 g), and the resultant solution was stirred at 80 °C for 5 min. The reaction mixture was cooled, and to this was added phenylboronic acid **IVa** (6.0 mmol, 0.725 g) as well as Na_2CO_3 (15.0 mmol, 1.59 g). Finally H_2O (10 mL) was added, and the resultant mixture was stirred at 80 °C for 12 h. At the end of the reaction, solvent was removed *in vacuo*, and the resultant crude product was purified using column chromatography (hexane) to give the product **Va** in 80% yield.

Crystal Structure Determination of [Pd(Bzpy)(Bmim)(Sacc)], Id, [Pd(Phpy)(Bmim)Br], IIb, [Pd(Phpy)(Bmim)(Sacc)], IId, and [Pd(Phpy)(Bmim)(Phthal)], IIe. Data collection for **Id**, **IIb**, **IId**, and **IIe** was performed at 100 K on a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 4.5 cm. Diffraction data were collected based on a ω scan run. A total of 2524 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package[42] and corrected for absorption with SADABS.[43] The structures were solved by direct methods[44] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms (Table 5 included as Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The X-ray coordinates (cif files) are available for complexes **Id**, **IIb**, **IId**, and **IIe**. Table 5 with crystal data and structure refinement for complexes **Id**, **IIb**, **IId**, and **IIe** is also included as Supporting Information. ^{1}H and ^{13}C NMR spectra for all the 9-arylphenanthrenes are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jose.serrano@upct.es.
*E-mail: ar.kapdi@ictmumbai.edu.in.

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Notes

The authors declare no competing financial interest.

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