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# Phosphorus-directed Rhodium-Catalyzed C–H Arylation of 1-Pyrenylphosphines Selective at the *K*-Region

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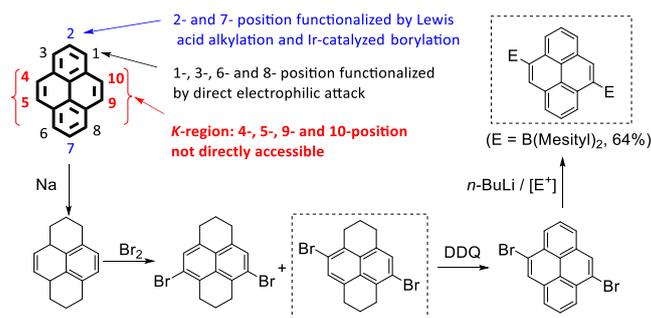
**Abstract.** C–H arylation of 1-pyrenylphosphine derivatives catalyzed by rhodium and directed by a diphenylphosphino group is selectively achieved at the *K*-region, *i.e.* 4-, 5-, 9-, or 10-position of the pyrene moiety. This *peri* C–H activation/arylation of pyrenes using (hetero)aryl bromide coupling partners tolerates both electron-donating and electron-withdrawing groups on the arene, and provides isolated yields of products between 25% to 90%, including from bulky polyaromatic bromoarene substrates. We achieved investigations directed at the formation and reactivity of pertinent intermediate species in this C–H arylation reaction. The P-ligand coordination at rhodium was established using <sup>31</sup>P NMR and XRD analysis, and we isolated five-membered rhodacycles as intermediates to the directed C–H functionalization. The data

obtained overall supported the occurrence of a cationic rhodium catalytic process. We further described the access to a large class of pyrenylphosphine ligands and their selenated derivatives. Phosphine selenation allows to rapidly estimate from <sup>1</sup>J<sub>P–Se</sub> values the basic character of the ligand in the perspective of their use as for coordination. Accordingly, linear P-coordinated Au(I) gold complexes were isolated, in addition to the variously coordinated Rh(III) complexes. The present methodology significantly extends the scope of polyaromatics that are functionalizable at the *K*-Region by direct C–H functionalization, beyond smaller-sized naphthalenes and aminopyrenes.

**Keywords:** PAH; Phosphorus; Rhodium; C–H Activation; Arylation

## Introduction

Polycyclic aromatic hydrocarbons (PAH) are building blocks useful in organic electronic and medicine, with applications within semiconductor devices, luminescence probes, and as cytotoxic agents.<sup>[1]</sup> The incorporation of main group elements (like B, N, Si, P, *etc.*) into these  $\pi$ -conjugated frameworks is a valuable strategy to extend their electronic and photophysical properties.<sup>[2]</sup> Especially, PAH which contain phosphorus atoms are valuable scaffold with regards to their wide applications as pharmaceuticals,<sup>[3]</sup> in ligands design for catalysis<sup>[4]</sup> and in material sciences.<sup>[5]</sup> In the synthesis of pyrene derivatives, generally 1-, 3-, 6- and 8-positions are substituted by using electrophilic reagents, such as in most common halogenation reactions (Scheme 1).



**Scheme 1.** Functionalization of pyrene derivatives by classical approaches: non-selective multistep halogenation/metalation reactions for accessing *K*-region.

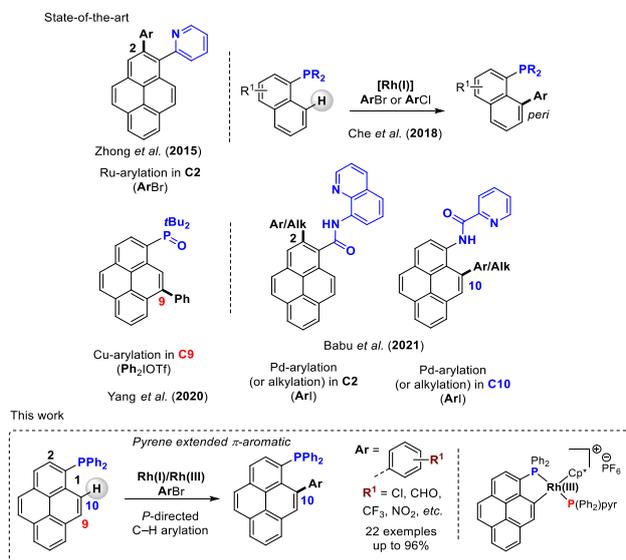
Alternatively, alkylation by aluminum reagents,<sup>[6]</sup> reactions with triflic acid,<sup>[7]</sup> and iridium-catalyzed borylation<sup>[8]</sup> occurs at 2- or 7-positions (Scheme 1). Conversely, the synthesis of pyrene derivatives substituted at the *K*-region (4-, 5-, 9- and 10-positions) usually requires tedious multistep metalation and halogenation procedures, which results in general in low overall yields.<sup>[9]</sup> For example, the preparation of 4,9-borylated pyrene from pyrene, is achieved in four

steps by sodium reduction, electrophilic bromination at the remaining  $sp^2$ -C  $K$ -sites, re-oxidation in the presence of DDQ, and electrophilic borylation via bromide/lithium exchange (Scheme 1). The bromination step also suffers from selectivity troubles.

On the other hand, selective direct metal-catalyzed C–H bond activation by transition metals opens more sustainable synthetic routes to reach extended  $\pi$ -systems and heteroatom-substituted derivatives.<sup>[10]</sup>

Accordingly, Zhong *et al.* reported the first example of  $N$ -directed arylation of pyrenes by using a ruthenium-catalyzed C–H activation, specifically selective at 2- (or 7)-position (Scheme 2).<sup>[11]</sup> More recently, Babu *et al.* described the selective arylation and alkylation in C2 and C10 positions of  $N$ -containing pyrene derivatives by palladium-catalyzed C–H functionalization using appropriate bidentate directing groups such as picolinamide and 8-quinoline carboxamide, respectively.<sup>[12]</sup> Yang *et al.* developed a copper-catalyzed (O)P-directed C–H arylation of PAH using hypervalent aryl iodanes,<sup>[13]</sup> illustrated in a single example to occur for a pyrene derivative in  $\gamma$ -position of the (O)P-directing group (C9–H arylation in  $K$ -region).

Interestingly, Yu and Che *et al.* employed a pendant phosphine as the directing group for arylation at the *peri*-position of naphthalene substrates, synthesizing thus in a single step reaction a class of bulky phosphine ligands structurally related to useful Buchwald biarylphosphines. They used with success a dimeric  $[\text{Rh}^{\text{I}}\text{Cl}_2(\text{COD})]_2$  precatalyst (Scheme 2).<sup>[14]</sup> The phosphine-directed functionalization proceeded in the presence of bromoarenes and chloroarenes as the coupling partner, with  $\text{KO}t\text{Bu}$  as the base in toluene at 110 °C and 150 °C, respectively.



**Scheme 2.** C–H functionalization and selectivity in extended  $\pi$ -aromatics by  $N$ - or  $P$ -ligand-directed C–H activation in transition metal catalysis (Ru, Rh, Cu, Pd).

The approach by Yu and Che was applied to anthracenyl moieties for yielding the corresponding PAH diphenylphosphine, but was not applied to more challenging extended  $\pi$ -aromatic scaffolds like pyrene derivatives.<sup>[1]</sup> This extension was potentially very

attractive since pyrenes are used in many instance as ligands and linkers for heterogenisation of catalytic systems because of their stacking affinity with current important materials like CNTs and graphene derivatives.<sup>[15]</sup> We disclose herein practical conditions for the selective rhodium-catalyzed direct C–H functionalization of pyrenes in C10-position using a preserved  $\text{Ph}_2\text{P}$ - directing group (Scheme 2, bottom). In addition, we investigated the formation and isolation of pertinent Rh species in this C–H arylation reaction by  $^{31}\text{P}$  NMR, and X-ray diffraction analysis. The data we collected overall support a cationic rhodium catalytic process for this C–H arylation of extended  $\pi$ -aromatic scaffold.

## Results and Discussion

*Peri*-functionalization of small size naphthalene aromatics,<sup>[14,16]</sup> and other  $P$ -directed functionalization studies,<sup>[17-18]</sup> oriented the present rhodium-catalyzed conditions that we optimized to selectively perform the functionalization on the  $K$ -region on pyrene scaffold. We first explored in details the Rh-catalyzed direct C–H<sup>10</sup> arylation of 1-diphenylphosphinopyrene **1** using 4-methoxybenzene bromide as coupling partner and various rhodium precatalysts, bases and solvent conditions (Table 1, see full optimization details in SI). The C–H bond activation at *peri*-position efficiently occurred in the presence of the precursors  $[\text{Rh}^{\text{I}}\text{Cl}(\text{COD})]_2$  dimer, the cationic monomer  $[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$ , and even starting from the high-oxidation state  $[\text{Rh}^{\text{III}}\text{Cl}_2\text{Cp}^*]_2$  (all in 5 mol% regarding the pyrene substrate).  $\text{KO}t\text{Bu}$  was used as the base in refluxing toluene to produce in excellent yield the arylated pyrenylphosphine **2** (up to 86%, Table 1, entries 1-3).

**Table 1.** Optimization of  $P$ -directed Rh-catalyzed arylation using 1-diphenylphosphine pyrene (**1**) and 4-bromoanisole as coupling partners.<sup>a)</sup>

Entry	[Rh] (5 mol%)	Base (3 equiv)	Solvent (0.16 M)	Conv. (%)	<b>2</b> (%)
1 <sup>[14]</sup>	$[\text{Rh}^{\text{I}}\text{Cl}(\text{COD})]_2$	$\text{KO}t\text{Bu}$	toluene	98	84
2	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{KO}t\text{Bu}$	toluene	98	86
3	$[\text{Rh}^{\text{III}}\text{Cl}_2(\text{Cp}^*)]_2$	$\text{KO}t\text{Bu}$	toluene	98	81
4 <sup>b)</sup>	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{KO}t\text{Bu}$	toluene	42	36
5 <sup>c)</sup>	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{KO}t\text{Bu}$	toluene	38	38
6	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{NaO}t\text{Bu}$	toluene	75	72
7	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{KOAc}$	toluene	22	22
8	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{K}_3\text{PO}_4$	toluene	99	87
9	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{K}_3\text{PO}_4$	1,4-dioxane	99	87
10	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{K}_3\text{PO}_4$	$\text{PhCF}_3$	99	90
11	$[\text{Rh}^{\text{I}}(\text{COD})_2]\text{BF}_4$	$\text{K}_3\text{PO}_4$	CPME	99	83

<sup>a)</sup> Conditions: 1-diphenylphosphine pyrene (0.5 mmol, 1 equiv), 4-methoxybenzene bromide (1.5 equiv), [Rh] precatalyst (5 mol%), base (3.0 equiv), solvent (0.16 M) at reflux, 18 h under argon. <sup>1</sup>H NMR yield.  $\text{PhCF}_3$ : trifluoromethylbenzene; CPME: methoxycyclopentane. <sup>b)</sup>  $\text{AgSbF}_6$  (20 mol%). <sup>c)</sup>  $\text{KPF}_6$  (20 mol%).

We observed that the addition of  $\text{AgSbF}_6$  and  $\text{KPF}_6$  salts as chloride abstractors dramatically affects the reaction, with only about 40% yield of **2** obtained

under these conditions (Table 1, entries 4-5). Both KO<sup>t</sup>Bu and K<sub>3</sub>PO<sub>4</sub> were found suitable as base, while conversely the use of NaO<sup>t</sup>Bu and KOAc slightly lowered the conversion in **2** (Table 1, entries 6-8). The solvents tested, toluene, 1,4-dioxane, trifluoromethylbenzene and methoxycyclopentane (CPME), showed little influence under the optimized conditions (Table 1, entries 8-11). Thus, in the presence of the monomeric cationic [Rh<sup>I</sup>(COD)<sub>2</sub>]BF<sub>4</sub> at 5 mol%, using K<sub>3</sub>PO<sub>4</sub> as the base, in refluxing PhCF<sub>3</sub> (102 °C), arylpyrenylphosphine **2** was isolated in 80% yield (Table 1, entry 10). Under these conditions, the nature of the aryl halide reagent deeply influences the conversion. Indeed, using 4-methoxybenzene chloride or the iodide analogue as coupling partners provided significantly lower yield of **2**, *i.e.* 37% and 79% yield respectively (Scheme 3).

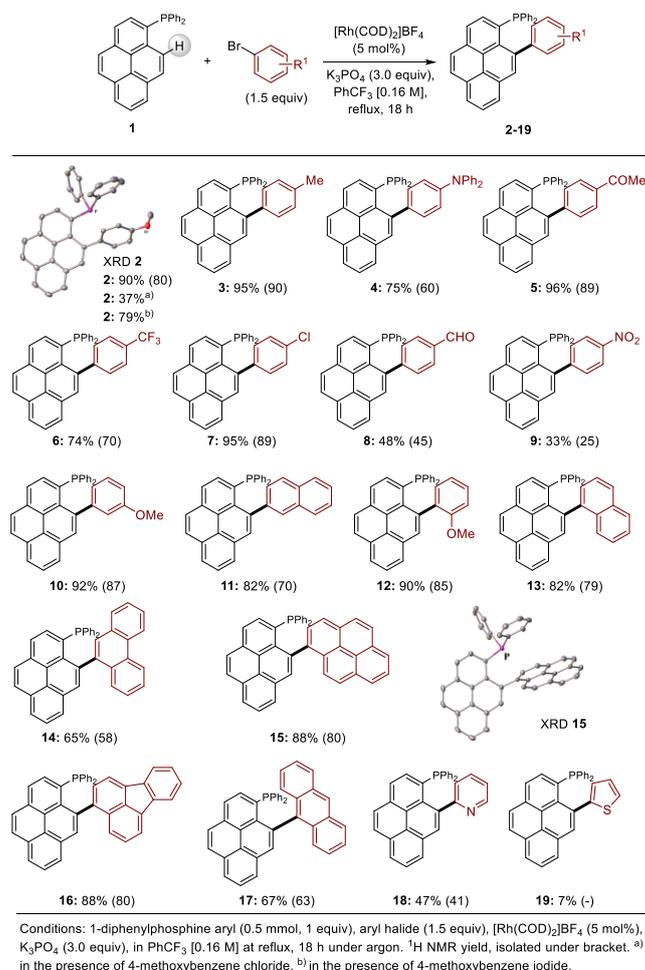
We further investigated the scope of functionalized (hetero)aryl bromides as coupling partners in the C–H arylation of 1-diphenylphosphine pyrene under the optimized conditions (Scheme 3). The formation of the aryl pyrenylphosphines **3** and **4** bearing in *para*-position of the aryl electron-donating methyl and diphenylamino groups, respectively, was achieved in 90 and 60% isolated yields, respectively. 4-Acetyl, 4-trifluoromethyl and 4-chloro groups were also tolerated functionalization in the bromoarene coupling partners, giving, respectively, the polyaromatic phosphines **5** (89%), **6** (70%) and **7** (89%) in isolated yields.

The presence of formyl and nitro groups in *para*-position of the bromide partner limited the coupling reaction, and **8** and **9** were isolated in somehow lower 45% and 25% yield, respectively. These polyaromatic phosphines were found to be more sensitive to oxidation under air, even in the solid state.

Using as coupling partners *meta*-substituted aryl bromides bearing a methoxy or a naphthyl group yielded **10** (87%) and **11** (70%) in isolated yields, respectively.

Bulky *ortho*-functionalized bromoarenes were equally tolerated, and 2-methoxyphenyl bromide coupling furnished **12** in a high 85% isolated yield. The steric congestion from polyaromatic bromides fortunately did not affected much the reaction, and in the presence of 2-naphthyl, 9-phenanthrenyl, 1-pyrenyl, 3-fluoranthenyl and 9-anthracenyl groups the corresponding coupling products **13** (79%), **14** (58%), **15** (80%), **16** (80%) and **17** (63%), respectively, were obtained in fairly good to excellent isolated yields.

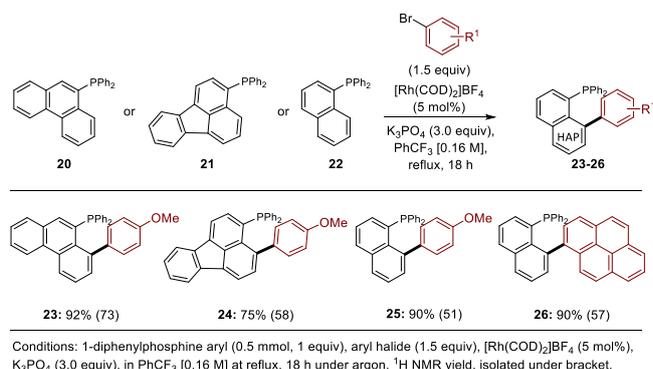
Concerning more electron-poor heteroaryl coupling partners, 2-pyridinyl bromide led to a moderate yield of 41% in **18** and 2-thienyl bromide gave a modest 7% yield in **19**. We tentatively attributed this limitation to a concurrent coordination of heteroaryl groups at the rhodium center.



**Scheme 3.** Selective arylation of *P*-directing 1-diphenylphosphine pyrene from functional aryl bromides.

The X-ray diffraction structure of the polyaromatic phosphines **2** and **15** (Scheme 3) confirmed the selectivity of the C–H bond arylation at the 10-position of the pyrene core. In <sup>1</sup>H NMR a singlet is observed at 7.96 ppm for the β-H<sup>9</sup> in **2**. Consistently, a similar <sup>1</sup>H NMR pattern was observed for all the 10-arylated pyrenylphosphines (**2-19**).

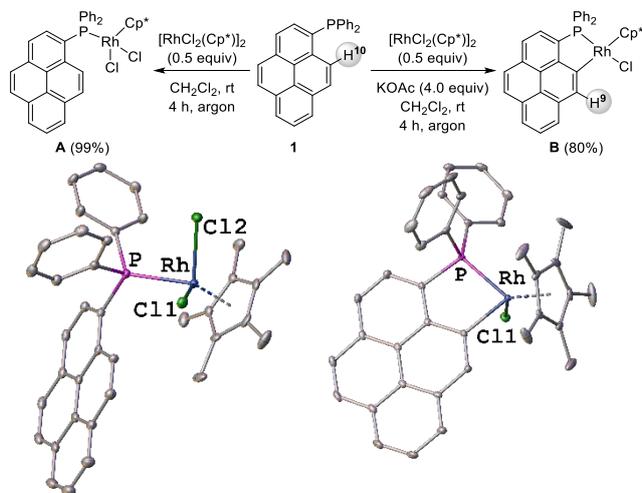
Other polyaromatic hydrocarbon diphosphines were tested under our optimized conditions (Scheme 4). Phenanthryl, fluoranthenyl and naphthyl phosphines gave isolated yield of 73%, 58% and 51% for **23**, **24** and **25** respectively in the presence of electron-rich 4-bromoanisole, and 57% for **26** using 1-bromopyrene as coupling partner.



**Scheme 4.** Selective arylation of other polyaromatic hydrocarbon diphosphines.

The similar efficiency of Rh(I) and Rh(III) precatalysts encouraged us to synthesize the pertinent Rh(III) complexes **A-C** (Scheme 5 and 6), which might be key intermediate of the catalytic process. We quantitatively synthesized the complex **A** (Scheme 5, top left) by reacting **1** with 0.5 equiv of the dimer complex  $[\text{Rh}^{\text{III}}\text{Cl}_2(\text{Cp}^*)]_2$  in  $\text{CH}_2\text{Cl}_2$  at room temperature. The chloride-bridged dimer breaks-up and rearranges from phosphorus coordination to the rhodium center in **A**. This was confirmed in the solid-state by XRD analysis (Scheme 5, bottom left,  $d$  P–Rh = 2.3629(9) Å), and in solution by  $^{31}\text{P}$  NMR with a singlet shift from –13.65 ppm in **1** to a doublet at 32.3 ppm in **A** ( $^1J_{\text{PRh}} = 145$  Hz). The Rh(III) metallacycle **B** (Scheme 6, top right) formally results from the selective C–H activation at the 10-position of pyrene in **A**. In the presence of KOAc used as the base, **B** was isolated pure in 80% yield.

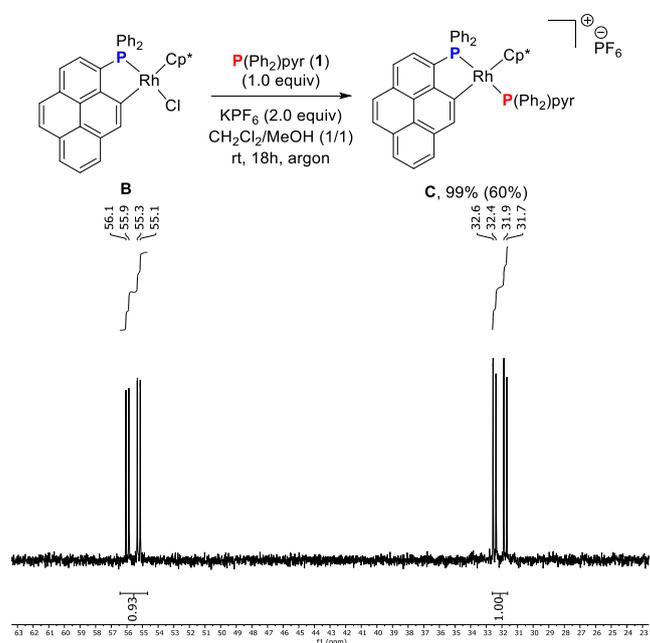
Single crystals XRD analysis of **B** (Scheme 5, bottom right) confirmed the five-membered ring formation with bond distances  $d$  C10–Rh = 2.063(2) Å and  $d$  P–Rh = 2.2630(5) Å.  $^{31}\text{P}$  NMR in solution confirmed the Rh (P, C)-chelation with a shift from –13.65 ppm in **1** to 66.4 ppm in **B** ( $^1J_{\text{PRh}} = 161$  Hz), and in  $^1\text{H}$  NMR with a singlet observed at 8.40 ppm for the  $\beta$ -H<sup>9</sup>.



**Scheme 5.** Synthesis of rhodium complex **A** (top left) and rhodium metallacycle **B** (top right). Molecular structures of complex **A** (bottom left) and complex **B** (bottom right);

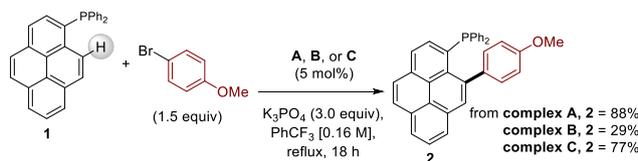
thermal ellipsoids at 30% probabilities. H atoms, two  $\text{CH}_2\text{Cl}_2$  for **A** and one  $\text{CH}_2\text{Cl}_2$  for **B** are omitted for clarity.

Because of the low metal:substrate ratio (1:20) which exists under the genuine catalytic conditions, we also tried to synthesize Rh complexes incorporating a second phosphine ligand, as a pertinent potential catalytic intermediate. From the precursor **B**, the Rh(III) cationic species **C** is easily formed and stabilized by a second P-coordinated pyrenylphosphine (Scheme 6). The reaction takes place in a mixture of  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1/1) using  $\text{KPF}_6$  as chloride abstractor. The complex **C** quantitatively formed and could be isolated pure in 60% yield by crystallization in  $\text{CH}_2\text{Cl}_2/\text{heptane}$ . We did not get single crystals suitable for XRD, but the  $^{31}\text{P}$  NMR spectra of **C** consistently displayed two signals as doublet of doublet at 55.6 ppm (rhodacycle phosphine,  $^1J_{\text{PRh}} = 140$  Hz and  $^2J_{\text{PP}'} = 38$  Hz) and 32.0 ppm ( $^1J_{\text{PRh}} = 148$  Hz and  $^2J_{\text{PP}'} = 38$  Hz).



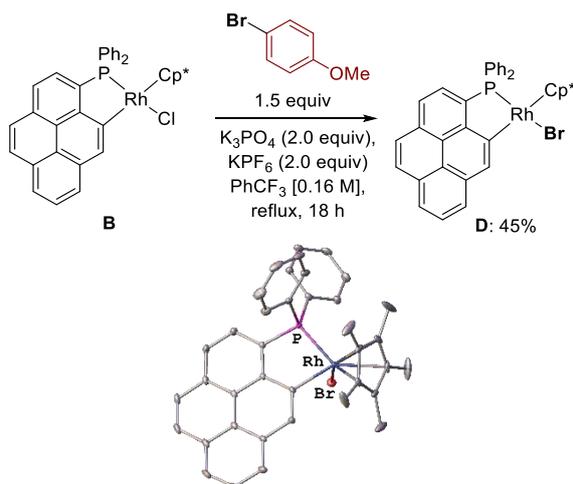
**Scheme 6.** Synthesis of the Rh(III) cationic metallacycle **C** and its  $^{31}\text{P}$  NMR spectra ( $\text{CDCl}_3$ , 202 MHz).

The complexes **A-C** were tested as catalyst (5 mol%) in the arylation reaction by using 1-diphenyl pyrene and 4-bromoanisole under the general conditions for coupling (Scheme 7). The Rh(III) nonmetallacycle complex **A** and the cationic metallacycle **C** achieved similar good yield (88% and 77%, respectively), while the metallacycle **B** provided a lower 29% yield. This suggests that **B**, and possibly neutral highly stable Rh(III) complexes in general, might be pitfall out-of-cycle resting states in the catalytic process. Conversely, complexes of type **A** still conserves the opportunity to form reactive Rh(III) cationic species like **C**.



**Scheme 7.** Peri-C–H arylation of 1-diphenylphosphine pyrene with 4-bromoanisole using preformed Rh(III) complexes **A–C**.

To better assess this proposal, the neutral Rh(III) metallacycle **B** was reacted with 1.5 equiv of 4-bromoanisole in both the presence of  $K_3PO_4$  and  $KPF_6$  (Scheme 8, top). After 18 h at reflux of  $PhCF_3$ , no evolution towards the expected coupling product **2** was observed, nor the formation of cationic rhodium species, but instead the formation of a new brominated Rh(III) neutral metallacycle complex **D** in 45% yield ( $^{31}P$  NMR 65.3 ppm,  $^1J_{PRh} = 162$  Hz) was achieved. In the solid state, the single crystals XRD analysis of **D** (Scheme 8, bottom) confirmed the conservation of the metallacycle structure with  $d$  C11–Rh = 2.065(2) Å and  $d$  P–Rh = 2.2631(6) Å (similar to values for **B**). In the structure, the chlorine atom has been replaced by a bromine with a  $d$  Rh–Br = 2.5222(4) Å ( $d$  Rh–Cl = 2.4025(5) Å for **B**).

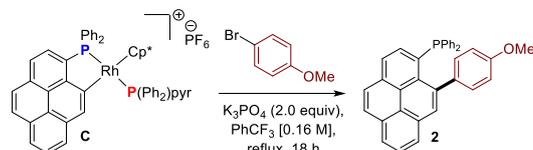


**Scheme 8.** Up: Stoichiometric reaction from metallacycle **B**. Bottom: molecular structure of complex **D**, thermal ellipsoids at 30% probabilities. H atoms, one  $CH_2Cl_2$  for **D** are omitted for clarity.

From **B** in the absence of  $KPF_6$  salt and base, no reaction occurred, while the dibrominated complex **A**<sub>2</sub> (analogous to **A**) was formed in 58% in the presence of  $K_3PO_4$  only. The lack of reactivity of complex **B** (and the formation of **D**) strongly suggests that the combination of both preformed **A** and the early presence of the base ( $K_3PO_4$ ) is an efficient way to form reactive cationic Rh(III) species, and avoid pitfall resting-states as neutral very stable Rh(III) metallacycle.

Conversely, the same reaction from the cationic complex **C** (Scheme 9), involving a direct addition of 1.5 equivalents of 4-bromoanisole, leads to the formation in 10% of the expected coupling product **2** (Table 2, line 1), supporting **C** as a pertinent catalytic intermediate. The formation of the expected

pyrenylphosphine **2** increased to 45% yield with an excess of 10 equiv of the arylated bromide (line 2). The addition of a halide abstractor (2 equiv of  $KPF_6$ , line 3) further increased this yield, and limited the formation of unidentified products.

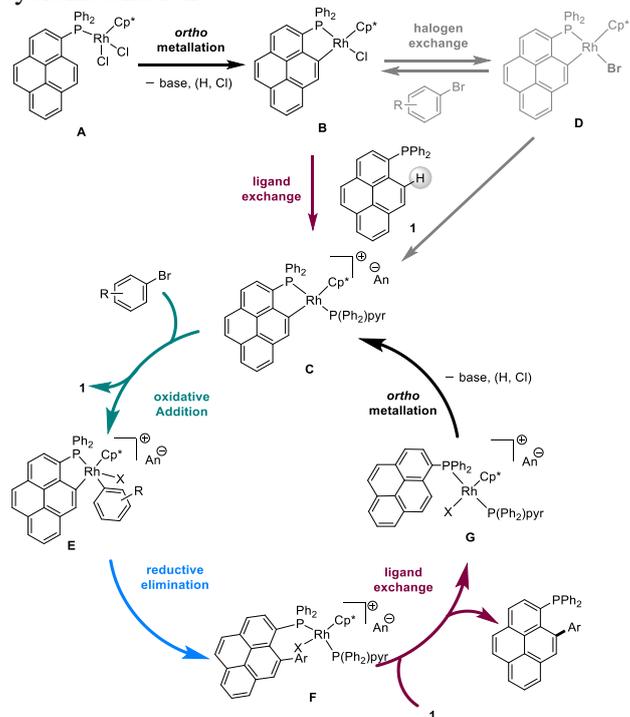


**Scheme 9.** Formation of **2** from 4-bromoanisole using the preformed Rh(III) cationic complex **C**.

4-bromoanisole added	<b>2</b>	<b>A</b> <sub>2</sub>	<b>C</b>	<b>D</b>	others <sup>b)</sup>
1.5 equiv.	10	42	16	18	14
10 equiv.	45	5	0	29	21
10 equiv. <sup>a)</sup>	57	2	0	30	11

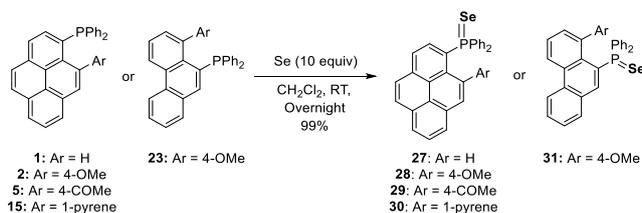
**A**<sub>2</sub> is  $[Rh^{III}Br_2(Cp^*)(1)]$ . <sup>a)</sup> Added  $KPF_6$  (2.0 equiv.); <sup>b)</sup> Unidentified products.

Based on these results, a tentative mechanism of the rhodium-catalyzed 10-arylation of PAH is proposed in Scheme 10. The *ortho*-metallation occurs from the complex **A** to **B** by a concerted metallation-deprotonation assisted by the base, which further leads to the formation of the active cationic species **C** stabilized by a second phosphine ligand. The oxidative addition of aryl bromide on **C** may form **E**,<sup>ACS Catal.</sup> 2018, 8, 242–257 which may give **F** by reductive elimination/C–C bond formation. The desired coupling product is released for a sterically less hindered non-arylated phosphine ligand, forming **G** that is ready for further cyclometallation.



**Scheme 10.** Catalytic cycle proposal for rhodium 10-arylation of polyaromatic phosphines.

We examined the impact that has the introduction of proximate aryl moieties on the Lewis basicity of the phosphino groups. This is achieved by phosphorus selenation and measurement of the  $^1J_{\text{P}=\text{Se}}$  spin-spin coupling constant (SSCC).<sup>[19,20]</sup> Quantitative selenation of the phosphorus is achieved from excess of Se powder in dichloromethane (Scheme 11, Table 2). We selected a complementary set of arylated-pyrenylphosphines which incorporate either electron-donating or electron-withdrawing group at the *peri*-aryl moiety: the compounds **2** bearing a OMe group, **5** bearing a COMe group, and **15** bearing another 1-pyrenyl moiety. The phenanthryl diphosphines **23** was also examined. The  $^{31}\text{P}$  NMR spectroscopy data for these compounds and their corresponding selenide derivatives are summarized in Table 2. As a benchmark, the SSCC  $^1J_{\text{P,Se}}$  value for triphenylphosphine selenide  $\text{Se}=\text{PPh}_3$  in  $\text{CDCl}_3$  is 730 Hz, which is higher than the SSCC for selenated-1-diphenylphosphine-pyrene  $\text{Se}=\mathbf{1}$   $^1J_{\text{P,Se}} = 722$  Hz, indicating that the phosphino group in **1** is slightly more electron-donating.<sup>[21]</sup> However, pure donating effects are strongly balanced by the functionalization at the  $\beta$ -position, as suggested by the values of SSCCs  $^1J_{\text{P,Se}}$  for **2**, **5**, **15** and **23** which ranges from 735 to 750 Hz. These clearly indicates less basic phosphines than **1**, with thus lower electron-transfer to phosphorus. This would be consistent with a better resistance to oxidation (more stable P-ligands).



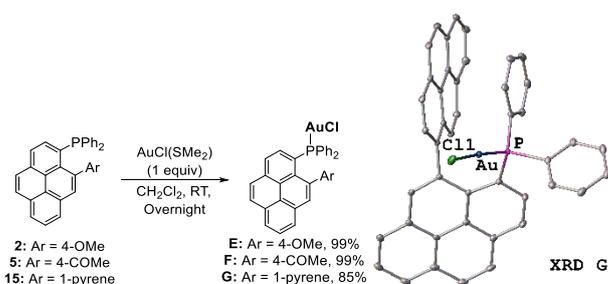
**Scheme 11.** Selenation of 10-arylated pyrene phosphines **1**, **2**, **5**, **15** and **23**.

We achieved the complexation of the bulky polyaromatic phosphines **2**, **5** and **15** to gold(I)chloride, illustrating thus the linear ligand property with Au(I) of this class of pyrenyl-based phosphines (Scheme 12, Table 2).<sup>[22]</sup>

**Table 2**  $^{31}\text{P}$  NMR data ( $\text{CDCl}_3$ , 202 MHz) for polyaromatic phosphines **1**, **2**, **5**, **15**, **23** and their corresponding selenium products and complexes with Au(I)Cl.<sup>a)</sup>

Ligand	$^{31}\text{P}$ (ppm)	$^{31}\text{P}=\text{Se}$ (ppm)	SSCC $^1J_{\text{P,Se}}$ (Hz)	Au(I) $^1J_{\text{Au-P}}$ (ppm)
<b>1</b>	-13.8	<b>27</b> : 31.7	722	-
<b>2</b>	-8.1	<b>28</b> : 38.8	750	<b>E</b> : 30.2
<b>5</b>	-9.2	<b>29</b> : 38.7	749	<b>F</b> : 34.8
<b>15</b>	-9.5	<b>30</b> : 38.4	735	<b>G</b> : 31.0
<b>23</b>	-6.8	<b>31</b> : 39.5	746	-

<sup>a)</sup> Benchmark SSCC  $^1J_{\text{P,Se}}$  value for  $(\text{Se})\text{PPh}_3 = 730$  Hz;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz) for  $[(\text{Ph}_3\text{P})\text{AuCl}] = 57.1$  ppm.<sup>[23]</sup> The coordination to gold was achieved by reacting the ligand with  $[\text{AuCl}(\text{SMe}_2)]$  in dichloromethane (Scheme 12).



**Scheme 12.** Au(I)Cl complexes **E**, **F** and **G** stabilized by pyrenylphosphines **2**, **5** and **15**, respectively. Molecular structure of complex **G** (thermal ellipsoids at 30% probabilities, H atoms and one  $\text{CH}_2\text{Cl}_2$  are omitted for clarity).

For pyrenylphosphines **2** and **5**, the reaction quantitatively leads to complexes **E** and **F**, respectively, and the complex **G** was obtained in 85% isolated yield by crystallization in a dichloromethane/heptane mixture. The single crystal XRD structure of **G**, beside a classical linear coordination of gold, revealed the conservation of phenyl/pyrenyl stacking interactions already evidenced from XRD of **15**.

## Conclusion

Overall, we report practical conditions for the efficient *peri*-functionalization of topical  $\pi$ -extended 1-pyrenylphosphine catalyzed by a cationic Rh(III) C-H arylation strategy. The arylation takes place at the *K*-region of pyrenyl fragments, which is hardly accessible by conventional organic synthesis. This atom-economic direct C-H arylation tolerates both electron-donating and electron-withdrawing groups on the (hetero)aryl bromide coupling partner, with the resulting products isolated in 25% to 90%. furnished good to high yields (up to 96%) even when bulky polyaromatic hydrocarbon bromides were used. General modification of the 1-pyrenylphosphines and other PAH, like presented herein, offers pertinent alternative to popular biphenylphosphine ligands used for transition metal catalysis, as well as potential perspectives to build luminescence probes, cytotoxic reagents and composite catalytic materials based on strong  $\pi$ -stacking of ligands and complexes incorporating pyrene moieties towards common  $sp^2$ -C-based supports.

## Experimental Section

Accession Codes. **2**: 2074194; **15**: 2074195; CCDC **A**: 2109009; CCDC **B**: 2074193; CCDC **D**: 2109022; CCDC **G**: 2074196 contain the supplementary crystallographic data for the paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**General Procedures.** All reagents were purchased from commercial suppliers and used without purifications. All reactions were performed under an atmosphere of dry argon in oven-dried glassware using Schlenk and vacuum-line techniques. Flash chromatography was performed on silica gel (40–63  $\mu\text{m}$ ). The identity and purity of the products were established at the “Chemical Analysis Platform and Molecular Synthesis University of Burgundy” (PACSMUB Platform – SATT SAYENS) using high-resolution mass spectrometry, elemental analysis and multinuclear NMR.  $^1\text{H}$  (500 MHz),  $^{31}\text{P}$  (202 MHz),  $^{18}\text{F}$  (407 MHz),  $^{13}\text{C}$  (125 MHz) spectra were recorded on Bruker AVANCE III instrument in  $\text{CDCl}_3$  solutions. Chemical shifts are reported in ppm relative to  $\text{CDCl}_3$  ( $^1\text{H}$ : 7.26 and  $^{13}\text{C}$ : 77.16) and coupling constants  $J$  are given in Hz. High resolution mass spectra (HRMS) were obtained on a Thermo LTQ-Orbitrap XL with ESI source.

**Synthesis of 1-(diphenylphosphino) polyaromatic (1, 20–22).** To a solution of 1-bromoaryl (1 equiv, 7.8 mmol) in dry diethyl ether (40 ml) cooled below  $-78\text{ }^\circ\text{C}$ ,  $n\text{-BuLi}$  (1.56 M in hexane, 1.2 equiv, 7.8 mmol) was added dropwise by syringe. After 10 min, chlorodiphenylphosphine (1.2 equiv, 7.8 mmol) was added. The reaction mixture was allowed to warm to room temperature after 30 min stirring at  $-0\text{ }^\circ\text{C}$  in an iced water bath. The solution was stirred for 12 h at room temperature. The crude compound was purified through a flash chromatography packed with silica gel eluted using a mixture  $\text{CH}_2\text{Cl}_2$ :hexane (1:2) and afforded the corresponding 1-(diphenylphosphino)aryl.

**Synthesis of 1-(diphenylphosphino) pyrene (1).** As a white solid (75%, 2.2 g)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.77 (dd,  $J = 4.8$  and  $9.2$  Hz, 1H), 8.23–8.17 (m, 2H), 8.13–7.98 (m, 5H), 7.55 (dd,  $J = 4.4$  and  $7.9$  Hz, 1H), 7.39–7.30 (m, 10H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-13.9$  (s).

**Synthesis of the arylated 1-polyaromatic phosphines (2–19, 23–26).** An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with 1-PAH phosphine (pyrene: 0.5 mmol, 1 equiv, 194 mg), aryl bromide (1.5 equiv),  $\text{K}_3\text{PO}_4$  (1.5 mmol, 3 equiv, 318 mg), and  $[\text{Rh}(\text{COD})_2]\text{BF}_4$  (0.025 mmol, 5 mol%, 10 mg), in trifluoromethylbenzene (0.16 M, 3 ml). The mixture was stirred at reflux under argon during 18 h. After extraction using a  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  mixture, the organic layer was concentrated in vacuum. The crude product was purified by column chromatography on silica using as eluent a mixture heptane:dichloromethane (4:1).

**1-(diphenylphosphino)-10-(4-methoxyphenyl) pyrene (2):** as a yellow solid (70%, 172 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.20 (d,  $J = 7.4$  Hz, 1H), 8.15 (d,  $J = 5.9$  Hz, 1H), 8.12 (d,  $J = 8.8$  Hz, 1H), 8.07–8.00 (m, 3H), 7.96 (bs, 1H), 7.73 (dd,  $J = 4.0$  and  $7.9$  Hz, 1H), 7.27–7.18 (m, 6H), 7.16 (d,  $J = 8.3$  Hz, 2H), 7.04 (t,  $J = 6.5$  Hz, 4H), 6.69 (d,  $J = 10.3$  Hz, 2H), 3.82 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-8.1$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 159.2, 140.2 (d,  $J_{\text{PC}} = 4.6$  Hz), 140.1 (d,  $J_{\text{PC}} = 17.4$  Hz), 136.5 (d,  $J_{\text{PC}} = 5.5$  Hz), 135.7 (d,  $J_{\text{PC}} = 21.0$  Hz), 135.6, 133.8, 133.6, 133.4 (d,  $J_{\text{PC}} = 28.0$  Hz), 131.9, 131.8 (d,  $J_{\text{PC}} = 6.9$  Hz), 131.6, 131.4, 130.5, 128.2 (d,  $J_{\text{PC}} = 6.4$  Hz), 128.1, 128.1, 127.8, 126.3, 126.2 (d,  $J_{\text{PC}} = 5.0$  Hz), 125.3 (d,  $J_{\text{PC}} = 28.2$  Hz), 125.3, 124.1 (d,  $J_{\text{PC}} = 1.0$  Hz), 113.5, 55.4. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 493.17212, found: 493.17164.

**1-(diphenylphosphino)-10-(4-methylphenyl) pyrene (3):** as a yellow solid (90%, 214 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.11 (t,  $J = 7.9$  Hz, 2H), 8.04 (d,  $J = 8.9$  Hz, 1H), 8.00–7.95 (m, 3H), 7.93 (d,  $J = 7.6$  Hz, 1H), 7.77 (dd,  $J = 4.0$  and  $7.9$  Hz, 1H), 7.24–7.15 (m, 8H), 7.05 (t,  $J = 6.9$  Hz, 4H), 6.94 (d,  $J = 7.7$  Hz, 2H), 2.38 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-8.6$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 141.2 (d,  $J_{\text{PC}} = 5.4$  Hz), 140.5 (d,  $J = 4.8$  Hz), 140.0 (d,  $J_{\text{PC}} = 17.2$  Hz), 136.7, 135.7, 135.7 (d,  $J_{\text{PC}} = 21.6$  Hz), 133.7, 133.6, 133.3 (d,  $J_{\text{PC}} = 30.0$  Hz), 131.9, 131.6, 131.3, 130.5 (d,  $J_{\text{PC}} = 6.9$  Hz), 130.4, 128.7, 128.1 (d,  $J_{\text{PC}} = 6.2$  Hz), 128.1, 128.0, 127.7, 126.3, 126.2 (d,  $J_{\text{PC}} = 5.2$  Hz), 125.4, 125.4 (d,  $J_{\text{PC}} = 29.4$  Hz), 124.1 (d,  $J_{\text{PC}} = 1.5$  Hz), 21.5. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 475.16156, found: 475.16073.

**1-(diphenylphosphino)-10-(4-diphenylaminophenyl) pyrene (4):** as a yellow solid (60%, 189 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.17 (d,  $J = 7.4$  Hz, 1H), 8.15 (d,  $J = 5.9$  Hz, 1H), 8.09 (d,  $J = 8.8$  Hz, 1H), 8.04–7.97 (m, 4H), 7.76 (dd,  $J = 4.1$  and  $8.0$  Hz, 1H), 7.29–7.14 (m, 16H), 7.10 (t,  $J = 6.8$  Hz, 4H), 7.02 (t,  $J = 6.9$  Hz, 2H), 6.96 (d,  $J = 8.4$  Hz, 2H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-7.6$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 148.0, 147.0, 140.2 (d,  $J_{\text{PC}} = 4.4$  Hz), 140.1 (d,  $J_{\text{PC}} = 18.1$  Hz), 138.6 (d,  $J_{\text{PC}} = 5.5$  Hz), 135.4 (d,  $J_{\text{PC}} = 4.7$  Hz), 135.3, 133.8, 133.7, 133.5 (d,  $J_{\text{PC}} = 28.4$  Hz), 131.9, 131.5 (d,  $J_{\text{PC}} = 7.3$  Hz), 131.5, 131.4, 130.4, 129.3, 128.3 (d,  $J_{\text{PC}} = 6.3$  Hz), 128.1, 127.8, 126.3, 126.2 (d,  $J_{\text{PC}} = 4.7$  Hz), 125.4 (d,  $J_{\text{PC}} = 22.9$  Hz), 125.4, 124.4, 124.2 (d,  $J_{\text{PC}} = 1.7$  Hz), 124.0, 122.7. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 630.23506, found: 630.23490.

**1-(diphenylphosphino)-10-(4-acetylphenyl) pyrene (5):** as a yellow solid (89%, 224 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.22 (d,  $J = 7.5$  Hz, 1H), 8.16 (d,  $J = 7.4$  Hz, 1H), 8.12 (d,  $J = 8.9$  Hz, 1H), 8.09–8.00 (m, 3H), 7.96 (s, 1H), 7.79 (dd,  $J = 4.0$  and  $7.9$  Hz, 1H), 7.71 (d,  $J = 8.2$  Hz, 2H), 7.37 (d,  $J = 8.2$  Hz, 2H), 7.27 (t,  $J = 6.7$  Hz, 2H), 7.21 (t,  $J = 7.4$  Hz, 4H), 7.03 (t,  $J = 7.1$  Hz, 4H), 2.60 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-9.2$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 198.0, 149.2 (d,  $J_{\text{PC}} = 4.9$  Hz), 139.4 (d,  $J_{\text{PC}} = 5.6$  Hz), 139.2 (d,  $J_{\text{PC}} = 15.9$  Hz), 135.9, 135.6, 135.1 (d,  $J_{\text{PC}} = 23.1$  Hz), 133.7, 133.5, 132.8 (d,  $J_{\text{PC}} = 26.7$  Hz), 132.0, 131.7, 131.3, 130.6 (d,  $J_{\text{PC}} = 7.1$  Hz), 130.0, 128.3 (d,  $J_{\text{PC}} = 6.1$  Hz), 128.3, 128.3, 128.2, 127.7, 126.5, 126.2 (d,  $J_{\text{PC}} = 5.7$  Hz), 125.9, 125.7, (d,  $J_{\text{PC}} = 32.8$  Hz), 124.2 (d,  $J_{\text{PC}} = 1.5$  Hz), 26.8. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 503.15647, found: 503.15585.

**1-(diphenylphosphino)-10-(4-trifluoromethylphenyl) pyrene (6):** as a yellow solid (70%, 186 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.21 (d,  $J = 7.4$  Hz, 1H), 8.13 (d,  $J = 8.1$  Hz, 1H), 8.12 (d,  $J = 8.9$  Hz, 1H), 8.08–7.99 (m, 3H), 7.94 (s, 1H), 7.78 (dd,  $J = 4.0$  and  $7.9$  Hz, 1H), 7.38–7.31 (m, 4H), 7.27 (t,  $J = 7.3$  Hz, 2H), 7.21 (t,  $J = 7.4$  Hz, 4H), 7.03 (t,  $J = 7.7$  Hz, 4H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-9.1$  (s).  $^{18}\text{F}\{^1\text{H}\}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-62.2$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 147.8 (d,  $J_{\text{PC}} = 6.2$  Hz), 139.2 (d,  $J_{\text{PC}} = 15.6$  Hz), 139.2 (d,  $J_{\text{PC}} = 5.0$  Hz), 136.1, 135.2 (d,  $J_{\text{PC}} = 23.1$  Hz), 133.7, 133.6, 132.7 (d,  $J_{\text{PC}} = 27.0$  Hz), 132.1, 132.0, 131.4, 130.9 (d,  $J_{\text{PC}} = 7.1$  Hz), 130.1, 129.3 (q,  $J_{\text{FC}} = 32.2$  Hz), 128.4, 128.4 (d,  $J_{\text{PC}} = 6.4$  Hz), 128.3, 127.8, 126.5, 126.2 (d,  $J_{\text{PC}} = 5.6$  Hz), 126.0 (d,  $J_{\text{PC}} = 33.5$  Hz), 125.7 (q,  $J_{\text{FC}} = 3.7$  Hz), 125.6, 124.9 (q,  $J_{\text{FC}} = 272.0$  Hz), 124.3 (d,  $J_{\text{PC}} = 1.5$  Hz). HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 531.14895, found: 531.14836.

**1-(diphenylphosphino)-10-(4-chlorophenyl) pyrene (7):** as a yellow solid (89%, 221 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.21 (d,  $J = 7.3$  Hz, 1H), 8.14 (d,  $J = 7.41$  Hz, 1H), 8.12 (d,  $J = 8.9$  Hz, 1H), 8.06–7.99 (m, 3H), 7.92 (s, 1H), 7.74 (dd,  $J = 4.0$  and  $7.9$  Hz, 1H), 7.27 (t,  $J = 7.3$  Hz, 2H), 7.22 (t,  $J = 7.4$  Hz, 4H), 7.16 (d,  $J = 8.3$  Hz, 2H), 7.09 (d,  $J = 8.3$  Hz, 2H), 7.04 (t,  $J = 7.7$  Hz, 4H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.3 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 142.3 (d,  $J_{\text{PC}} = 5.3$  Hz), 139.3 (d,  $J_{\text{PC}} = 4.7$  Hz), 139.3 (d,  $J_{\text{PC}} = 14.3$  Hz), 135.6, 135.1 (d,  $J_{\text{PC}} = 21.5$  Hz), 133.8, 133.6, 133.3, 132.8 (d,  $J_{\text{PC}} = 25.4$  Hz), 132.0, 132.0 (d,  $J_{\text{PC}} = 7.0$  Hz), 131.8, 131.3, 130.2, 128.4, 128.3 (d,  $J_{\text{PC}} = 6.5$  Hz), 128.2, 128.1, 127.8, 126.4, 126.2 (d,  $J_{\text{PC}} = 5.2$  Hz), 125.8, 125.6 (d,  $J_{\text{PC}} = 24.7$  Hz), 124.2 (d,  $J_{\text{PC}} = 1.6$  Hz). HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 497.12259, found: 497.11965.

**1-(diphenylphosphino)-10-(4-benzaldehyde) pyrene (8):** as a yellow solid (70%, 110 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 9.99 (s, 1H), 8.17 (d,  $J = 7.6$  Hz, 1H), 8.11–7.95 (m, 5H), 7.92 (s, 1H), 7.78 (dd,  $J = 4.0$  and  $7.9$  Hz, 1H), 7.61 (d,  $J = 8.1$  Hz, 2H), 7.40 (d,  $J = 7.9$  Hz, 2H), 7.24 (d,  $J = 7.3$  Hz, 2H), 7.19 (t,  $J = 7.2$  Hz, 4H), 7.01 (t,  $J = 7.1$  Hz, 4H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.7 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 192.2, 150.5 (d,  $J_{\text{PC}} = 4.8$  Hz), 139.2 (d,  $J_{\text{PC}} = 5.5$  Hz), 139.0 (d,  $J_{\text{PC}} = 15.7$  Hz), 135.7, 135.0, 134.8 (d,  $J_{\text{PC}} = 22.9$  Hz), 133.6, 133.5, 132.7 (d,  $J_{\text{PC}} = 26.7$  Hz), 132.0, 131.8, 131.2, 131.0 (d,  $J_{\text{PC}} = 7.2$  Hz), 129.9, 129.5, 128.4, 128.3 (d,  $J_{\text{PC}} = 6.9$  Hz), 128.2, 127.7, 126.4, 126.1 (d,  $J_{\text{PC}} = 5.5$  Hz), 126.0 (d,  $J_{\text{PC}} = 33.5$  Hz), 125.5 (d,  $J_{\text{PC}} = 0.8$  Hz), 124.2. HRMS + p ESI (m/z)  $[\text{M}-\text{H}]^+$  calcd.: 489.14083, found: 489.14056.

**1-(diphenylphosphino)-10-(4-nitrophenyl) pyrene (9):** as an orange solid (25%, 63 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.27 (d,  $J = 7.6$  Hz, 1H), 8.20 (d,  $J = 7.4$  Hz, 1H), 8.16 (d,  $J = 8.9$  Hz, 1H), 8.11–8.05 (m, 3H), 7.95 (d,  $J = 7.6$  Hz, 2H), 7.94 (s, 1H), 7.75 (dd,  $J = 4.0$  and  $7.9$  Hz, 1H), 7.39 (d,  $J = 8.6$  Hz, 2H), 7.28 (t,  $J = 7.3$  Hz, 2H), 7.22 (t,  $J = 8.0$  Hz, 4H), 6.99 (t,  $J = 7.1$  Hz, 4H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.7 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 151.0 (d,  $J_{\text{PC}} = 4.8$  Hz), 147.0, 138.6 (d,  $J_{\text{PC}} = 14.8$  Hz), 138.4 (d,  $J_{\text{PC}} = 5.6$  Hz), 135.8, 134.6 (d,  $J_{\text{PC}} = 22.9$  Hz), 133.7, 133.6, 132.5 (d,  $J_{\text{PC}} = 26.2$  Hz), 132.2, 132.1, 131.4, 131.3 (d,  $J_{\text{PC}} = 7.3$  Hz), 129.9, 128.6 (d,  $J_{\text{PC}} = 6.6$  Hz), 128.5, 128.4, 127.9, 126.7, 126.4, 126.2 (d,  $J_{\text{PC}} = 5.6$  Hz), 126.0 (d,  $J_{\text{PC}} = 22.5$  Hz), 124.4 (d,  $J_{\text{PC}} = 1.6$  Hz), 123.3. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 508.14664, found: 508.14633.

**1-(diphenylphosphino)-10-(3-methoxyphenyl) pyrene (10):** as a yellow solid (87%, 214 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.04 (d,  $J = 7.5$  Hz, 1H), 8.01 (d,  $J = 7.5$  Hz, 1H), 7.96 (d,  $J = 8.8$  Hz, 1H), 7.93–7.84 (m, 4H), 7.65 (dd,  $J = 3.9$  and  $8.0$  Hz, 1H), 7.13–7.00 (m, 7H), 6.95 (t,  $J = 7.5$  Hz, 2H), 6.88 (q,  $J = 7.0$  Hz, 3H), 6.76 (dd,  $J = 2.3$  and  $8.2$  Hz, 1H), 6.55 (s, 1H), 3.32 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.6 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 159.3, 145.5 (d,  $J_{\text{PC}} = 5.4$  Hz), 140.7 (d,  $J_{\text{PC}} = 18.2$  Hz), 140.3 (d,  $J_{\text{PC}} = 4.7$  Hz), 139.5 (d,  $J_{\text{PC}} = 16.9$  Hz), 136.0, 135.4 (d,  $J_{\text{PC}} = 21.8$  Hz), 133.5 (d,  $J_{\text{PC}} = 6.5$  Hz), 133.5 (d,  $J_{\text{PC}} = 6.5$  Hz), 133.3 (d,  $J_{\text{PC}} = 28.4$  Hz), 132.0, 131.5, 131.4, 130.2, 129.4, 128.3 (d,  $J_{\text{PC}} = 6.5$  Hz), 128.2 (d,  $J_{\text{PC}} = 5.8$  Hz), 128.2, 128.0, 127.8, 126.4, 126.1 (d,  $J_{\text{PC}} = 5.4$  Hz), 125.6, 125.5 (d,  $J_{\text{PC}} = 29.6$  Hz), 124.2 (d,  $J_{\text{PC}} = 1.6$  Hz), 123.5 (d,  $J_{\text{PC}} = 7.7$  Hz), 115.5 (d,  $J_{\text{PC}} = 7.1$  Hz), 113.7, 54.9. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 493.17212, found: 493.17143.

**1-(diphenylphosphino)-10-(2-naphthyl) pyrene (11):** as a yellow solid (70%, 179 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.23 (d,  $J = 7.4$  Hz, 1H), 8.18 (d,  $J = 8.2$  Hz, 1H), 8.16 (d,  $J = 8.2$  Hz, 1H), 8.09 (d,  $J = 7.6$  Hz, 2H), 8.07–8.02 (m, 2H), 7.87 (d,  $J = 8.2$  Hz, 1H), 7.82 (d,  $J = 8.3$  Hz, 1H), 7.76 (dd,  $J = 4.2$  and  $8.0$  Hz, 1H), 7.65 (d,  $J = 8.3$  Hz, 1H), 7.50–7.44 (m, 2H), 7.34 (q,  $J = 7.7$  and  $8.2$  Hz, 2H), 7.24–7.14 (m, 4H), 7.09 (t,  $J = 7.1$  Hz, 2H), 6.93 (t,  $J = 6.9$  Hz, 2H), 6.85 (t,  $J = 7.3$  Hz, 2H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.2 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 141.5 (d,  $J_{\text{PC}} = 5.2$  Hz), 140.5 (d,  $J_{\text{PC}} = 5.0$  Hz), 140.4 (d,  $J_{\text{PC}} = 17.9$  Hz), 138.6 (d,  $J_{\text{PC}} = 14.2$  Hz), 135.7, 135.5 (d,  $J_{\text{PC}} = 21.5$  Hz), 133.8 (d,  $J_{\text{PC}} = 20.5$  Hz), 133.7 (d,  $J_{\text{PC}} = 20.5$  Hz), 133.5 (d,  $J_{\text{PC}} = 20.4$  Hz), 133.3, 133.3 (d,  $J_{\text{PC}} = 26.9$  Hz), 132.7, 132.1, 132.0, 131.4, 130.7 (d,  $J_{\text{PC}} = 6.9$  Hz), 130.4, 129.5 (d,  $J_{\text{PC}} = 6.7$  Hz), 129.4 (d,  $J_{\text{PC}} = 7.6$  Hz), 128.4, 128.3 (d,  $J_{\text{PC}} = 5.8$  Hz), 128.2, 128.1, 128.1 (d,  $J_{\text{PC}} = 6.9$  Hz), 128.0, 127.8, 127.6 (d,  $J_{\text{PC}} = 9.4$  Hz), 126.4, 126.2 (d,  $J_{\text{PC}} = 5.2$  Hz), 125.9, 125.7, 125.6, 125.5 (d,  $J_{\text{PC}} = 30.9$  Hz), 124.2 (d,  $J_{\text{PC}} = 1.4$  Hz). HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 513.17721, found: 513.17593.

**1-(diphenylphosphino)-10-(2-methoxyphenyl) pyrene (12):** as a yellow solid (85%, 210 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.21 (d,  $J = 7.5$  Hz, 1H), 8.16 (d,  $J = 7.5$  Hz, 1H), 8.16 (d,  $J = 8.9$  Hz, 1H), 8.07–8.00 (m, 3H), 7.98 (s, 1H), 7.72 (dd,  $J = 3.4$  and  $7.3$  Hz, 1H), 7.40 (t,  $J = 7.6$  Hz, 1H), 7.29 (sb, 3H), 7.22 (t,  $J = 7.0$  Hz, 1H), 7.16–7.13 (m, 4H), 7.04 (d,  $J = 7.0$  Hz, 1H), 6.87 (t,  $J = 6.9$  Hz, 2H), 6.80 (t,  $J = 7.2$  Hz, 2H), 3.48 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.3 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 158.5 (d,  $J_{\text{PC}} = 6.3$  Hz), 140.1 (d,  $J_{\text{PC}} = 19.7$  Hz), 139.8 (d,  $J_{\text{PC}} = 16.4$  Hz), 137.2 (d,  $J_{\text{PC}} = 5.2$  Hz), 135.3 (d,  $J_{\text{PC}} = 21.2$  Hz), 135.0, 134.0 (d,  $J_{\text{PC}} = 21.3$  Hz), 133.6 (d,  $J_{\text{PC}} = 20.6$  Hz), 133.0, 133.0 (d,  $J_{\text{PC}} = 21.3$  Hz), 132.3, 132.2 (d,  $J_{\text{PC}} = 5.3$  Hz), 132.0, 131.5, 130.5, 129.3, 128.3 (d,  $J_{\text{PC}} = 5.9$  Hz), 128.1 (d,  $J_{\text{PC}} = 6.4$  Hz), 128.0, 128.0 (d,  $J_{\text{PC}} = 5.9$  Hz), 128.0, 126.1, 126.0 (d,  $J_{\text{PC}} = 5.1$  Hz), 125.4, 125.4 (d,  $J_{\text{PC}} = 33.1$  Hz), 124.5 (d,  $J_{\text{PC}} = 1.8$  Hz), 120.3, 110.3. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 493.17212, found: 493.17117.

**1-(diphenylphosphino)-10-(1-naphthyl) pyrene (13):** as a yellow solid (79%, 203 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.26 (d,  $J = 7.0$  Hz, 1H), 8.18 (d,  $J = 8.2$  Hz, 1H), 8.16 (d,  $J = 7.5$  Hz, 1H), 8.12–8.03 (m, 4H), 7.92 (t,  $J = 6.4$  Hz, 2H), 7.66 (t,  $J = 3.6$  and  $7.9$  Hz, 1H), 7.42 (t,  $J = 7.6$  Hz, 2H), 7.25–7.12 (m, 7H), 7.07 (t,  $J = 7.4$  Hz, 2H), 6.78 (t,  $J = 7.7$  Hz, 2H), 6.67 (t,  $J = 6.8$  Hz, 2H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -7.7 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 141.5 (d,  $J_{\text{PC}} = 5.1$  Hz), 140.1 (d,  $J_{\text{PC}} = 1.1$  Hz), 139.2 (d,  $J_{\text{PC}} = 20.1$  Hz), 138.4 (d,  $J_{\text{PC}} = 16.8$  Hz), 135.8 (d,  $J_{\text{PC}} = 21.6$  Hz), 135.4, 134.9 (d,  $J_{\text{PC}} = 9.9$  Hz), 133.7, 133.6, 133.4, 133.3 (d,  $J_{\text{PC}} = 30.2$  Hz), 132.4, 132.3, 131.5, 130.4, 128.8 (d,  $J_{\text{PC}} = 9.9$  Hz), 128.3, 128.3, 128.2, 128.2 (d,  $J_{\text{PC}} = 6.0$  Hz), 128.1, 128.0 (d,  $J_{\text{PC}} = 6.8$  Hz), 126.7, 126.7 (d,  $J_{\text{PC}} = 30.6$  Hz), 126.0 (d,  $J_{\text{PC}} = 5.2$  Hz), 125.9, 125.7 (d,  $J_{\text{PC}} = 28.3$  Hz), 125.7 (d,  $J_{\text{PC}} = 24.4$  Hz), 125.6, 124.6 (d,  $J_{\text{PC}} = 1.8$  Hz). HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 513.17721, found: 513.17593.

**1-(diphenylphosphino)-10-(9-phenanthryl) pyrene (14):** as a yellow solid (58%, 163 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.78 (d,  $J = 8.2$  Hz, 1H), 8.74 (d,  $J = 8.3$  Hz, 1H), 8.25 (d,  $J = 7.5$  Hz, 1H), 8.19–8.13 (m, 3H), 8.12–8.07 (m, 2H), 8.03 (t,  $J = 7.6$  Hz, 1H), 7.67–7.58 (m, 4H), 7.46 (t,  $J = 7.3$  Hz, 1H), 7.39–7.30 (m, 3H), 7.19–7.09 (m,

2H), 7.09–6.98 (m, 4H), 6.68 (t,  $J = 6.8$  Hz, 2H), 6.54 (t,  $J = 7.2$  Hz, 2H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-7.1$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 140.3 (d,  $J_{\text{PC}} = 20.9$  Hz), 140.0 (d,  $J_{\text{PC}} = 4.9$  Hz), 138.4 (d,  $J_{\text{PC}} = 5.1$  Hz), 138.2 (d,  $J_{\text{PC}} = 14.8$  Hz), 135.8 (d,  $J_{\text{PC}} = 21.8$  Hz), 135.3, 134.6 (d,  $J_{\text{PC}} = 10.3$  Hz), 134.3 (d,  $J_{\text{PC}} = 19.7$  Hz), 133.8 (d,  $J_{\text{PC}} = 20.6$  Hz), 133.6 (d,  $J_{\text{PC}} = 7.3$  Hz), 133.5 (d,  $J_{\text{PC}} = 6.5$  Hz), 133.2 (d,  $J_{\text{PC}} = 29.6$  Hz), 132.4, 132.3, 132.0, 131.6, 130.7, 130.5, 130.4, 129.1 (d,  $J_{\text{PC}} = 6.7$  Hz), 129.0, 128.8 (d,  $J_{\text{PC}} = 7.1$  Hz), 128.3, 128.2 (d,  $J_{\text{PC}} = 5.5$  Hz), 128.1, 128.0, 128.0 (d,  $J_{\text{PC}} = 7.0$  Hz), 127.5 (d,  $J_{\text{PC}} = 1.7$  Hz), 126.6, 126.5 (d,  $J_{\text{PC}} = 7.0$  Hz), 126.4, 126.2, 126.1 (d,  $J_{\text{PC}} = 5.1$  Hz), 125.7 (d,  $J_{\text{PC}} = 32.0$  Hz), 125.6, 124.6 (d,  $J_{\text{PC}} = 1.8$  Hz), 122.9, 122.6. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 563.19286, found: 563.19309.

**1-(diphenylphosphino)-10-(1-pyrenyl) pyrene (15):** as a yellow solid (80%, 234 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.29 (d,  $J = 7.5$  Hz, 1H), 8.24–8.16 (m, 3H), 8.13–8.06 (m, 5H), 7.03–7.95 (m, 4H), 7.86 (d,  $J = 7.7$  Hz, 1H), 7.67 (dd,  $J = 3.6$  and 7.9 Hz, 1H), 7.63 (d,  $J = 9.2$  Hz, 1H), 7.53 (d,  $J = 9.2$  Hz, 1H), 7.19 (t,  $J = 7.3$  Hz, 1H), 7.11 (t,  $J = 7.3$  Hz, 2H), 6.84 (t,  $J = 7.4$  Hz, 1H), 6.72 (t,  $J = 7.1$  Hz, 2H), 6.65 (t,  $J = 7.0$  Hz, 2H), 6.43 (t,  $J = 7.2$  Hz, 2H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-9.5$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 139.8 (d,  $J_{\text{PC}} = 17.6$  Hz), 139.1 (d,  $J_{\text{PC}} = 5.0$  Hz), 138.9 (d,  $J_{\text{PC}} = 5.2$  Hz), 138.7 (d,  $J_{\text{PC}} = 18.9$  Hz), 136.3 (d,  $J_{\text{PC}} = 22.1$  Hz), 135.8, 133.5 (d,  $J_{\text{PC}} = 28.5$  Hz), 133.4, 133.3, 133.1, 133.0, 132.3, 131.6 (d,  $J_{\text{PC}} = 3.8$  Hz), 131.2, 131.2 (d,  $J_{\text{PC}} = 3.8$  Hz), 130.4, 129.5 (d,  $J_{\text{PC}} = 7.6$  Hz), 128.3, 128.1 (d,  $J_{\text{PC}} = 6.0$  Hz), 128.0, 127.9, 127.7, 127.7 (d,  $J_{\text{PC}} = 6.2$  Hz), 127.3, 127.2, 126.5, 126.1, 126.1, 125.8 (d,  $J_{\text{PC}} = 1.1$  Hz), 125.6 (d,  $J_{\text{PC}} = 4.9$  Hz), 125.1 (d,  $J_{\text{PC}} = 9.1$  Hz), 124.9 (d,  $J_{\text{PC}} = 1.9$  Hz), 124.6, 124.6. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 587.19286, found: 587.19228.

**1-(diphenylphosphino)-10-(3-fluoranthenyl) pyrene (16):** as a yellow solid (80%, 234 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.26 (d,  $J = 7.4$  Hz, 1H), 8.19–8.13 (m, 3H), 8.10 (dd,  $J = 4.3$  and 8.4 Hz, 2H), 8.04 (t,  $J = 7.6$  Hz, 1H), 7.93 (dd,  $J = 4.5$  and 7.7 Hz, 2H), 7.86 (d,  $J = 6.5$  Hz, 1H), 7.70 (m, 1H), 7.62 (d,  $J = 7.0$  Hz, 1H), 7.43–7.38 (m, 2H), 7.38–7.29 (m, 3H), 7.24 (t,  $J = 6.1$  Hz, 1H), 7.16 (t,  $J = 7.5$  Hz, 2H), 7.09 (t,  $J = 7.3$  Hz, 1H), 7.01 (t,  $J = 7.5$  Hz, 2H), 6.81 (t,  $J = 6.9$  Hz, 2H), 6.65 (t,  $J = 8.0$  Hz, 2H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-8.1$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 141.5 (d,  $J_{\text{PC}} = 4.9$  Hz), 139.8, 139.4, 139.4 (d,  $J_{\text{PC}} = 19.9$  Hz), 138.7 (d,  $J_{\text{PC}} = 16.2$  Hz), 137.1 (d,  $J_{\text{PC}} = 5.4$  Hz), 136.6, 136.5, 135.9 (d,  $J_{\text{PC}} = 21.9$  Hz), 135.2, 133.5 (d,  $J_{\text{PC}} = 20.6$  Hz), 133.3 (d,  $J_{\text{PC}} = 9.2$  Hz), 133.2 (d,  $J_{\text{PC}} = 28.9$  Hz), 133.1 (d,  $J_{\text{PC}} = 10.4$  Hz), 132.5, 131.9, 131.2 (d,  $J_{\text{PC}} = 9.1$  Hz), 131.2, 129.9, 129.8 (d,  $J_{\text{PC}} = 7.54$  Hz), 128.0, 127.8 (d,  $J_{\text{PC}} = 5.9$  Hz), 127.8 (d,  $J_{\text{PC}} = 6.2$  Hz), 127.6 (d,  $J_{\text{PC}} = 5.7$  Hz), 127.6, 127.2, 127.1, 126.1, 125.7 (d,  $J_{\text{PC}} = 5.2$  Hz), 125.6, 125.4 (d,  $J_{\text{PC}} = 34.4$  Hz), 125.2, 124.2 (d,  $J_{\text{PC}} = 1.8$  Hz), 121.3 (d,  $J_{\text{PC}} = 3.9$  Hz), 119.8, 119.6. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 587.19286, found: 587.19312.

**1-(diphenylphosphino)-10-(9-anthracenyl) pyrene (17):** as a yellow solid (70%, 177 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.63 (s, 1H), 8.31 (d,  $J = 7.5$  Hz, 1H), 8.23 (d,  $J = 8.9$  Hz, 1H), 8.18–8.06 (m, 5H), 8.02 (d,  $J = 8.5$  Hz, 2H), 7.63 (dd,  $J = 3.3$  and 7.9 Hz, 1H), 7.37 (d,  $J = 8.8$  Hz, 2H), 7.29 (t,  $J = 7.2$  Hz, 2H), 7.04 (t,  $J = 7.3$  Hz, 2H), 6.93 (m, 6H), 6.35 (t,  $J = 7.1$  Hz, 4H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202

MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-9.7$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 139.2 (d,  $J_{\text{PC}} = 19.9$  Hz), 138.2 (d,  $J_{\text{PC}} = 4.3$  Hz), 136.4 (d,  $J_{\text{PC}} = 5.2$  Hz), 136.3 (d,  $J_{\text{PC}} = 19.8$  Hz), 135.8 (d,  $J_{\text{PC}} = 0.6$  Hz), 133.4 (d,  $J_{\text{PC}} = 0.9$  Hz), 133.1 (d,  $J_{\text{PC}} = 21.6$  Hz), 133.1 (d,  $J_{\text{PC}} = 30.3$  Hz), 132.5 (d,  $J_{\text{PC}} = 23.9$  Hz), 132.4, 132.0, 131.6, 130.5, 128.4, 128.3, 128.1, 128.0 (d,  $J_{\text{PC}} = 6.1$  Hz), 127.6, 127.3 (d,  $J_{\text{PC}} = 1.2$  Hz), 127.1, 126.5, 126.3 (d,  $J_{\text{PC}} = 5.25$  Hz), 125.8, 125.7, 125.5, 125.1 (d,  $J_{\text{PC}} = 18.1$  Hz), 124.8 (d,  $J_{\text{PC}} = 1.9$  Hz). HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 563.19286, found: 563.19281.

**1-(diphenylphosphino)-10-(2-pyridinyl) pyrene (18):** as a brown solid (41%, 95 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.40 (d,  $J = 4.7$  Hz, 1H), 8.23 (t,  $J = 6.7$  Hz, 2H), 8.18 (s, 1H), 8.14 (d,  $J = 8.8$  Hz, 1H), 8.11–8.02 (m, 3H), 7.85 (dd,  $J = 3.9$  and 7.9 Hz, 1H), 7.41 (td,  $J = 1.6$  and 7.6 Hz, 1H), 7.39 (d,  $J = 7.7$  Hz, 1H), 7.24 (m, 7H), 7.11 (t,  $J = 6.7$  Hz, 4H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-9.0$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 162.5 (d,  $J_{\text{PC}} = 1.9$  Hz), 149.8, 139.9 (d,  $J_{\text{PC}} = 15.6$  Hz), 139.6 (d,  $J_{\text{PC}} = 5.7$  Hz), 136.7, 136.4, 135.7 (d,  $J_{\text{PC}} = 25.2$  Hz), 133.8, 133.6, 138.8 (d,  $J_{\text{PC}} = 24.6$  Hz), 132.4, 132.3, 131.6, 130.4, 128.5 (d,  $J_{\text{PC}} = 6.1$  Hz), 128.3, 128.0, 126.6, 126.5, 126.3, 126.2, 125.8, 125.5 (d,  $J_{\text{PC}} = 8.6$  Hz), 124.8 (d,  $J_{\text{PC}} = 1.4$  Hz), 122.3. HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  calcd.: 464.15681, found: 464.15625.

**1-(diphenylphosphino)-10-(4-methoxyphenyl) phenanthrene (23):** as a yellow solid (73%, 179 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.77 (d,  $J = 8.4$  Hz, 1H), 8.72 (d,  $J = 8.4$  Hz, 1H), 7.67–7.62 (m, 2H), 7.56–7.50 (m, 2H), 7.41–7.39 (m, 2H), 7.26 (t,  $J = 7.3$  Hz, 2H), 7.20 (t,  $J = 7.4$  Hz, 4H), 7.03 (t,  $J = 7.0$  Hz, 4H), 6.99 (d,  $J = 8.4$  Hz, 2H), 6.60 (d,  $J = 8.6$  Hz, 2H), 3.78 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-6.88$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 159.2, 142.0 (d,  $J_{\text{PC}} = 3.7$  Hz), 139.6 (d,  $J_{\text{PC}} = 16.8$  Hz), 139.0, 135.9 (d,  $J_{\text{PC}} = 5.3$  Hz), 134.4, 134.2, 134.0 (d,  $J_{\text{PC}} = 21.0$  Hz), 133.3, 133.1, 132.4 (d,  $J_{\text{PC}} = 6.7$ ), 131.6 (d,  $J_{\text{PC}} = 4.1$  Hz), 131.2, 131.1, 130.9, 128.7, 128.3, 128.2 (d,  $J_{\text{PC}} = 6.5$  Hz), 127.6, 126.3, 125.6, 123.0, 122.3 (d,  $J_{\text{PC}} = 1.0$  Hz), 113.1, 55.3. HRMS + p ESI (m/z)  $[\text{M}+\text{Na}]^+$  calcd.: 491.15352, found: 491.15317.

**1-(diphenylphosphino)-10-(4-methoxyphenyl) naphthalene (24):** as a yellow solid (58%, 149 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.92 (t,  $J = 7.2$  Hz, 2H), 7.87 (d,  $J = 6.8$  Hz, 1H), 7.80 (d,  $J = 7.2$  Hz, 1H), 7.41–7.35 (m, 3H), 7.28–7.20 (m, 7H), 7.03 (m, 6H), 6.67 (d,  $J = 8.6$  Hz, 2H), 3.84 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-8.5$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 159.2, 141.9 (d,  $J_{\text{PC}} = 1.2$  Hz), 139.4, 139.1 (d,  $J_{\text{PC}} = 15.3$  Hz), 139.0, 138.3, 137.5, 137.0, 136.8 (d,  $J_{\text{PC}} = 30.4$  Hz), 134.8, 134.7, 134.2 (d,  $J_{\text{PC}} = 20.7$  Hz), 133.4 (d,  $J_{\text{PC}} = 5.7$  Hz), 132.6 (d,  $J_{\text{PC}} = 20.4$  Hz), 132.2, 132.1 (d,  $J_{\text{PC}} = 5.9$  Hz), 128.4, 128.3 (d,  $J_{\text{PC}} = 6.6$  Hz), 128.1, 127.6, 121.6, 121.3, 119.9, 119.7, 113.1, 55.5. HRMS + p ESI (m/z)  $[\text{M}+\text{Na}]^+$  calcd.: 515.15352, found: 515.15392.

**1-(diphenylphosphino)-10-(4-methoxyphenyl) naphthalene (25):** as a yellow solid (90%, 198 mg)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.91 (t,  $J = 8.3$  Hz, 2H), 7.50 (t,  $J = 7.5$  Hz, 1H), 7.36–7.23 (m, 2H), 7.26–7.20 (m, 2H), 7.20 (m, 5H), 7.01–6.95 (m, 6H), 6.63 (d,  $J = 8.5$  Hz, 2H), 3.81 (s, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =  $-8.10$  (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) =

159.1, 141.2 (d,  $J_{PC} = 2.3$  Hz), 139.8 (d,  $J_{PC} = 18.0$  Hz), 137.3, 135.9 (d,  $J_{PC} = 5.4$  Hz), 135.6, 135.4, 135.4, 135.0, 134.0 (d,  $J_{PC} = 20.8$  Hz), 132.1 (d,  $J_{PC} = 6.8$  Hz), 130.9, 130.4, 128.8, 128.1 (d,  $J_{PC} = 6.4$  Hz), 125.3, 124.9, 113.0, 55.4. HRMS + p ESI (m/z) [M+Na]<sup>+</sup> calcd.: 441.13787, found: 441.13769.

**1-(diphenylphosphino)-10-(1-pyrene) naphthalene (26):** as a yellow solid (57%, 152 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.16 (d,  $J = 8.7$  Hz, 1H), 8.10–8.00 (m, 5H), 7.96 (t,  $J = 7.6$  Hz, 1H), 7.90 (d,  $J = 7.8$  Hz, 1H), 7.69–7.57 (m, 3H), 7.49 (d,  $J = 8.5$  Hz, 1H), 7.43–7.32 (m, 2H), 7.20 (t,  $J = 7.9$  Hz, 1H), 7.17–7.09 (m, 3H), 6.83 (t,  $J = 7.4$  Hz, 1H), 6.70 (t,  $J = 8.3$  Hz, 2H), 6.64 (t,  $J = 6.9$  Hz, 2H), 6.35 (t,  $J = 8.2$  Hz, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ (ppm) = -9.57 (s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 139.6 (d,  $J_{PC} = 4.2$  Hz), 139.4 (d,  $J_{PC} = 17.1$  Hz), 138.7 (d,  $J_{PC} = 4.6$  Hz), 138.4 (d,  $J_{PC} = 18.3$  Hz), 137.5, 136.4 (d,  $J_{PC} = 21.2$  Hz), 135.7 (d,  $J_{PC} = 29.9$  Hz), 135.0 (d,  $J_{PC} = 4.7$  Hz), 133.5 (d,  $J_{PC} = 22.7$  Hz), 133.4 (d,  $J_{PC} = 24.0$  Hz), 131.9, 131.6, 131.3 (d,  $J_{PC} = 8.1$  Hz), 131.2 (d,  $J_{PC} = 12.1$  Hz), 130.8, 129.6 (d,  $J_{PC} = 7.5$  Hz), 129.6 (d,  $J_{PC} = 1.8$  Hz), 128.0 (d,  $J_{PC} = 6.2$  Hz), 128.0, 127.7, 127.7 (d,  $J_{PC} = 2.6$  Hz), 127.3, 127.0, 126.0, 125.8, 125.6, 125.1, 124.9 (d,  $J_{PC} = 1.7$  Hz), 124.7, 124.1. HRMS + p ESI (m/z) [M+Na]<sup>+</sup> calcd.: 535.15916, found: 535.15814.

**Synthesis of the rhodium complex A:** In an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with 1-pyrene phosphine (0.259 mmol, 1 equiv, 100 mg), the dimeric rhodium [RhCl<sub>2</sub>Cp\*]<sub>2</sub> (0.129 mmol, 0.5 equiv, 80 mg), and degassed before addition of CH<sub>2</sub>Cl<sub>2</sub> (0.25 M, 10 ml). The solution was stirred at 60 °C under argon for 4 h. The solvent was removed in vacuum to give the corresponding rhodium complex as a reddish solid (99%, 145 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.77 (d,  $J = 9.5$  Hz, 1H), 8.27 (d,  $J = 7.6$  Hz, 1H), 8.21 (t,  $J = 8.1$  Hz, 2H), 8.12 (dd,  $J = 8.7$  and 17.5 Hz, 2H), 8.09–8.04 (m, 1H), 7.98 (d,  $J = 9.3$  Hz, 1H), 7.90–7.76 (m, 3H), 7.52–7.40 (m, 3H), 7.18–7.10 (m, 2H), 1.23 (s, 15H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 32.2 (d,  $J_{PRh} = 144.6$  Hz). Insolubility troubles precluded proper NMR, especially for <sup>13</sup>C NMR. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 135.0, 133.6, 133.5, 130.7, 129.7, 129.3, 129.2, 129.1, 128.1, 127.3, 126.7, 126.2, 124.3, 123.7, 9.1, 1.2. HRMS + p ESI (m/z) [M-HCl-Cl]<sup>+</sup> calcd.: 623.13694, found: 623.13590.

**Synthesis of the rhodium metallacycle B:** An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with 1-pyrene phosphine (0.259 mmol, 1 equiv, 100 mg), the dimeric rhodium [RhCl<sub>2</sub>Cp\*]<sub>2</sub> (0.129 mmol, 0.5 equiv, 80 mg), KOAc (0.777 mmol, 4 equiv, 76 mg), and degassed before addition of CH<sub>2</sub>Cl<sub>2</sub> (0.25 M, 10 ml). The solution was stirred at 60 °C under argon for 4 h. The solvent was removed in vacuum to give the corresponding rhodium complex, which was further purified through a flash chromatography packed with silica gel and eluted with a mixture of CH<sub>2</sub>Cl<sub>2</sub>:diethyl ether (9:1) and by crystallization operated using CH<sub>2</sub>Cl<sub>2</sub> solution and slow addition of heptane as a reddish solid (80%, 129 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.40 (s, 1H), 8.32–8.24 (m, 3H), 8.21 (dt,  $J = 4.9$  and 10.4 Hz, 3H), 8.16–8.12 (m, 2H), 8.06 (t,  $J = 7.6$  Hz, 1H), 7.58 (d,  $J = 5.1$  Hz, 3H), 7.38 (t,  $J = 7.3$  Hz, 1H), 7.30 (t,  $J = 8.4$  Hz, 2H), 7.06–7.00 (m, 2H), 1.68 (s, 15H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 66.4

(d,  $J_{PRh} = 161$  Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 164.5 (dd,  $J = 10.2$  and 32.1 Hz), 151.0 (dd,  $J = 1.6$  and 37.4 Hz), 136.3 (dd,  $J = 1.0$  and 44.6 Hz), 135.8 (d,  $J = 1.4$  Hz), 135.7 (d,  $J = 10.8$  Hz), 133.6 (d,  $J = 2.1$  Hz), 133.2, 132.5 (d,  $J = 9.8$  Hz), 132.1 (dd,  $J = 2.4$  and 33.0 Hz), 131.1, 131.0 (dd,  $J = 2.4$  and 133.0 Hz), 129.6 (d,  $J = 47.0$  Hz), 129.3, 128.4, 128.4 (dd,  $J = 10.3$  and 23.0 Hz), 126.3, 126.1, 124.9 (d,  $J = 7.6$  Hz), 123.9, 123.7 (d,  $J = 17.5$  Hz), 123.1, 122.6, 100.6 (dd,  $J = 3.2$  and 4.8 Hz), 9.3. HRMS + p ESI (m/z) [M-Cl]<sup>+</sup> calcd.: 623.13749, found: 623.13667.

**Synthesis of the rhodium cationic metallacycle C:** An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with metallacycle **B** (0.076 mmol, 1 equiv, 49.8 mg), 1-(diphenylphosphino) pyrene (**1**) (0.076 mmol, 1 equiv, 30.5 mg), KPF<sub>6</sub> (0.152 mmol, 2 equiv, 28 mg), and degassed before addition of a solution MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1/1, 0.25 M, 3 ml). The solution was stirred at RT under argon overnight. The solvent was removed in vacuum to give the corresponding rhodium complex, which was further purified by crystallization operated using CH<sub>2</sub>Cl<sub>2</sub> solution and slow addition of heptane as a reddish solid (60%, 46 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.77 (dd,  $J = 17.8$ , 7.8 Hz, 1H), 8.51 (d,  $J = 7.6$  Hz, 1H), 8.41 (d,  $J = 7.6$  Hz, 2H), 8.36 (d,  $J = 8.9$  Hz, 1H), 8.34–8.29 (m, 2H), 8.28 (s, 1H), 8.25–8.20 (m, 2H), 8.12 (d,  $J = 8.9$  Hz, 1H), 7.97–7.91 (m, 3H), 7.79–7.73 (m, 2H), 7.67 (t,  $J = 7.9$  Hz, 1H), 7.42 (m, 4H), 7.33–7.28 (m, 2H), 7.23 (m, 3H), 6.51 (d,  $J = 9.5$  Hz, 1H), 6.42 (t,  $J = 7.3$  Hz, 1H), 1.43 (t,  $J = 3.0$  Hz, 15H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 56.1 (dd,  $J_{PP} = 38.3$  Hz,  $J_{PRh} = 146.8$  Hz), 32.6 (dd,  $J_{PP} = 38$  Hz,  $J_{PRh} = 140$  Hz), -133.5 (PF<sub>6</sub>, hept,  $J_{PF} = 712$  Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 140.7, 140.4, 139.5 (d,  $J_{PC} = 3.1$  Hz), 135.4 (d,  $J_{PC} = 2.4$  Hz), 133.9, 133.3, 133.2, 132.6 (d,  $J_{PC} = 8.2$  Hz), 132.1, 131.9, 131.5 (d,  $J_{PC} = 3.8$  Hz), 131.1, 131.0, 130.5 (d,  $J_{PC} = 2.8$  Hz), 130.3, 129.9, 129.8, 129.7, 129.2 (d,  $J_{PC} = 10.2$  Hz), 129.1 (d,  $J_{PC} = 3.2$  Hz), 128.9 (d,  $J_{PC} = 10.6$  Hz), 128.3 (d,  $J_{PC} = 9.4$  Hz), 127.9, 127.6 (d,  $J_{PC} = 4.1$  Hz), 127.5 (d,  $J_{PC} = 16.1$  Hz), 126.9, 126.8, 126.7, 125.8 (d,  $J_{PC} = 8.2$  Hz), 125.2, 124.3 (d,  $J_{PC} = 16.7$  Hz), 124.1, 123.7, 122.8, 106.2, 31.1, 9.7. HRMS + p ESI (m/z) [M-2H-e]<sup>+</sup> calcd.: 1009.25938, found: 1009.25943.

**Synthesis of rhodium metallacycle D:** An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with the metallacycle **B** (0.026 mmol, 1 equiv, 100 mg), 4-bromoanisole (0.040 mmol, 1.5 equiv, 5 μl), K<sub>3</sub>PO<sub>4</sub> (0.052 mmol, 2 equiv, 11.0 mg), KPF<sub>6</sub> (0.052 mmol, 2 equiv, 9.6 mg), and degassed before addition of CH<sub>2</sub>Cl<sub>2</sub> (0.25 M, 10 ml). in trifluoromethylbenzene (0.16 M, 3 ml). The mixture was stirred at reflux under argon during 18 h. After extraction using a CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O mixture, the organic layer was concentrated in vacuum to give the corresponding rhodium complex, which was further purified by crystallization using a CH<sub>2</sub>Cl<sub>2</sub> solution and heptane as a reddish solid (45%, 7 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.27 (s, 1H), 8.20–8.12 (m, 7H), 8.08 (dd,  $J = 4.0$ , 8.3 Hz, 2H), 7.98 (t,  $J = 7.6$  Hz, 1H), 7.51 (m,  $J = 4.6$ , 3H), 7.33–7.29 (m, 1H), 7.22 (td,  $J = 2.2$  and 7.8 Hz, 2H), 6.94 (t,  $J = 10.9$  Hz, 2H), 1.68 (s, 15H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 65.3 (d,  $J_{PRh} = 161.7$  Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 136.7, 135.9 (d,  $J_{PC} = 10.6$  Hz), 133.6, 133.1, 132.6 (d,  $J_{PC} = 9.8$  Hz), 131.1, 130.9, 129.8,

129.3, 128.6, 128.3 (d,  $J_{PC} = 7.3$  Hz), 128.2 (d,  $J_{PC} = 6.7$  Hz), 126.4, 126.1, 124.8, 124.8, 123.8, 123.1, 122.6, 100.6, 31.1, 9.6. HRMS + p ESI (m/z) [M-Br]<sup>+</sup> calcd.: 623.13694, found: 623.13525.

**Synthesis of the pyrenylphosphine selenides.**<sup>[20]</sup> A round flask (50 ml) equipped with a magnetic stirring bar was charged with 50 mg (0.125 mmol) of phosphine and an excess of elemental selenium powder (1.25 mmol, 100 mg) in 20 ml of dichloromethane. The solution was stirred at room temperature overnight, and the mixture was filtrated on Celite and rinsed with dichloromethane. The solvent was removed under vacuum to give the corresponding selenide phosphine.

**1-(diphenylphosphino)pyrene selenide (27):**<sup>[20]</sup> as a yellow solid (99%, 57 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.83 (d,  $J = 9.3$  Hz, 1H), 8.23 (dd,  $J = 7.6$  and 14.2 Hz, 2H), 8.16 (d,  $J = 8.9$  Hz, 1H), 8.06–8.00 (m, 4H), 7.91 (dd,  $J = 7.4$  and 13.7 Hz, 4H), 7.61 (dd,  $J = 8.0$  and 14.9 Hz, 1H), 7.54 (t,  $J = 7.1$  Hz, 2H), 7.47 (t,  $J = 7.5$  Hz, 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 31.7 ( $J_{PSe} = 722$  Hz).

**1-(diphenylphosphino)-10-(4-methoxyphenyl) pyrene selenide (28):** as a yellow solid (99%, 71 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.24–2.18 (m, 4H), 8.08 (t,  $J = 8.6$  Hz, 2H), 8.02 (t,  $J = 7.6$  Hz, 1H), 7.91 (s, 1H), 7.44 (dd,  $J = 7.7$  and 13.1 Hz, 4H), 7.31 (t,  $J = 7.2$  Hz, 2H), 7.22–7.20 (m, 4H), 7.03 (sb, 2H), 6.50 (sb, 2H), 3.80 (s, 3H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ = 38.8 ( $J_{PSe} = 750$  Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 139.3 (d,  $J_{PC} = 4.4$  Hz), 135.1, 134.9 (d,  $J_{PC} = 7.1$  Hz), 133.5 (d,  $J_{PC} = 11.8$  Hz), 133.0 (d,  $J_{PC} = 6.2$  Hz), 132.2, 131.9 (d,  $J_{PC} = 10.1$  Hz), 131.3, 131.1, 130.8, 130.5 (d,  $J_{PC} = 2.8$  Hz), 129.5, 128.4 (d,  $J_{PC} = 15.8$  Hz), 128.1 (d,  $J_{PC} = 12.3$  Hz), 127.2, 126.9, 126.7 (d,  $J_{PC} = 10.5$  Hz), 126.4, 126.0, 126.0, 125.4, 124.0 (d,  $J_{PC} = 14.2$  Hz), 123.5 (d,  $J_{PC} = 0.7$  Hz), 113.7, 55.3. HRMS + p ESI (m/z) [M+H]<sup>+</sup> Calcd.: 573.08865, Found: 573.08541.

**1-(diphenylphosphino)-10-(4-acetylphenyl) pyrene selenide (29):** as a yellow solid (99%, 75 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.33 (d,  $J = 7.5$  Hz, 1H), 8.30–8.09 (m, 6H), 8.03 (s, 1H), 7.55 (sb, 2H), 7.46 (dd,  $J = 7.8$  and 13.2 Hz, 4H), 7.39 (t,  $J = 7.1$  Hz, 2H), 7.31–7.23 (m, 6H), 2.64 (s, 3H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ = 38.70 ( $J_{PSe} = 749$  Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 198.0, 149.2 (d,  $J_{PC} = 4.9$  Hz), 139.4 (d,  $J_{PC} = 5.7$  Hz), 138.2 (d,  $J_{PC} = 15.9$  Hz), 135.9, 135.6, 135.1 (d,  $J_{PC} = 23.1$  Hz), 133.7, 133.5, 132.8 (d,  $J_{PC} = 26.7$  Hz), 132.0, 131.8, 131.3, 130.6 (d,  $J_{PC} = 7.1$  Hz), 130.1, 128.3, 128.3, 128.3, 128.2, 127.7, 126.5, 126.2 (d,  $J_{PC} = 5.7$  Hz), 125.9, 125.7 (d,  $J_{PC} = 32.7$  Hz), 124.2 (d,  $J_{PC} = 1.5$  Hz), 26.8. HRMS + p ESI (m/z) [M+Na]<sup>+</sup> calcd.: 607.07059, found: 607.07010.

**1-(diphenylphosphino)-10-(1-pyrenyl) pyrene selenide (30):** as a yellow solid (99%, 82 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.98 (s, 1H), 8.35 (d,  $J = 7.5$  Hz, 1H), 8.34–8.28 (m, 3H), 8.19 (d,  $J = 8.9$  Hz, 1H), 8.16–8.02 (m, 5H), 7.96 (t,  $J = 8.8$  Hz, 3H), 7.70 (dd,  $J = 8.0$  and 15.8 Hz, 1H), 7.45 (d,  $J = 9.3$  Hz, 1H), 7.33 (t,  $J = 7.2$  Hz, 1H), 7.22–7.09 (m, 6H), 6.59 (d,  $J = 8.5$  Hz, 1H), 6.18 (sb, 2H), 6.05 (sb, 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 38.3 ( $J_{PSe} = 735$  Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 138.7 (d,  $J_{PC} = 5.5$  Hz), 137.6, 135.9 (d,  $J_{PC} = 8.7$  Hz), 135.0, 134.0 (d,  $J_{PC} = 4.7$  Hz), 134.0 (d,  $J_{PC} = 34.7$  Hz), 132.5 (d,  $J_{PC} = 9.9$  Hz), 131.3, 132 (sb), 131.1, 131.0, 130.7 (d,  $J_{PC} = 2.8$  Hz), 130.5, 130.4, 130.0 (sb), 129.8 (sb), 129.2 (d,  $J_{PC} =$

3.0 Hz), 128.2 (d,  $J_{PC} = 12.2$  Hz), 127.5, 127.3, 127.2, 127.0, 127.0, 126.6 (d,  $J_{PC} = 10.4$  Hz), 126.6, 126.3 (d,  $J_{PC} = 13.2$  Hz), 125.9, 125.4, 125.3, 125.2, 124.8, 124.7, 124.5, 123.9, 123.4, 123.3 (d,  $J_{PC} = 13.0$  Hz). HRMS + p ESI (m/z) [M+H]<sup>+</sup> calcd.: 667.10938, found: 667.10751.

**1-(diphenylphosphino)-10-(4-methoxyphenyl)**

**phenanthrene selenide (31):** as a yellow solid (99%, 68 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.76 (d,  $J = 8.2$  Hz, 1H), 8.72 (d,  $J = 8.4$  Hz, 1H), 8.20 (d,  $J = 20.6$  Hz, 1H), 7.77 (t,  $J = 7.7$  Hz, 1H), 7.72–7.66 (m, 2H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.43–7.37 (m, 5H), 7.30–7.25 (m, 2H), 7.17 (td,  $J = 3.1$  and 7.8 Hz, 4H), 6.15 (s, 2H), 3.89 (s, 3H), 3.75 (s, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 40.0 ( $J_{PSe} = 753$  Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 152.4, 142.3 (d,  $J_{PC} = 2.7$  Hz), 141.2 (d,  $J_{PC} = 11.1$  Hz), 137.4, 137.2, 132.2 (d,  $J_{PC} = 8.0$  Hz), 131.8, 131.7, 130.9, 130.5 (d,  $J_{PC} = 2.8$  Hz), 130.0 (d,  $J_{PC} = 15.5$  Hz), 129.6, 129.4, 128.8, 128.3 (d,  $J_{PC} = 6.3$  Hz), 128.2, 128.0 (d,  $J_{PC} = 12.4$  Hz), 127.6, 126.8, 123.0, 122.1, 108.0, 60.9, 55.8. HRMS + p ESI (m/z) [M+H]<sup>+</sup> calcd.: 549.08865, found: 549.08871.

**Synthesis of the Au(I)Cl complexes (E-G).**<sup>[22d]</sup> A round flask (50 ml) equipped with a magnetic stirring bar was charged with 100 mg of phosphine (0.17 mmol) and 50 mg of gold precursor [AuCl(SMe<sub>2</sub>)] (0.17 mmol) in 5 ml dichloromethane. The solution was stirred at room temperature overnight, and the mixture was filtrated on Celite and washed with dichloromethane. The solvent was removed under vacuum to give the corresponding complex. Crystallization was operated using CH<sub>2</sub>Cl<sub>2</sub> solution, and slow addition of heptane in the case of complex G.

**Au(I)Cl complex (E) stabilized by 1-(diphenylphosphino)-10-(4-methoxyphenyl) pyrene (2):**

as a yellow solid (99%, 116 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.31 (d,  $J = 7.6$  Hz, 1H), 8.26 (d,  $J = 8.6$  Hz, 2H), 8.11 (t,  $J = 7.8$  Hz, 3H), 8.01 (s, 1H), 7.77 (dd,  $J = 8.1$  and 14.8 Hz, 1H), 7.47 (t,  $J = 6.4$  Hz, 2H), 7.41–7.31 (m, 8H), 7.11 (d,  $J = 8.0$  Hz, 2H), 6.64 (d,  $J = 8.5$  Hz, 2H), 3.89 (s, 3H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 35.2 (s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 159.1, 138.6 (d,  $J_{PC} = 5.0$  Hz), 134.9 (d,  $J_{PC} = 9.1$  Hz), 134.8 (d,  $J_{PC} = 8.6$  Hz), 134.7 (d,  $J_{PC} = 1.1$  Hz), 134.1, 134.0, 133.6 (d,  $J_{PC} = 2.6$  Hz), 133.2, 132.8, 132.2, 131.8 (d,  $J_{PC} = 1.7$  Hz), 131.4 (d,  $J_{PC} = 2.3$  Hz), 131.1 (d,  $J_{PC} = 0.7$  Hz), 130.5, 128.9 (d,  $J_{PC} = 11.9$  Hz), 127.1 (d,  $J_{PC} = 8.4$  Hz), 126.8, 126.7 (d,  $J_{PC} = 9.1$  Hz), 124.4 (d,  $J_{PC} = 11.6$  Hz), 123.3, 122.5, 122.0, 114.6, 55.5. HRMS + p ESI (m/z) [M-Cl]<sup>+</sup> calcd.: 689.130863, found: 689.130851.

**Au(I)Cl complex (F) stabilized by 1-(diphenylphosphino)-10-(4-acetylphenyl) pyrene (5):**

as a yellow solid (99%, 118 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.36 (d,  $J = 7.6$  Hz, 1H), 8.33–8.27 (m, 2H), 8.18–8.12 (m, 3H), 8.09 (s, 1H), 7.81 (dd,  $J = 8.1$  and 14.6 Hz, 1H), 7.67 (d,  $J = 8.2$  Hz, 2H), 7.50 (t,  $J = 7.1$  Hz, 2H), 7.40–7.31 (m, 10H), 2.70 (s, 3H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 34.8 (s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 197.9, 146.7, 137.9 (d,  $J_{PC} = 5.3$  Hz), 135.5, 135.1 (d,  $J_{PC} = 8.7$  Hz), 134.1, 134.1 (d,  $J_{PC} = 3.6$  Hz), 134.0, 133.7 (d,  $J_{PC} = 2.6$  Hz), 132.1, 131.7 (d,  $J_{PC} = 2.4$  Hz), 131.6, 131.1 (d,  $J_{PC} = 0.8$  Hz), 130.7 (d,  $J_{PC} = 1.7$  Hz), 130.2, 130.0, 129.1, 129.1 (d,  $J_{PC} = 12.1$  Hz), 127.4 (d,  $J_{PC} = 10.2$  Hz), 127.3, 124.2, 126.7 (d,  $J_{PC} = 9.2$  Hz), 124.8 (d,  $J_{PC} = 11.4$

Hz), 123.6 (d,  $J_{PC}$  = 1.0 Hz), 122.3, 121.8, 27.0. HRMS + p ESI (m/z) [M-Cl]<sup>+</sup> calcd.: 701.13086, found: 701.13055. **Au(DCl) complex (G) stabilized by 1-(diphenylphosphino)-10-(1-pyrenyl) pyrene (15):** as a yellow solid (85%, 113 mg) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 9.28 (d,  $J$  = 7.7 Hz, 1H), 8.39–8.29 (m, 4H), 8.19–8.07 (m, 4H), 8.03 (s, 2H), 7.91 (d,  $J$  = 2.1 Hz, 2H), 7.55 (dd,  $J$  = 8.0 and 13.8, 8.0 Hz, 1H), 7.37 (d,  $J$  = 9.3 Hz, 1H), 7.28 (d,  $J$  = 6.2 Hz, 1H), 7.16–7.11 (m, 2H), 6.83 (dd,  $J$  = 7.4 and 13.9 Hz, 2H), 6.76 (dd,  $J$  = 7.8 and 12.4 Hz, 2H), 6.49 (d,  $J$  = 9.3 Hz, 1H), 6.19 (t,  $J$  = 8.8 Hz, 2H), 6.02 (t,  $J$  = 7.3 Hz, 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>):  $\delta$  = 31.0(s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 136.4 (d,  $J_{PC}$  = 3.2 Hz), 136.2, 136.2 (d,  $J_{PC}$  = 12.1 Hz), 133.3, 133.0 (d,  $J_{PC}$  = 10.7 Hz), 133.0, 132.4 (d,  $J_{PC}$  = 12.9 Hz), 130.8 (d,  $J_{PC}$  = 15.1 Hz), 130.7, 130.2 (d,  $J_{PC}$  = 2.5 Hz), 130.2, 130.1 (d,  $J_{PC}$  = 0.9 Hz), 129.6, 129.1, 128.9, 128.7 (d,  $J_{PC}$  = 2.5 Hz), 127.7 (d,  $J_{PC}$  = 11.3 Hz), 126.5 (d,  $J_{PC}$  = 2.2 Hz), 126.3, 126.1, 126.1, 126.0, 125.9, 125.8, 124.9 (d,  $J_{PC}$  = 10.1 Hz), 124.8, 124.3, 124.0, 123.7, 123.6, 123.3 (d,  $J_{PC}$  = 10.6 Hz), 123.0, 122.8, 122.5 (d,  $J_{PC}$  = 0.9 Hz), 120.9, 120.5. HRMS + p ESI (m/z) [M+H]<sup>+</sup> calcd.: 783.15159, found: 783.15187.

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Phosphorus-directed Rhodium-Catalyzed C–H  
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