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Heteropolymetallic Complexes Linked to a 9,10-Dihydroanthracenyl Frame. Ruthenium as Active Spectator for Palladium Reactivity

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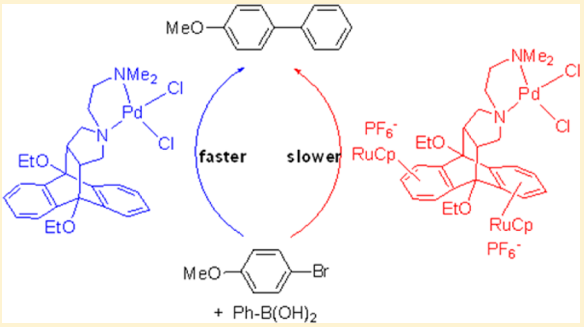
Supporting Information

ABSTRACT: New monometallic Pd(II) (**3**, **4**) and heteropolymetallic Pd(II)/Ru(II) complexes (**5**, **6**) linked to an original 9,10-dihydroanthracenyl−pyrrolidine scaffold were synthesized and fully characterized. For monometallic complexes, *exo*-**3** and *endo*-**4** conformers were exclusively obtained from $Pd(OAc)_2$ and $[PdCl_2(COD)]$, respectively. The formation of the sterically hindered *endo*-**4** was justified by the positive noncovalent intramolecular Cl−π interaction, observed by X-ray diffraction. The reaction of *endo*-**4** with 1 and 2 equiv of $[RuCp(NCMe)_3]PF_6$ led to complexes **5** and **6**, respectively. It is worth noting that lower conversions in the Suzuki−Miyaura coupling were found using **5** and **6** as catalysts, in comparison to those with monometallic palladium complexes. This behavior could be related to the higher stabilization of Pd(II) species for the heteropolymetallic complexes, as proven by electrochemical analyses.



INTRODUCTION

Catalysis represents the key approach to convert raw materials into valuable products. Mimicking nature seems to be the elegant way to conceive polyfunctional assemblies leading to "synergic" catalysts. Imitating biocatalysts, several research groups have developed polymetallic catalysts, finding cooperative effects between the different metal centers.[1] The design of versatile bimetallic catalysts containing robust ancillary frames seems to be an appropriate strategy for cooperative purposes.[2] The successful design of polymetallic catalysts, most of them bimetallic, where metals are linked to the same structure ligand, has been accomplished, proving their positive cooperative effect in a large number of organic transformations.[3] In this context, N-heterocyclic carbenes appear as suitable ligands.[4] In the last years, the Peris group has developed homo- and heterobimetallic complexes containing the straightforward 1,2,4-trimethyltriazolyldiylidene ligand acting as a Janus-type skeleton, able to coordinate two different metals.[5] Electrochemical studies proved weak electronic coupling between the two metal centers.[5e]

However, π interactions between the ligand and metals are hardly represented.[6−8] Among them, the most relevant bimetallic systems are those described by the Marks group, which are constituted by constrained binuclear complexes;[7] the metal is coordinated to an indenyl or cyclopentadienyl moiety by π coordination and a nitrogen atom by a dative bond. An interesting effect was also observed by the fragment "$Mn(CO)_3$" coordinated through a π interaction to a palladium phosphino oxazoline complex, increasing both the activity and selectivity of the Pd-catalyzed catalytic process in relation to the related Mn-free monometallic palladium complex.[6] A similar behavior was observed in Ru-catalyzed alkene metathesis reactions upon π coordination of "$Cr(CO)_3$" to the monometallic complex.[8b]

In particular, we have been intrigued by structures containing both aromatic groups able to favor metal π coordination and flexible frameworks assisting metal−ligand dative interactions, with the aim to prepare heteropolymetallic complexes for cooperative effects in catalysis. Triptycene, a rigid molecule containing three aromatic rings, has attracted attention from a coordination standpoint since the pioneering work of Pohl and Willeford in 1970,[9] followed by the independent studies of Mislow[10] and Toyota[11] reporting the first X-ray crystal structures of mono-, bi-, and trimetallic complexes through π interactions with metal fragments such as $Cr(CO)_3$ and $Co_4(CO)_9$;[12] triptycene complexes containing $[RuCp^*]^+$ moieties have been previously described, without a full structural characterization.[13] More recently, triptycene-based phosphane and seleno ligands, able to coordinate transition metals (Pd, Pt, Ir), have found interesting applications in catalysis.[14] The versatility of triptycene led us to consider dihydroanthracene−dicarboximides as appropriate candidates for coordination chemistry purposes, where one of the aromatic groups is replaced by a five-membered ring which allows an easy functionalization.

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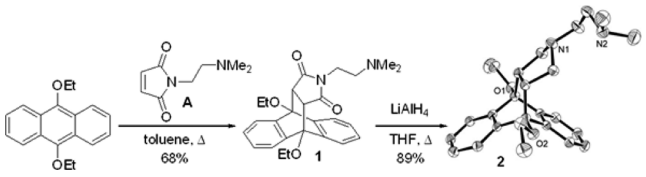
We have reported the first studies concerning the coordination chemistry of functionalized 9,10-dihydroanthracene ligands[15] and their applications in catalysis. Therefore, Pd(II) and Rh(I) monometallic complexes containing chiral phosphite or NHC moieties have been successfully applied in asymmetric Pd-catalyzed allylic alkylations and Rh-catalyzed hydroformylation reactions[16a] and in Rh-catalyzed conjugate additions of unsaturated carbonyls.[16b] Concerning polymetallic complexes, we have been initially interested in the study of the π coordination of these multifunctional ligands, offering different ways to link metallic fragments.[17] Selective synthesis of mono-, bi-, and trimetallic Ru complexes by π coordination was effectively achieved using the organometallic precursor $[RuCp(NCMe)_3]PF_6$, known for its affinity toward η^6 coordination.[18] These studies encouraged us to design heteropolymetallic complexes based on novel scaffolds allowing different coordination modes, in order to search for positive catalytic cooperative effects. In the present work, we describe the synthesis of Pd(II)/Ru(II) polymetallic complexes **5** and **6** starting from the monometallic Pd(II) complex *endo*-**4** and their effect on Pd-catalyzed Suzuki–Miyaura C–C cross-coupling.

RESULTS AND DISCUSSION

Synthesis of Ligands. The diamine ligand **2** was prepared by a two-step sequence on the basis of published methodologies (Scheme 1).[15b] Therefore, the imide **1** was first

Scheme 1. Synthesis of 9,10-Dihydroanthracene-Based Compounds 1 and 2[a]



[a]For **2**, the molecular view is given (ellipsoids drawn at the 50% probability level), where hydrogen atoms are omitted for clarity.

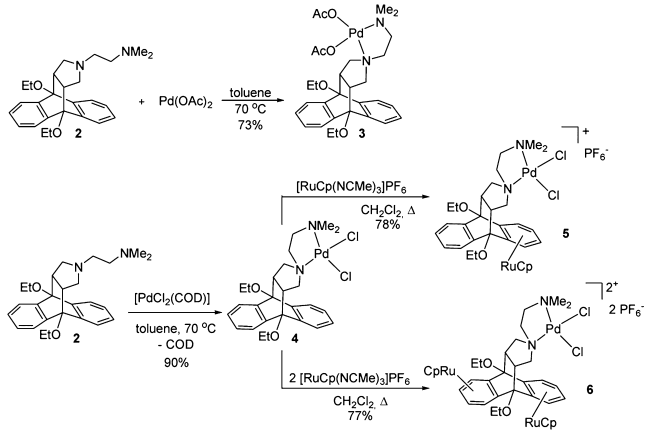
prepared by a [4 + 2] cycloaddition of 9,10-diethoxyanthracene with the *N*,*N*-dimethylethylenemaleimide **A** in toluene under thermal conditions (68% yield). Imide **1** was then reduced by $LiAlH_4$, giving the pyrrolidine **2** in high yield (89%).

Compounds **1** and **2** were fully characterized both in solution (by means of NMR and high-resolution mass spectrometry) and the solid state. Suitable crystals for an X-ray diffraction analysis were obtained for **2** from a diisopropyl ether solution. The heterocycle adopts an envelope conformation, where the nitrogen atom presents an unambiguous pyramidalization ($\sum^{\circ}_{N}$ = 332°). Ethoxide groups of the dihydroanthracenyl skeleton point out of the pyrrolidine cycle (Scheme 1).

Synthesis of Complexes. With the goal of preparing heteropolymetallic complexes, we started by the coordination of Pd(II) precursors to the diamine fragment of **2** by dative nitrogen–metal interactions (complexes **3** and **4**, Scheme 2), pursuing the coordination of $RuCp^+$ fragments to the 9,10-dihydroanthracenyl frame to lead to the corresponding bi- and trimetallic complexes **5** and **6**, respectively (Scheme 2). All of the complexes were fully characterized in solution (NMR) and in the solid state (X-ray diffraction).

First, we isolated monometallic palladium complexes by reaction of ligand **2** with $Pd(OAc)_2$ and $[PdCl_2(COD)]$, giving

Scheme 2. Synthesis of Monometallic Pd(II) Complexes 3 and 4 and Pd(II)/Ru(II) Heteropolymetallic Complexes 5 and 6



the corresponding complexes **3** and **4** in high yields (73 and 90%, respectively). Both complexes gave only one isomer, according to the NMR and X-ray diffraction analyses. The corresponding crystal structures showed a distorted-square-planar geometry around the palladium as expected. The torsion angles between the two five-membered cycles connected by the nitrogen atoms of these structures are 83.46 and 75.89° for **3** and **4**, respectively; the difference observed can be attributed to the steric hindrance for **3** being higher than that for **4**. The structure of **3** showed that the five-membered palladacycle formed by coordination of the two nitrogen atoms of ligand **2** to the palladium atom points out of the 9,10-dihydroanthracenyl backbone, adopting an *exo* arrangement (Figure 1). This

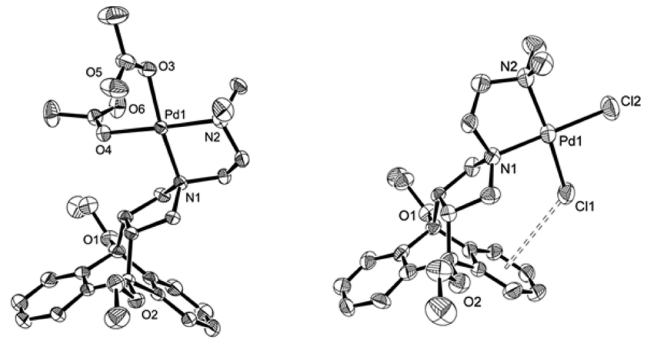


Figure 1. Molecular views (ellipsoids drawn at the 50% probability level) of palladium monometallic complexes **3** (left) and **4** (right). Hydrogen atoms and molecules of solvent are omitted for clarity. For **4**, the dashed line indicates the noncovalent Cl–π interaction: the Cl–π bond length is 3.528(4) Å, and the angle of the Cl–centroid axis to the plane of the ring is 80.2°.

exo conformer is also confirmed in solution by NOE NMR experiments (Figure S1 in the Supporting Information). The *exo* arrangement precludes the formation of a trimetallic complex. The calculated relative energy for the two plausible isomers (DFT level, B3LYP 6-31G*), *exo*-**3** and *endo*-**3**, indicated that the *exo* form is the most stable conformation, probably due to steric reasons (Figure 2).

We then envisaged the use of a less hindered ligand, chlorine instead of acetate, favoring the formation of the desired *endo* conformation. Actually, the *endo*-**4** conformer was exclusively

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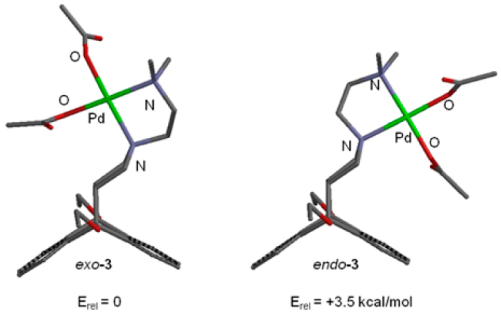

Figure 2. Calculated structures (DFT, B3LYP 6-31G*) for the conformers *exo*-**3** and *endo*-**3**. Hydrogen atoms are omitted for clarity. Energy values are relative to the most stable isomer.

obtained when ligand **2** reacted with $[PdCl_2(COD)]$, as proven by its crystal structure (Figure 1); in solution, only one isomer was also observed (Figure S2 in the Supporting Information). In addition, the X-ray diffraction analysis revealed an intramolecular interaction between one of the chlorine atoms linked to the metal center and one of the aromatic rings of the 9,10-dihydroanthracenyl skeleton. This interaction could be the responsible for the stabilization of the *endo* conformer in relation to the *exo* form (see below for a more detailed discussion).

Due to the different coordination behavior between both palladium complexes **3** and **4**, only that adopting the *endo* conformation is appropriate to synthesize bi- and trimetallic complexes (through π interactions between the aromatic rings of the 9,10-dihydroanthracenyl backbone and the electrophilic metallic moiety $RuCp^+$). On the basis of our previous work on the synthesis of homopolymetallic π complexes,[17] we decided to treat **4** with 1 and 2 equiv of $[RuCp(NCMe)_3]PF_6$ to give the corresponding Pd(II)/Ru(II) heteropolymetallic complexes (Scheme 2). Therefore, the palladium complex **4** reacted with $[RuCp(NCMe)_3]PF_6$ under reflux of dichloromethane to selectively afford the bi- (**5**) and trimetallic (**6**) complexes, in high yields (ca. 80%). These two complexes were fully characterized both in solution and in the solid state, in particular by XRD on single crystals (Figure 3). The bimetallic

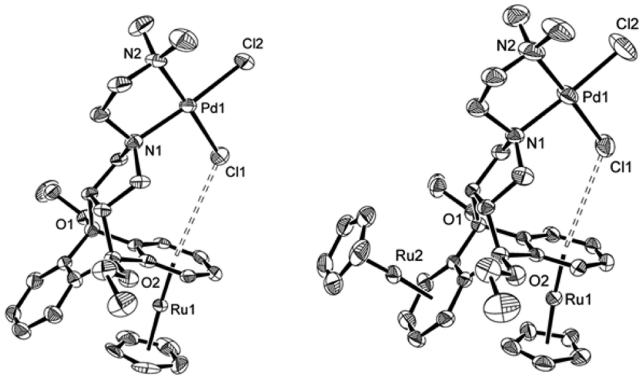

Figure 3. Molecular views (ellipsoids drawn at the 50% probability level) of the cations corresponding to bimetallic **5** (left) and trimetallic **6** (right) complexes. Hydrogen atoms and molecules of solvent are omitted for clarity. Dashed lines indicate the noncovalent Cl–π interactions. For **5**the Cl–π distance is 3.731(3) Å and the angle of the Cl–centroid axis to the plane of the ring is 79.8°; for **6**, the Cl–π distance is 3.628(2) Å and the angle of the Cl–centroid axis to the plane of the ring is 78.9°.

complex **5** was obtained as a mixture of two isomers in a ca. 7/3 ratio (determined by ^1H NMR; see Figure S3 in the Supporting Information). The interaction of 1 equiv of $RuCp^+$ with the complex **4** could lead to three isomers, depending on the coordination to the dissymmetric 9,10-dihydroanthracenyl skeleton. On the basis of the corresponding calculated structures (Figure S4 in the Supporting Information), the two low-energy complexes could be associated with the observed isomers. The most stable isomer corresponds to that observed by X-ray diffraction analysis.

The coordination of the diamine fragment to the metal was proven by $\{^1H,^{15}N\}$-HMBC NMR experiments at natural abundance of the ^{15}N isotope for the ligand **2** and complexes **4** and **5** (unfortunately, complex **6** was not soluble enough for this kind of experiment). As reported for Pd(II) complexes containing N-donor ligands,[19] the nitrogen chemical shifts for complexes are shielded (by ca. 5–7 ppm) in relation to the free ligand (Figure S5 in the Supporting Information).

The spatial arrangements of the three structures having the same metallacycle, **4**–**6**, are quite similar with regard to the palladium coordination, as proven by the relative angle between the two five-membered cycles in the spiro frame (75.89, 75.25, and 78.23° for **4**–**6**, respectively) and the noncovalent Cl–π interaction.

Actually, complexes **4**–**6** seem to exhibit noncovalent intramolecular Cl–π interactions (see above), showing Cl–π distances in the range 3.52–3.73 Å with angles of the Cl–centroid axis to the plane of the ring between 78.9 and 80.2°, comparable to those reported for intermolecular interactions between chloride anion and pyridine rings in polymetallic copper complexes (3.46–3.69 Å, 75–82°).[20] However, the interactions observed for complexes **4**–**6** are weaker than those observed involving electron-deficient aromatic rings such as triazine[21] or imidazolyl rings[22] but similar to those observed for the intramolecular Cl–π interaction, where the aromatic ring is a pentafluorophenoxide group (Cl–π distance 3.725 Å).[23]

The noncovalent Cl–π interactions are proposed to occur from a negatively charged species (in our case the chloride ligand) to an electron-deficient aromatic ring (for us, the six-membered ring of the 9,10-dihydroanthracenyl frame) by Coulombic attraction.[24] Calculations of charges (natural atomic population, NAP, by DFT M06 6-31G*) of the aromatic ring close to the chloride ligand indicated that, even for the monometallic complex **4**, the net charge of the six-membered ring is positive (NAP data: for **4**, +0.0260; for **5**, +0.2403; for **6**, +0.2817), proving the electron-deficient character of this moiety and consequently favoring the Cl–π contact.

Palladium Reactivity. With the aim of analyzing the effect of $RuCp^+$ fragments in the palladium reactivity, we evaluated the catalytic activity of complexes **3**–**6** in the Suzuki–Miyaura cross-coupling between 4-bromoanisole and phenylboronic acid as a benchmark reaction, in toluene at 65 °C using 1 mol % of Pd (Table 1). Monometallic complexes **3** and **4** showed a similar catalytic behavior, giving high conversions (91–99%) after 2.5 and 5 h, respectively (entries 1 and 2). While complex **4** exclusively gave the desired product **B** (entry 2), complex **3** led to the formation of byproducts (up to 6% of anisole and biphenyl) together with the major cross-coupling product, **B** (entry 1).

Heteropolymetallic complexes **5** and **6** with one and two Ru fragments, respectively, exhibited lower conversions than **4** (entries 3 and 4). After 5 h of reaction, 27% and 11% of conversion were respectively achieved. Longer times did not

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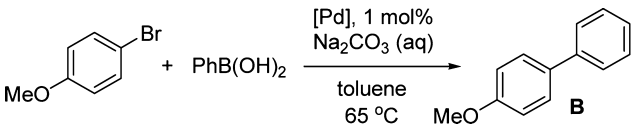
Table 1. Pd-Catalyzed Suzuki–Miyaura Cross-Coupling Reactions Using Complexes 3–6 as Catalytic Precursors[a]



entry	complex	conversn (%)[b]	B/biphenyl/anisole (%)[b]
1[c]	3	99	94/4/2
2[d]	4	99	100/0/0
3	5	27	100/0/0
4	6	11	98/2/0

[a]Reaction conditions: 4-bromoanisole/$PhB(OH)_2$/Na_2CO_3/Pd = 100/150/200/1, 2 mL of toluene, 0.5 mL of H_2O, 65 °C, 5 h. [b]Determined by ^1H NMR. [c]Catalytic data for 2.5 h. [d]For 2.5 h, 60% conversion.

improve the catalytic activity. These results are in contrast with those previously reported using pincer ferrocene and ruthenocene bimetallic catalysts[25a,b] and pincer Pd/Ru complexes applied as catalytic precursors in cross-coupling reactions.[25c]

The observed reactivity trend seems to indicate a higher stabilization of Pd(II) species in relation to the corresponding Pd(0) species, when $RuCp^+$ moieties are present. This fact could consequently trigger a catalytic activity decrease in the studied cross-coupling reaction. Following this reasoning, the reduction of Pd(II) to Pd(0) could turn more difficult in the presence of ruthenium fragments. In order to make this behavior clearer, we decided to analyze by voltammetry the different species involved.

Electrochemical Studies. We decided to study the electrochemical behavior of complexes **4**–**6**. In order to evaluate the effect of the ligand skeleton on both metals, we first considered the monometallic palladium complex **4** and monometallic ruthenium complexes **7**[17] and **8** (Figure 4), for

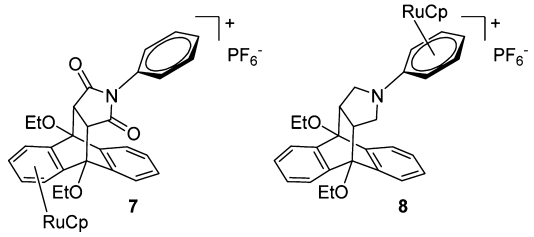


Figure 4. Monometallic Ru(II) complexes **7** and **8**.

comparative purposes. Monometallic ruthenium complexes permitted us to analyze the stability of the involved species when Ru is linked to different kinds of six-membered neutral aromatic rings through metal–π interactions: complex **7** coordinated to an aromatic cycle of the 9,10-dihydroanthracenyl skeleton and complex **8** to a phenyl group present as a substituent of the pyrrolidine heterocycle.

The cyclic voltammogram of complex **8** exhibited an irreversible Ru(II)/Ru(III) oxidation wave at +1.6 V. After the oxidized Ru(III)–**8** species was generated, a reversible wave at +1.1 V was observed, which corresponds to the Ru(III)/Ru(II) process of the organometallic precursor $[RuCp(NCMe)_3]PF_6$ (Figure 5) (for the cyclic voltammogram corresponding to $[RuCp(NCMe)_3]PF_6$, see Figure S6 in the Supporting Information).[26] This fact evidences the lability of

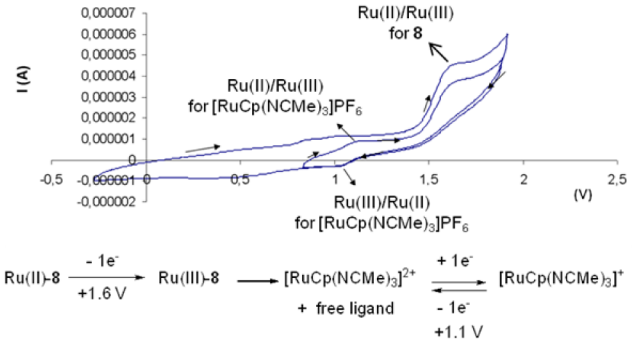


Figure 5. Cyclic voltammogram for the oxidation region (glassy-carbon electrode; scan rate 200 mV s^{-1}) for complex **8** in acetonitrile (top) and a schematic representation of the generated species (bottom).

the CpRu–Ph bond, the ligand being shifted by acetonitrile, used as solvent. In addition, in the reduction potential region, two irreversible waves were observed (at −1.72 and −2.05 V corresponding to Ru(II)/Ru(I) and Ru(I)/Ru(0) processes, respectively), closer to those exhibited by the precursor $[RuCp(NCMe)_3]PF_6$ (see Figure S6 in the Supporting Information). However, complex **7**, coordinated to the ligand through the aromatic moiety of the 9,10-dihydroanthracenyl ligand, showed two irreversible reduction waves, corresponding to Ru(II)/Ru(I) (at −1.76 and −2.1 V), and one irreversible oxidation wave at +2.6 V, associated with the oxidation of the ligand (Figures S7 and S8 in the Supporting Information). No metal deposition was observed. These facts point to a higher stabilization of the Ru(II) species and also a higher robustness of the Ru–(aromatic cycle) η^6 bond when the metal is coordinated to the 9,10-dihydroanthracenyl fragment complex **7** rather than through the phenyl group as in complex **8** (see Figure S9 in the Supporting Information for comparisons among **7**, **8**, and the precursor $[RuCp(NCMe)_3]PF_6$).

With regard to palladium, both the precursor $[PdCl_2(COD)]$ and the monometallic complex **4** only exhibited one wave corresponding to the Pd(II)/Pd(0) reduction (at −0.44 and −1.30 V, respectively);[27] actually, this reduction becomes more difficult upon coordination to the ligand **2** (see Figure S10 in the Supporting Information). For both complexes, palladium deposition occurred.

For the heteropolymetallic complexes **5** and **6**, as expected, three irreversible reduction waves were observed corresponding to Pd(II)/Pd(0), Ru(II)/Ru(I), and Ru(I)/Ru(0), at potentials close to those observed for **4** and **7** (Figure 6; see Figure S11 in the Supporting Information for the full electrochemical study of complexes **5** and **6**). However, no palladium deposition was observed. In addition, with regard to the Pd(II)/Pd(0) reduction, the waves were broader than those observed for **4**, pointing to a higher stabilization of the Pd(II) oxidation state when the $RuCp^+$ fragment is present in the corresponding complexes. The NAP calculated charges on metal, nitrogen, and chlorine atoms remain practically unchanged for complexes **4**–**6**, in agreement with the similar potentials observed (Table S1 in the Supporting Information).

This electrochemical behavior is in agreement with the low catalytic reactivity observed for the C–C cross-coupling when **5** and **6** were involved as catalytic precursors in relation to **4**, because the Pd(II) oxidation state is more stable toward

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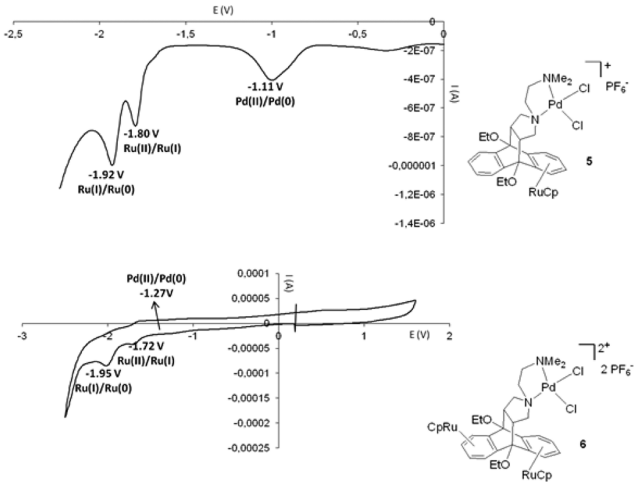

Figure 6. Electrochemical study of the oxidation potential region of complexes **5** and **6**: (top) scanning voltammogram (Pt electrode; 20 mV s^{-1}) for complex **5**; (bottom) cyclic voltammogram (glassy-carbon electrode; 5000 mV s^{-1}) for complex **6**.

reduction and then the formation of Pd(0) active catalytic species turns more difficult.

CONCLUDING REMARKS

In this work, we have described the synthesis of new monometallic palladium complexes (*exo*-**3** and *endo*-**4**), linked to the ligand **2** containing a 9,10-dihydroanthracenyl−pyrrolidine skeleton. The *endo*-**4** conformer was exclusively formed, probably due to the presence of a positive noncovalent intramolecular Cl−π interaction, observed by X-ray diffraction analyses. This complex **4** led selectively to the formation of bi- and triheteropolymetallic complexes (**5** and **6**). The catalytic activity of **5** and **6** was compared to that observed using monometallic complexes **3** and **4**, in Suzuki−Miyaura cross coupling, in order to analyze the effect of the $RuCp^+$ fragment on the Pd-assisted reactivity. Heteropolymetallic complexes showed catalytic activity lower than that observed using monometallic palladium systems. It seems that a higher stabilization of the Pd(II) center occurs in the presence of electrophilic $RuCp^+$ moieties in the complex, as proven by the electrochemical study. The coordination of $RuCp^+$ in the frame increases the stability of Pd(II) species, and consequently the reduction to give Pd(0) catalytically active species becomes more difficult.

Further studies concerning heteropolymetallic complexes to be applied in multistep catalytic processes looking for cooperative effects are currently under way.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out under argon using standard Schlenk techniques and high vacuum, unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS, MBraun). All other reagents were used as received from commercial suppliers. NMR spectra were recorded on 300 or 500 MHz spectrometers at room temperature unless otherwise stated. IR spectra were recorded on a FTIR instrument. Elemental analyses were carried out at the University of Barcelona. The mass spectra were recorded on instruments to analyze the samples by chemical ionization or electrospray; for all metallic complexes, PF_6^- was detected as a single counteranion. Theoretical studies were carried out using the following software: SPARTAN'14 for Windows and Linux (Wavefunction, Inc. 18401 Von Karmaan Avenue, Suite 307, Irvine, CA 92612, USA). Calculations were carried out with density functional B3LYP or M06 using the basis set 6-31G*.

Synthesis of Maleimide A. To a solution of maleic anhydride (999.1 mg, 10.195 mmol) in toluene (120 mL) was added *N,N*-dimethylethylenediamine (1.1 mL, 10.195 mmol). The solution was refluxed over molecular sieves for 24 h. The reaction mixture was then cooled to room temperature and filtered. After the evaporation of the solvent, compound **A** was isolated as a yellow solid (904.2 mg, 5.382 mmol, 53%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67 (s, 2H, C*H*), 3.62 (t, $^3J_{H-H}$ = 6.6 Hz, 2H, CH_2), 2.47 (t, ^3J = 6.6 Hz, 2H, CH_2), 2.24 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 170.8 (C═O), 134.1 (CH), 57.0 (CH_2), 45.4 (CH_3), 35.8 (CH_2).

Synthesis of 1. To a solution of 9,10-diethoxyanthracene (408.0 mg, 1.534 mmol) in toluene (80 mL) was added maleimide **A** (258.0 mg, 1.534 mmol). The solution was refluxed for 96 h. After evaporation of the solvent the crude reaction mixture was purified by column chromatography (eluent dichloromethane/methanol, from 100/0 to 98/2, R_f = 0.3). The compound was isolated as a white solid (449.3 mg, 1.035 mmol, 68%). For NMR labeling, see Figure S12 in the Supporting Information.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (m, 2H, H_{arom}), 7.41 (m, 2H, H_{arom}), 7.21 (m, 2H, H_{arom}), 7.14 (m, 2H, H_{arom}), 4.59 (dq, $^3J_{H-H}$ = 7.0 Hz, $^2J_{H-H}$ = 8.6 Hz, 2H, $H_{23(a)}$, $H_{25(a)}$), 4.15 (dq, $^3J_{H-H}$ = 7.0 Hz, $^2J_{H-H}$ = 8.6 Hz, 2H, $H_{23(b)}$, $H_{25(b)}$), 3.69 (s, 2H, H_{15}, H_{16}), 3.17 (m, 2H, H_{20}), 2.09 (s, 6H, H_{21}, H_{22}), 1.62−1.67 (m, 8H, H_{19}, H_{24}, H_{26}). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 173.7 (C_{17}, C_{18}), 141.3 (C_{11}, C_{12} or C_{13}, C_{14}), 138.3 (C_{11}, C_{12} or C_{13}, C_{14}), 126.7 (CH_{arom}), 126.4 (CH_{arom}), 121.4 (CH_{arom}), 121.3 (CH_{arom}), 79.4 (C_9, C_{10}), 61.0 (C_{23}, C_{25}), 55.2 (C_{19}), 46.4 (C_{15}, C_{16}), 45.1 (C_{21}, C_{22}), 35.8 (C_{20}), 15.3 (C_{24}, C_{26}). IR (KBr, υ cm^{-1}): 3072, 3026 (═C−H), 2971, 2942, 2861, 2825 (C−H), 1701 (C═O), 1458 (C═C), 1150 (C−N), 1077 (C−O). High-resolution mass spectrometry (CI, CH_4, CH_2Cl_2): calcd mass 435.2284, found mass 435.2287 ($C_{26}H_{31}N_2O_4$).

Synthesis of 2. This compound was prepared according to a previously reported procedure.[15b] To a solution of compound **1** (449 mg, 1.035 mmol) in THF (55 mL) at 0 °C was added $LiAlH_4$ (590 mg, 15.52 mmol) in small portions. The reaction mixture was then refluxed for 24 h. The reaction mixture was then cooled to 0 °C, diethyl ether (40 mL) was added, and then Na_2SO_4 aqueous saturated solution was added dropwise. The formed precipitate was filtered off and the filtrate washed three times with water. The combined organic layers were dried on anhydrous Na_2SO_4 and filtered off and the solvent evaporated, leading to a white powder (372.1 mg, 0.916 mmol, 89%). Single crystals suitable for X-ray analysis were obtained from a diisopropyl ether solution of **2**. For NMR labeling, see Figure S12 in the Supporting Information.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (m, 2H, H_5, H_8), 7.31 (m, 2H, H_1, H_4), 7.12−7.16 (m, 4H, H_2, H_3, H_6, H_7), 4.11 (dq, $^3J_{H-H}$ = 7.0 Hz, $^2J_{H-H}$ = 8.6 Hz, 2H, $H_{23(a)}$, $H_{25(a)}$), 3.84 (dq, $^3J_{H-H}$ = 7.0 Hz, $^2J_{H-H}$ = 8.6 Hz, 2H, $H_{23(b)}$, $H_{25(b)}$), 3.19 (m, 2H, H_{15}, H_{16}), 3.01 (m, 2H, $H_{17(a)}$, $H_{18(a)}$), 2.22 (m, 4H, H_{19}, H_{20}), 2.15 (s, 6H, H_{21}, H_{22}), 1.65 (m, 2H, $H_{17(b)}$, $H_{18(b)}$), 1.52 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, H_{24}, H_{26}). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.6 (C_{11}, C_{12} or C_{13}, C_{14}), 140.9 (C_{11}, C_{12} or C_{13}, C_{14}), 125.6 (C_2, C_3 or C_6, C_7), 125.5 (C_2, C_3 or C_6, C_7), 121.9 (C_5, C_8), 120.7 (C_1, C_4), 80.9 (C_9, C_{10}), 60.0 (C_{23}, C_{25}), 57.9 (C_{19}), 56.3 (C_{17}, C_{18}), 54.2 (C_{20}), 45.7 (C_{21}, C_{22}), 45.2 (C_{15}, C_{16}), 15.7 (C_{24}, C_{26}). IR (KBr, υ cm^{-1}): 3065, 3037 (═C−H), 2970, 2925, 2876, 2805 (C−H), 1449 (C═C), 1142 (C−N), 1074 (C−O). High-resolution mass spectrometry (CI, CH_4, CH_2Cl_2): calcd mass 407.2699, found mass 407.2693 ($C_{26}H_{35}N_2O_2$). Anal. Calcd for $C_{26}H_{34}N_2O_2$ (406.26): C, 76.81; H, 8.43; N, 6.89. Found: C, 76.60; H, 8.35; N, 6.70.

Synthesis of 3. This compound was prepared according to a previously reported procedure.[15b] Ligand **2** (200.5 mg, 0.4938 mmol) was dissolved in 30 mL of toluene, and $Pd(OAc)_2$ (110.8 mg, 0.4938 mmol) was then added. This mixture was stirred for 1 h at 70 °C. The solvent was then evaporated to give a green solid. Recrystallization from dichloromethane/diethyl ether (1/5) at 4 °C afforded the complex **3** as yellow crystals (226.2 mg, 0.359 mmol, 73%). Single

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crystals suitable for X-ray analysis were obtained by cooling a dichloromethane/diethyl ether (1/5) solution of **3**. For NMR labeling, see Figure S12 in the Supporting Information.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (m, 2H, H_{arom}), 7.26 (m, 2H, H_{arom}), 7.11−7.16 (m, 4H, H_{arom}), 4.16 (dq, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 8.6 Hz, 2H, $H_{23(a)}$, $H_{25(a)}$), 4.08 (m, 2H, $H_{17(a)}$, $H_{18(a)}$), 3.87 (dq, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 8.6 Hz, 2H, $H_{23(b)}$, $H_{25(b)}$), 3.50 (m, 2H, H_{15}, H_{16}), 2.62 (s, 6H, H_{21}, H_{22}), 2.37 (m, 2H, H_{20}), 2.26 (m, 2H, H_{19}), 1.89 (s, 3H, CH_3−COO), 1.79 (s, 3H, CH_3−COO), 1.67 (m, 2H, $H_{17(b)}$, $H_{18(b)}$), 1.52 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, H_{24}, H_{26}). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 178.4 (CH_3−COO), 178.3 (CH_3−COO), 141.9 (C_{11}, C_{12} or C_{13}, C_{14}), 140.2 (C_{11}, C_{12} or C_{13}, C_{14}), 126.0 (CH_{arom}), 125.9 (CH_{arom}), 122.4 (CH_{arom}), 120.9 (CH_{arom}), 80.5 (C_9, C_{10}), 63.3 (C_{17}, C_{18}), 62.5 (C_{20}), 61.7 (C_{19}), 60.5 (C_{23}, C_{25}), 50.7 (C_{21}, C_{22}), 44.7 (C_{15}, C_{16}), 23.0 (C_{28}), 22.9 (C_{30}), 15.5 (C_{24}, C_{26}). IR (KBr, ν cm^{-1}): 3447 (=C−H), 2973, 2928 (C−H), 1617, 1600 (C=O), 1451 (C=C), 1073, 1024 (C−O). Anal. Calcd for $C_{30}H_{40}N_2O_6Pd$ (631.5): C, 57.01; H, 6.33; N, 4.44. Found: C, 56.86; H, 6.51; N, 4.49.

Synthesis of 4. Ligand **2** (100 mg, 0.246 mmol) was dissolved in 15 mL of toluene, and [$PdCl_2$(COD)] (70.2 mg, 0.246 mmol) was then added. This mixture was stirred for 15 h at 70 °C. The solvent was then evaporated, and the obtained solid was washed with diethyl ether. After it was dried under vacuum, the complex was isolated as a yellow solid (129.2 mg, 0.222 mmol, 90%). Single crystals suitable for X-ray analysis were obtained from a dichloromethane/diethyl ether (1/2) solution of **4**. For NMR labeling, see Figure S12 in the Supporting Information.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.51 (m, 2H, H_{arom}), 7.14−7.19 (m, 6H, H_{arom}), 4.10−4.18 (dq+m, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 8.6 Hz, 4H, $H_{23(a)}$, $H_{25(a)}$ and $H_{17(a)}$, $H_{18(a)}$), 3.76−3.86 (dq+m, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 8.6 Hz, 4H, $H_{23(b)}$, $H_{25(b)}$ and H_{15}, H_{16}), 2.76 (s, 6H, H_{21}, H_{22}), 2.42 (m, 2H, H_{20}), 2.14 (br, 2H, H_{19}), 1.95 (m, 2H, $H_{17(b)}$, $H_{18(b)}$), 1.53 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, H_{24}, H_{26}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.9 (C_{11}, C_{12} or C_{13}, C_{14}), 140.4 (C_{11}, C_{12} or C_{13}, C_{14}), 129.0 (CH_{arom}), 128.2 (CH_{arom}), 126.1 (CH_{arom}), 125.3 (CH_{arom}), 80.9 (C_9, C_{10}), 65.1 (C_{17}, C_{18}), 63.7 (C_{20}), 63.4 (C_{19}), 60.7 (C_{23}, C_{25}), 51.8 (C_{21}, C_{22}), 45.8 (C_{15}, C_{16}), 15.5 (C_{24}, C_{26}). IR (KBr, ν cm^{-1}): 3447 (=C−H), 2974, 2928 (C−H), 1459 (C=C), 1078, 1025 (C−O). High-resolution mass spectrometry (ES$^+$, methanol): calcd mass 547.1351 [M − Cl]$^+$, found mass 547.1353 [M − Cl]$^+$ ($C_{26}H_{34}ClN_2O_2Pd$). Anal. Calcd for $C_{26}H_{34}Cl_2N_2O_2Pd\cdot CH_2Cl_2$ (667.486): C, 48.54; H, 5.39; N, 4.19. Found: C, 49.78; H, 5.70; N, 3.90.

Synthesis of 5. To a solution of **2** (25 mg, 0.043 mmol) in 5 mL of degassed dichloromethane was added [$RuCp(NCMe)_3$]PF_6 (18.6 mg, 0.043 mmol). The resulting mixture was refluxed overnight. After evaporation of the solvent the resulting complex was isolated as an orange solid (29.9 mg, 0.033 mmol, 78%). Single crystals suitable for X-ray analysis were obtained from an acetone solution of **5**. For NMR labeling, see Figure S12 in the Supporting Information.

^{31}P{^{1}H} NMR (121.4 MHz, $(CD_3)_2CO$): δ −144.5 ppm. IR (KBr, ν cm^{-1}): 3481 (=C−H), 2976, 2930 (C−H), 1458 (C=C), 1068 (C−O), 841 (P−F). High-resolution mass spectrometry (ES$^+$, methanol): calcd mass 750.0480, found mass 750.0475 ($C_{31}H_{39}Cl_2N_2O_2PdRu$). High-resolution mass spectrometry (ES$^-$, methanol): calcd mass 144.9642, found mass 144.9644 ([PF_6]$^-$). Anal. Calcd for $C_{31}H_{39}Cl_2F_6N_2O_2PPdRu\cdot CH_2Cl_2$ (979.923): C, 39.19; H, 4.18; N, 2.86. Found: C, 39.83; H, 4.59; N, 2.40.

Data for *maj*-**5** (70%) are as follows. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.48 (m, 2H, H_{arom}), 7.23 (m, 2H, H_{arom}), 7.17 (m, 2H, H_{arom}), 6.32 (m, 2H, H_{arom}), 5.49 (s, 5H, Cp), 4.13 (m, 4H, H_{23}, H_{25}), 3.65 (m, 2H, H_{20}), 3.55 (m, 2H, H_{15}, H_{16}), 2.96 (m, 4H, H_{17}, H_{18}), 2.83 (m, 2H, H_{19}), 2.70 (s, 6H, H_{21}, H_{22}), 1.48−1.56 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, H_{24}, H_{26}). ^{13}C{^{1}H} NMR (75 MHz, $(CD_3)_2CO$): δ 142.0 (C_{11} or C_{14}), 139.0 (C_{11} or C_{14}), 129.7, 127.9, 127.5, 122.7 (C_1, C_2, C_3, C_4), 113.6 (C_{12}, C_{13}), 87.3 (CH_{arom}), 83.2 (Cp), 83.0, 82.9, 82.0 (CH_{arom}), 80.5 (C_9, C_{10}), 66.3 (C_{17}, C_{18}), 61.9 (C_{23}, C_{25}), 61.4 (C_{19}), 60.8 (C_{20}), 52.0 (C_{21}, C_{22}), 44.8 (C_{15}, C_{16}), 16.8 (C_{24}, C_{26}).

Data for *min*-**5** (30%) are as follows. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.57 (m, 2H, H_{arom}), 7.35 (m, 2H, H_{arom}), 6.52 (m, 2H, H_{arom}), 6.20 (m, 2H, H_{arom}), 5.70 (s, 5H, Cp), 4.00 (m, 4H, H_{23}, H_{25}), 3.68 (m, 2H, H_{20}), 3.53 (m, 2H, H_{15}, H_{16}), 3.06 (m, 4H, H_{17}, H_{18}), 2.83 (m, 2H, H_{19}), 2.73 (s, 6H, H_{21}, H_{22}), 1.52 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, H_{24}, H_{26}). ^{13}C{^{1}H} NMR (75 MHz, $(CD_3)_2CO$): δ 145.5 (C_{11} or C_{14}), 144.7 (C_{11} or C_{14}), 127.7, 124.2, 123.9 (C_1, C_2, C_3, C_4), 110.0 (C_{12}, C_{13}), 89.1, 87.3, 87.1, 84.6 (C_5, C_6, C_7, C_8), 83.5 (Cp), 80.6 (C_9, C_{10}), 64.9 (C_{17}, C_{18}), 63.0 (C_{23}, C_{25}), 61.2 (C_{19}), 60.8 (C_{20}), 52.5 (C_{21}, C_{22}), 44.5 (C_{15}, C_{16}), 16.9 (C_{24}, C_{26}).

Synthesis of 6. To a solution of **2** (20 mg, 0.034 mmol) in 5 mL of degassed dichloromethane was added [$RuCp(NCMe)_3$]PF_6 (29.8 mg, 0.068 mmol). The resulting mixture was refluxed overnight. After the evaporation of the solvent the resulting complex was isolated as a brown solid (31.8 mg, 0.026 mmol, 77%). Single crystals suitable for X-ray analysis were obtained from an acetone solution of **6**. For NMR labeling, see Figure S12 in the Supporting Information.

^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 6.36 (m, 4H, H_{arom}), 6.30 (m, 2H, H_{arom}), 6.27 (m, 2H, H_{arom}), 5.50 (s, 10H, Cp), 4.11 (m, 4H, H_{23}, H_{25}), 3.67 (m, 2H, H_{20}), 3.10 (m, 2H, H_{19}), 2.78 (m, 6H, H_{15}, H_{16}, H_{17}, H_{18}), 2.70 (s, 6H, H_{21}, H_{22}), 1.52 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, H_{24}, H_{26}). ^{13}C{^{1}H} NMR (75 MHz, $(CD_3)_2CO$): δ 153.8, 131.7 (C_{11}, C_{12}, C_{13}, C_{14}), 89.1 (CH_{arom}), 87.3 (CH_{arom}), 86.6 (CH_{arom}), 85.2 (CH_{arom}), 84.2 (Cp), 80.7 (C_9, C_{10}), 65.6 (C_{17}, C_{18}), 63.1 (C_{23}, C_{25}), 61.5 (C_{19}), 60.9 (C_{20}), 52.1 (C_{21}, C_{22}), 44.5 (C_{15}, C_{16}), 16.7 (C_{24}, C_{26}). ^{31}P{^{1}H} NMR (121.4 MHz, $(CD_3)_2CO$): δ −144.5 ppm. IR (KBr, ν cm^{-1}): 3479 (=C−H), 2974, 2928 (C−H), 1459 (C=C), 1065 (C−O), 842 (P−F). High-resolution mass spectrometry (ES$^+$, methanol): calcd mass 1005.3069, found mass 1005.3076 ($C_{36}H_{44}N_2O_2ClPdRu_2PF_5$). High-resolution mass spectrometry (ES$^-$, methanol): calcd mass 144.9642, found mass 144.9642 ([PF_6]$^-$).

Synthesis of 8. To a solution of the corresponding aniline ligand[17] (20 mg, 0.049 mmol) in 3 mL of degassed dichloroethane was added [$RuCp(NCMe)_3$]PF_6 (21 mg, 0.049 mmol). The resulting mixture was refluxed overnight. After the evaporation of the solvent the resulting solid was purified by recrystallization in a dichloromethane/diethyl ether mixture (1/2). Yield: 20 mg (61%).

^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.59 (m, 2H, H_{arom}), 7.41 (m, 2H, H_{arom}), 7.19−7.23 (m, 4H, H_{arom}), 5.95 (m, 3H, H_{arom}), 5.72 (m, 2H, H_{arom}), 5.11 (s, 5H, Cp), 4.20 (m, 2H, CH_2−CH_3), 3.92 (m, 2H, CH_2−CH_3), 3.59 (m, 2H, CH_2−N), 2.90 (m, 4H, CH and CH_2−N), 1.55 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, CH_2−CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, $(CD_3)_2CO$): δ −143.7 ppm. IR (KBr, ν cm^{-1}): 3113 (=C−H), 2973, 2927 (C−H), 1551, 1468 (C=C), 1070 (C−O), 836 (P−F).

Procedure for Pd-Catalyzed Suzuki−Miyaura Cross-Coupling. Palladium complex (1 mol %), phenylboronic acid (91.5 mg, 0.75 mmol), and Na_2CO_3 (106 mg, 1.0 mmol) dissolved in 0.5 mL of deoxygenated water were dissolved in 2 mL of dried toluene. 4-Bromoanisole (93.5 mg, 0.5 mmol) was then added. The mixture was heated to 65 °C for the corresponding time. A 15 mL portion of diethyl ether was added, and the organic phase was consecutively washed with a NaOH aqueous solution (1 M) and water. The organic phase was dried on Na_2SO_4, filtered, concentrated under vacuum, and analyzed by gas chromatography and ^{1}H NMR.

Electrochemical Measurements. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface or a glassy-carbon disk 1 mm in diameter. The solutions used during the electrochemical studies were typically 10^{-3} mol L^{-1} in complex compound and 0.1 mol L^{-1} in supporting electrolyte. The supporting electrolyte (nBu$_4$N)[PF_6] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Acetonitrile was used from the MBraun SPS-800 solvent purification system. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Potentials are given vs the Fc$^+$/Fc couple as internal standard ($E_{1/2}$ = 0.4 V/SCE).

X-ray Diffraction Data Collection and Structure Solution Refinement. The X-ray data (see the Supporting Information, Table S2) for single crystals of ligand **2** and complexes **3**−**6** were obtained at

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a temperature of 193(2) K, using a 30 W air-cooled microfocus source with focusing multilayer optics and Mo Kα radiation (λ = 0.71073 Å). ψ and ω scans were used. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[28] The structures were solved by direct methods, using SHELXS-97 and refined using the least-squares method on F^2 with SHELXL-97.[29] All non-H atoms were treated anisotropically. The hydrogen atoms were fixed geometrically and treated as a riding model.

CCDC-967241 (**2**), CCDC-967240 (**3**), CCDC-967244 (**4**), CCDC-967242 (**5**), and CCDC-967243 (**6**) contain supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Tables S1 and S2, Figures S1−S12, and CIF files giving NMR, electrochemical, theoretical, and crystallographic data for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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