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Electrochemically Driven and Acid-Driven Pyridine-Directed *ortho*-Phosphorylation of C(sp^2)−H Bonds

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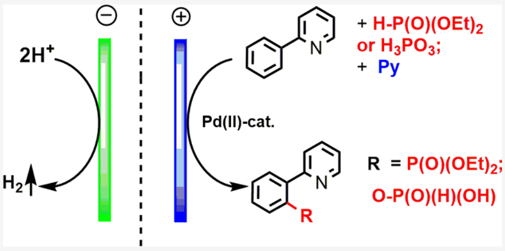

ABSTRACT: The key intermediate palladacycles (mono-, bi-, and tetranuclear) with phosphonate, acetate, and other counterions in C(sp^2)−H phosphonation are analyzed in terms of their redox properties, mutual transitions, reactivity, and reaction pathways for the selective production of the desired products. It was found that, in the presence of pyridine, the reaction proceeds through a mononuclear palladacycle, which at a relatively high electrolysis potential gives the product of *ortho*-phosphonation of the arene with a C−P bond in good yield. Under acidic conditions, the process involves the tetrapalladium intermediate and leads to a product with a C−O−P bond. Phosphorous acid gives inorganic phosphoric derivatives of 2-phenylpyridine. The electrochemical data on the redox properties of key palladacycles **4** and **5** and their potentials and energy gaps are confirmed by DFT calculations.

1. INTRODUCTION

Palladium remains one of the most widely used transition metals, catalyzing a large variety of reactions that occur both under oxidizing and reducing, as well as seemingly redox neutral, conditions.[1] As a rule, it is believed that such universal palladium reactivity is associated with several factors, primarily with the ability to form diverse complexes in 0, I, II, III, or IV oxidation states, which consequently can be easily involved in one- and two-electron redox processes,[2] facilitate substrate binding and release through ligand exchange, and form catalytically active high-order Pd intermediate clusters or complexes that are mono- or polynuclear.[2,3] Over the past decade, metal-catalyzed functionalization of C−H bonds including ligand-directed reactions has emerged as a powerful strategy for the construction of important molecules, such as pharmaceuticals, biologically active molecules, universal ligands in catalytic reactions, and functional materials.[1]

Dehydrogenative (hetero)arene phosphonation triggered by Pd^{II} and other metals, C(sp^2)−H/P−H coupling, is an important atom-economical and environmentally friendly process.[4] Phosphorus-containing moieties, such as the phosphonic acid residue RP, comprise a part of numerous structurally diverse natural compounds involved in different biological reactions. Phosphonic acid moieties are also present in many potential pharmaceutical agents having anticancer, antibacterial, or antiviral activity, including anti-HIV potential, increasing their bioavailability.[4a] In view of the synthetic value of phosphorylated aromatics, the development of methods for constructing C−P or C−OP bonds is of ongoing interest. The electrochemical C−H/P−H cross-coupling methodology can be regarded as environmentally friendly, since the only byproducts formed in these reactions are protons (H$^+$) or hydrogen (H$_2$) under oxidative or reductive conditions, respectively, under ideal conditions with an electron as a traceless reagent, the strength of which is easily controlled by the potential of the electrode.[4a,d−s]

Factors controlling the stability and reactivity of mononuclear or binuclear Pd(II) complexes and palladacycles (as catalyst precursors or intermediates) in C−H functionalization catalysis have been investigated and established in each particular case.[5] However, the identification and characterization of the true catalytically active species and intermediates are extremely difficult in many Pd-catalyzed transformations. As a result, the identity of the active Pd structures in various widely utilized cross-coupling and C−H functionalization reactions still remains under active discussion. However, there are a few papers in which all transformations are traced, starting from electrosynthesis and mutual transformations of intermediates, confirmed by physicochemical methods and DFT calculations. Such methods include electrochemistry, which gives experimental values of the redox potentials and energies of the boundary molecular orbitals, information on the stability of oxidized (reduced) forms, and the number of participating electrons in each stage.[4i,j,q,s]

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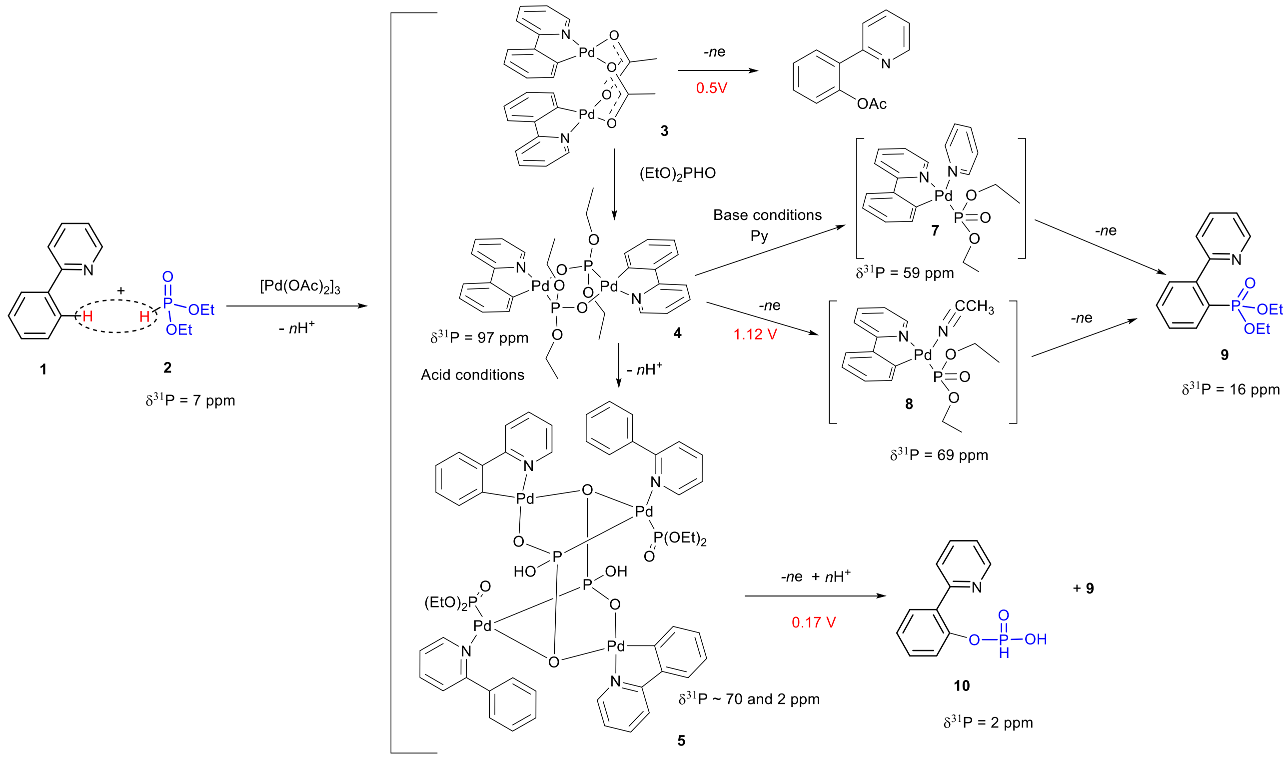
Scheme 1. *ortho*-Phosphorylation of 2-Phenylpyridine Involving Dipalladacycle Intermediates



Yu[6] and Murakami[4c] reported catalytic ligand-directed aromatic C−H phosphonation in 12−66% yields and showed that dialkyl-*H*-phosphonates and *α*-hydroxyphosphonate were phosphorylating reagents. However, these reactions required high temperatures (120 °C), an excess of oxidants (expensive silver salts), bases, and additives (*N*-methylmaleimide, 1,4-benzoquinone, etc.) probably to promote a reductive elimination step. One of the main problems arising in the chemistry of Pd in the high oxidation state III/IV is that applied co-oxidizing agents either are expensive (Ag or other metal salts) or are hardly separable from the reaction mixture (organic oxidants). In addition, all of them are insufficiently selective. An electrochemical approach has several advantages over conventional organic syntheses. Recently, an electrocatalytic method for the phosphonation of 2-phenylpyridine has been developed by the authors' team, but apart from obvious advantages such as room temperature and the absence of traditional oxidizers, the best yields (up to 78%) have been achieved only in the presence of additives: bases NaOAc (4 equiv) and benzoquinoline (2 equiv) or lutidine (4 equiv) and 2,2′-bpy (1 equiv).[4i] These conditions have been found empirically, and they are difficult to explain in terms of understanding the mechanism of the catalytic cycle. The desire to simplify the reaction conditions, increase the yield of phosphorylation products, and find out the nature of other previously unidentified products stimulated further research. This report demonstrates the possibility of managed, controlled, and convenient production of organic and inorganic phosphorylated derivatives of arenes under mild Pd-catalyzed conditions of C(sp^2)−H/P(O)−H cross-coupling on the basis of a detailed analysis of the reactions of 2-phenylpyridine as a model arene with dialkyl-*H*-phosphonates or H_3PO_3, palladacyclic intermediates, and their redox properties combined with computational confirmation of the reactivity.

2. RESULTS AND DISCUSSION

2.1. Palladacycles. Traditional catalytic C−H functionalization is carried out by mixing reaction partners with the catalyst, cocatalyst, oxidizer, and additives, followed by the reaction stage under certain temperature conditions while controlling the conversion of the original reagents. the palladium reactivity is attributed also to its ability to form catalytically active high-order aggregates (including Pd clusters) of specific sizes.[3,7] Low process selectivity and yields may be associated with the divergence of the reaction paths through different metal−organic intermediates with different reactivities. Understanding how to eliminate unwanted intermediates is very important for choosing the best conditions. We have started the research by analyzing all palladium derivatives, palladacycles, which are formed in a three-component system used in C−H phosphonation: palladium salt $Pd(OAc)_2$ (existing as a trimer[8] $[Pd(OAc)_2]_3$), diethyl-*H*-phosphonate, and 2-phenylpyridine (1:1:1 Pd:P:phpy). Three palladacycles with different structures have been identified from this reaction mixture (Scheme 1): the clamshell $Pd_2(phpy)_2(OAc)_2$ (**3**), the phosphonate-bridged $Pd_2(phpy)_2[P(O)(OEt)_2]_2$ (**4**), and the unusual tetranuclear $Pd_4(phpy)_4[P(O)(OEt)_2P(O)(OH)O]$ (**5**). Their structures have been confirmed using X-ray single-crystal diffraction (Figure 1). Monitoring the formation of products and the consumption of precursors on the basis of ^{31}P NMR data dynamics, including the integrated signal intensity in the ^{31}P NMR spectrum of the reaction mixture, is a very convenient method (see details in the Supporting Information). The nature of each isolated product is then confirmed by

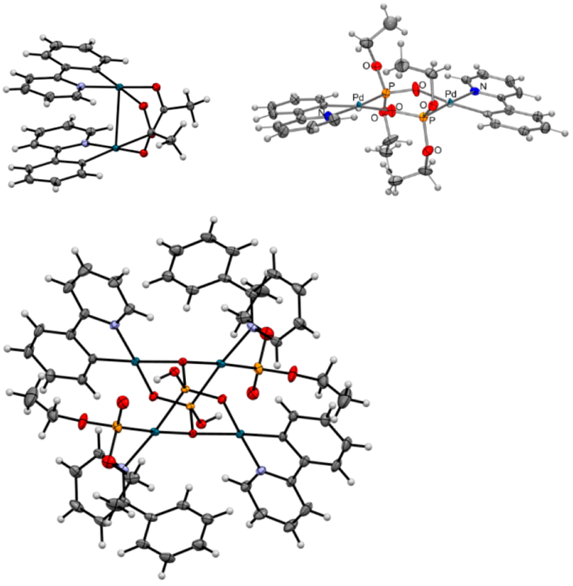


Figure 1. ORTEP drawings of Pd cycles **3** (top left),[3f] **4** (top right),[4i] and **5** (bottom).

a combination of physicochemical methods, including X-ray structural analysis.

Compound **3** gradually disappears (over 1 h, if $(EtO)_2PHO$ is taken in excess) and completely turns into palladacycles with phosphonate counterions. Since the formation of the palladacycle releases the acid AcOH, it provokes some dealkylation of dialkyl phosphorus fragments in palladium complexes during aging. The addition of this acid to the reaction mixture increases the content of **5**. Despite the lack of Pd−Pd bonds and π-stacking interactions between the aromatic substituents at the palladium in **4** and **5** (in contrast to **3**), they were believed to enhance the stability of palladacycles;[9] phosphonate-bridged **4** and tetranuclear **5** are stable and retain their structure for a long time. The structures and NMR data for the isolated crystals of **4** and **5** remain unchanged for at least 1 year.

The tetranuclear palladium complex **5** includes palladium in different environments, two palladacycles and two palladium atoms with the coordination bond Pd−N and two bonds Pd−P, one of them with dealkylated phosphorus and one with phosphorus with ethoxy substituents.

The study of the redox properties of palladacycles **3**−**5** using cyclic voltammetry in both solution and solid form (using a carbon-paste electrode, CPE) has shown that the oxidation potential of Pd(II) is highly dependent on the nature of the bridging ligand and the structure of the complex in general (Table 1). Since potentials also depend on the electrode nature, we conducted a study on two electrodes: Pt, which is used in preparative synthesis, and glassy carbon, which is usually similar in properties to carbon paste. The CPE was mainly used for insoluble or poorly soluble complexes.

The electrochemical properties of complexes **3** and **4** were first described in refs 4i, j, and s. Interestingly, oxidation of complex **5** is noticeably easier than that of diphosphonate-bridged dipalladacycles **4**. This is somewhat surprising, as in tetranuclear palladium complex **5** there are no Pd−Pd bonds usually facilitating oxidation. The extension (blurring) of the first oxidation peak for **5** is related to the presence of different palladium ions with different environments. Since the current at potentials of the first reduction peak is 2 times higher than the current at potentials of the first oxidation peak, hence the reduction is two-electron, $Pd^{II/0}$, and the oxidation is one-electron at the first stage, $Pd^{II/II}$, as was previously demonstrated and confirmed.[4i,j,s,10,11] Thus, in a number of binuclear palladacycles, acetate-bridged **3** is oxidized more easily than diethylphosphonate-bridged **4**. Among phosphonate palladacycles **4** and **5**, the palladacycle with inorganic phosphorus substitutes **5** (tetrapalladium complex) undergoes the easiest oxidation. In order to confirm the more difficult oxidation of palladium with a $Pd-P(O)O(OEt)_2$ bond in comparison to the easier oxidation of fragments with inorganic substituents in palladium, the model compound $bpyPd[P(O)(OEt)_2]_2$ (**6**) has been synthesized. Its structure has been confirmed by single-crystal XRD (Figure 2).

Table 1. Electrochemical Data for Palladacycles 3−7: Oxidation Potentials E_p (V vs Fc^+/Fc)[a]

complex	Pt[4s]	GC	CPE
$Pd_2(phpy)_2(OAc)_2$ (**3**)	0.50	0.39	0.42
	1.09	0.89	0.80
$Pd_2(phpy)_2[P(O)(OEt)_2]_2$ (**4**)	1.12	0.61	0.55
	1.62	1.70	0.99
$Pdbpy[P(O)(OEt)_2]_2$ (**6**)		1.09	0.99
		1.41	1.44
Pd-4 (**5**)	0.50	0.61	0.17
		0.79	1.08
$Pd(phpy)Py[P(O)(OEt)_2]$ (**7**)		0.82	no crystal
		1.32	
$[phpyPd(H_3PO_3)]$ (**11**)			0.25
			1.07

[a] Conditions: CH_3CN; glassy carbon (GC), carbon paste (CPE), or Pt electrodes.

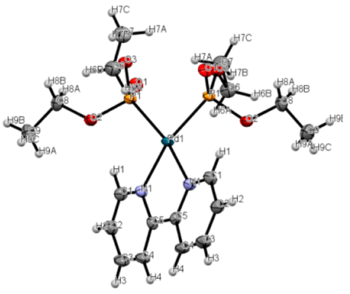


Figure 2. ORTEP drawing of $bpyPdP(O)(OEt)_2$ (**6**).

A voltammetric study of $bpyPd[P(O)(OEt)_2]_2$ (**6**) has shown that it is oxidized at a relatively high potential of about 1.09 V (Table 1). The palladium complex obtained through mixing phpy, $Pd(OAc)_2$, and H_3PO_3, which does not produce crystals suitable for X-ray structural analysis, is oxidized very easily at 0.25 V (CPE), which confirms its instability and propensity for oxidation even by oxygen in the air.

Thus, there are various palladium intermediates—palladacycles with different oxidation abilities in the mixture of arene, phosphorylating agent (e.g., $(EtO)_2P(O)H$), and the salt of the palladium catalyst $Pd(OAc)_2$ under conditions of C−H phosphonation. Under conditions of chemical reaction with the added oxidizer $K_2S_2O_8$[4c,6] or under electrochemical oxidation, this leads to a mixture of products of *ortho*-substituted 2-phpy: cycle **3** will produce an *ortho*-acetoxylated product, cycle **4** (its E_{ox} is above those of **3** and **5**) *ortho*-phosphonated **9**, and cycle **5** a mixture of phosphorylation products **9** and **10**. Since the most easily oxidized cycles are those undesired in terms of obtaining product **9**, the yield of the latter has never been very high: 12−66% in the papers of Yu and 72−78% in our works.[4c,i,6]

The palladacycles **3** and **4** are the key intermediates of electrocatalytic C−H functionalization, acetoxylation (**3**) and phosphonation (**4**) of 2-phenylpyridine, which was previously reported in refs 4i, j, s, and 11. It can be assumed that, in order to increase the selectivity of the *ortho*-dialkylphosphonation reaction, it is necessary to exclude the formation of cycles **3** and **5**, as well as to provide conditions for the oxidation of key intermediate **4**, i.e. to use higher electrosynthesis potentials corresponding to this process, or to choose stronger oxidizers (in classical organic synthesis). To eliminate the presence of acetate-bridged palladacycle **3**, which gives the product of aromatic C−H acetoxylation during oxidation (with low potentials), it is necessary to age the mixture for some time before oxidation (chemical or electrochemical) in order to turn **3** into phosphonate palladacycle **4**, which is easy enough. The next step should be neutralization of acetic acid, which was released during the formation of phosphonate palladacycle **4**. For this purpose, oxidation processes were carried out in the presence of a base (pyridine). When pyridine is added to the bridge phosphonate palladacycle **4**, the latter breaks down to the monometallic palladacycle **7**, which appears in the ^{31}P NMR spectrum as a singlet at δ_P 59.7 ppm in acetonitrile solution. The assumption of the monomeric structure of the intermediates with δ_P 69.5 (**8**) and 59 ppm (**7**) was proved by the proximity of these values to the chemical shifts of other mononuclear palladium phosphonate complexes, such as Stockland's arylpalladium complexes $bu_2bpyPd(Ar)(P(O)(OR)_2)$ (δ_P 70.8−78.8 ppm).[12] Monomerization of $[(phpy)Pd(OEt)_2P(O)]_2$ (**4**) into $(phpy)Pd(CH_3CN)[P(O)(OEt)_2]$ (**8**; the most likely structure) induced by an electron transfer reaction is unusual and is described in ref 4j. Monomeric palladium complexes are known to be oxidized usually at potentials more positive than dimeric complexes with the same ligand environment.[4s,11,13,] We assume and confirm that the same trend is valid for phosphonate complexes (Table 1). Indeed, the addition of pyridine to $Pd_2(phpy)_2[P(O)(OEt)_2]_2$ (**4**) results in the disappearance of its oxidation peaks on CVA and the emergence of new peaks with more positive potentials (Figure 3). We attribute these new peaks to the oxidation of monometallic $Pd(phpy)Py[P(O)(OEt)_2]$ (**7**).

Subsequent electrochemical oxidation of palladacycle **7** proceeds selectively with the formation of diethyl (2-(pyridin-2-yl)phenyl)phosphonate (**9**) with a good yield (86%) (Scheme 2).

In the absence of base during electrolysis, the ^{31}P NMR spectrum shows two singlet signals with δ_P 16.2 and 2.3 ($^1J_{PH}$ = 626 Hz) ppm. Apparently, the presence of acetic acid in the reaction mixture promotes the formation of tetranuclear palladium complex **5**, which breaks down into two products with further electrochemical oxidation: *ortho*-phosphorylated 2-phenylpyridines **9** and **10** (Scheme 1).

To establish the possibility of obtaining inorganic phosphorus derivatives of arenes under electrocatalytic conditions, we performed phosphorylation of 2-phenylpiridine **1** using phosphorous acid H_3PO_3 as a phosphorylating reagent (2*F* of electricity per mole of acid) and $Pd(OAc)_2$ as catalyst. In the ^{31}P NMR spectrum of the reaction mixture, the original H_3PO_3 is completely absent, and there is a signal of the product with δ_P 2.4 ppm. Registration of spectrum without proton suppression revealed that compound **10** with δ_P 2.4 m.d. had a P−H bond ($^1J_{PH}$ 650 Hz), i.e. a product with an *ortho*-$C(sp^2)$−O-P bond is formed (Scheme 3).

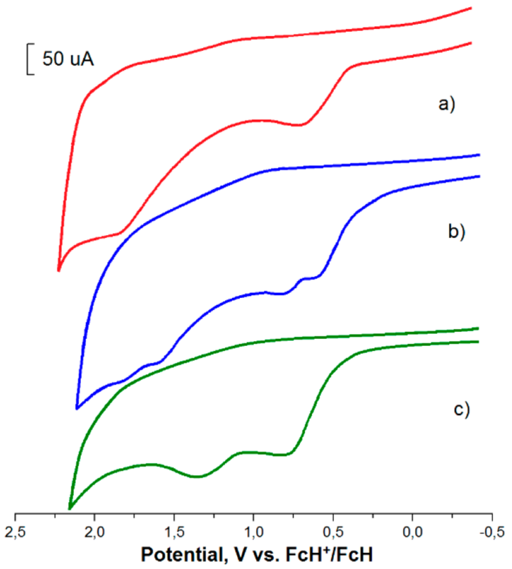
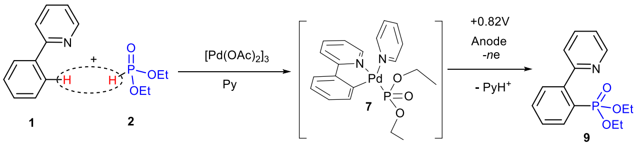
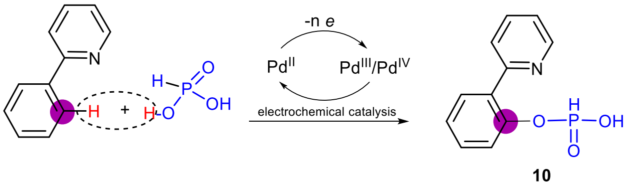


Figure 3. Cyclic voltammograms of palladacycle **4** (5×10^{-4} M) on a GC electrode in CH_3CN (a, red), in the presence of Py (1×10^{-4} M) (b, blue), and in the presence of Py (1×10^{-3} M) (c, green).

Scheme 2

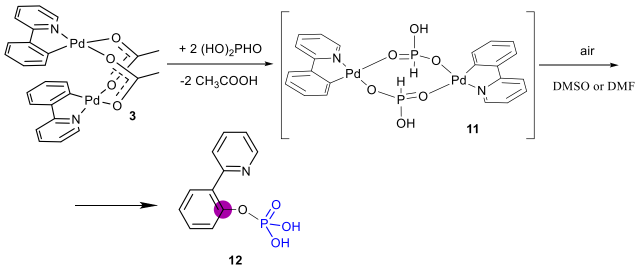


Scheme 3



Since dipalladium phosphonate-bridged complex **4** lies in the way ofelectrocatalytic phosphorylation of 2-phenylpyridine (**1**) with diethyl phosphite (**2**), we have assumed the formation of a similar dipalladium complex when using phosphoric acid H_3PO_3. Such s complex was formed during mixing of 2-phenylpyridine (**1**), palladium acetate, and phosphoric acid. However, on the basis of the analysis of ^{31}P NMR spectra of the reaction mixture (δ_P 3.82 ppm, $^1J_{PH}$ = 637 Hz), one can assume the formation of bridged dipalladium complex **11** having P−H fragments (Scheme 4). The dipalladium complex **11** is not very stable and is hardly soluble in organic solvents. Aging in solvents such as DMSO and DMF over 1 day results in the formation of a black powder sediment of Pd(0). After the precipitate is filtered, the signal with δ_P 3.82 ppm disappears in the ^{31}P NMR spectrum of a solution of complex **11**, and there is a new singlet with δ_P 1.89 ppm (splitting from

Scheme 4



protons is not observed). Apparently, complex **11** is easily oxidized by atmospheric oxygen in DMSO or DMF, which leads to the release of Pd(0) and the formation of compound **12** (Scheme 4).

2.2. Electrochemical vs DFT Calculations.

Electrochemical data for palladacycles **4** and **5** in the solid state show that complex **5** oxidizes noticeably more easily than diphosphonate-bridged dipalladacycles **4**, and the value of its electrochemical gap (Table 2 and Figure 4), associated with the energy difference between HOMO and LUMO orbitals, is less than that for **5**. That is, according to voltammetry, complex **5** is more easily polarizable and reactive. To confirm these observations, to establish more stable forms, and to understand the distribution of electron density in Pd complexes, we performed a quantum chemical study of these phosphoric palladacycles with known X-ray structures. Previously, computational density functional theory was successfully used to calculate the HOMO−LUMO energies, redox potentials, stability of metal complexes, and factors controlling the stability and reactivity of dimeric Pd(II) complexes, including metal cycles of nickel and palladium.[4s,5a,13,15]

Table 2. Electrochemical Data for Palladacycles 4 and 5 in the Solid State: Oxidation and Reduction Peak Potentials (E_p, V vs Fc$^+$/Fc)^a

complex	oxidation E_p^a, V	reduction E_p^c, V	electrochemical gap, $\Delta E_g = E_p^a - E_p^c$, V
4	0.55	−2.20	2.75
5	0.17	−2.22	2.39

^{a}Conditions: carbon-paste electrode (graphite + ionic liquid + palladacycle)[14] in 2 mL of CH$_3$CN (0.1 M Bu$_4$NBF$_4$).

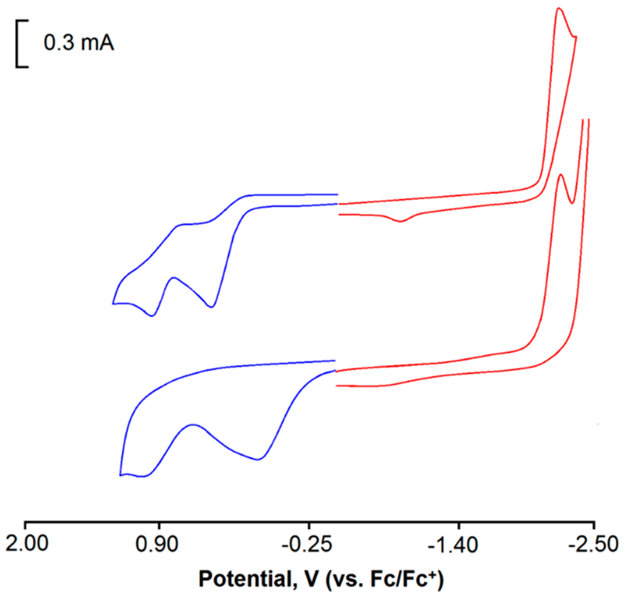


Figure 4. CVs data for palladacycles **4** (upper CV) and **5** (at the bottom) in carbon-paste electrodes (CPE): oxidation and reduction peak potentials (E_p, V vs Fc$^+$/Fc). Conditions: CPE (graphite + ionic liquid + palladacycle)[14] in 2 mL of CH$_3$CN (0.1 M Bu$_4$NBF$_4$).

Structures of palladacycles **4** and **5** for the calculation of the energy of frontier orbitals were taken from the X-ray diffraction data. The calculations were performed in solvent (CH$_3$CN) by DFT using the M06L density functional,[16] which has shown itself well for the transition-metal energy calculations.[17] Calculations of the energies of frontier orbitals of complex **4** were performed in the singlet ground state; the corresponding HOMO and LUMO energies as well as the energy gap value, Δ*E*, are given in Table 3. According to the presented data, the computational level M06L/LACV3Psspp with the diffuse functions included in the valence shell basis set provides excellent agreement with the experimental data for ΔE_g as well as for the energies of the frontier orbitals.

The contour plots for the HOMO and LUMO are given in Figure 5. HOMO orbital covers both Pd atoms, while the LUMO is concentrated mostly on phosphonate groups.

For complex **5**, the calculations performed with the assumption that the complex ground state is a singlet gave unreasonable estimations for Δ*E*. A study[18] of the stability of Pd$_n$ clusters in the gas phase established a state with multiplicity, *M*, equal to 3 to have minimal energy for the Pd$_2$ and Pd$_4$ clusters; at the same time the energy differences between the cases $M = 3$ and $M = 1$ are 0.0018 and 0.017 eV, respectively. As the difference for complex **4** is negligibly small (an order of magnitude smaller than for $M = 3$), the presence of ligands as well as solvent may change the most stable state of the Pd$_2$ cluster. We have examined this assumption and obtained that for complex **4** the state with $M = 1$ is 2.7 eV more stable than that with $M = 3$. The corresponding calculations for complex **5** demonstrated that in this case, in contrast, the state with $M = 3$ is more stable, though the energy difference in this case is 0.12 eV. Thus, the calculated values of Δ*E* and frontier orbital energies presented in Table 3 correspond to the state with $M = 3$. These data demonstrate reasonable agreement with electrochemical data; the LUMO energy is quite close to the value obtained on the basis of electrochemical data. The ΔE_g value for complex **5** estimated on the basis of electrochemistry is shown to be notably smaller than that for complex **4**, and this tendency does hold for the computational estimations: ΔE_g is found to be 0.34 eV greater for complex **4**. The visualizations of the HOMO and LUMO for complex **5** demonstrate that the HOMO covers mostly all four Pd atoms, primarily the pair of Pd atoms bonded with *ortho*-phosphonate fragments, while the LUMO is completely placed on palladacycles.

■ CONCLUSION

The key intermediates of ligand-directed aromatic phosphonation catalyzed by palladium, palladacycles, are distinguished by their structure, chemical and electrochemical reactivities, and redox properties, which determine the final products and their yields. The reasons for the usually low yields of C−H *ortho*-functionalization under oxidizing conditions, with uncontrolled intermediates and the oxidizing power of the reagents, have been established. The possibility of controlled phosphorylation of an arene (2-phenylpyridine) in the

Table 3. Energies of Frontier Orbitals and the Energy Difference between Them (in eV) Calculated in Acetonitrile and Estimated Electrochemically (Exp)

	complex **4**			complex **5**		
	Exp	M06L/LACV3Pss	M06L/LACV3Psspp	Exp	M06L/LACV3Pss	M06L/LACV3Psspp
E(HOMO)	−5.35	−5.33	−5.35	−4.97	−4.99	−5.09
E(LUMO)	−2.60	−2.52	−2.55	−2.58	−2.59	−2.63
ΔE_g	−2.75	−2.81	−2.80	−2.39	−2.40	−2.46

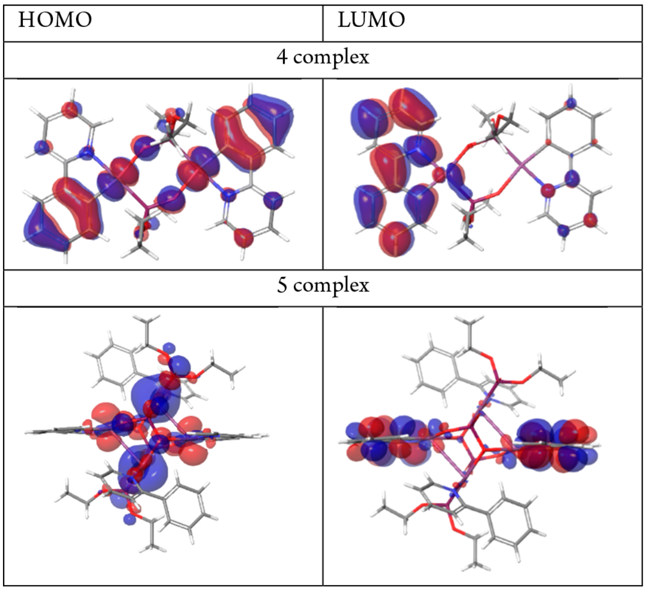


Figure 5. Contour plots for the HOMO and LUMO (M06L/LACV3Psspp in ACN) of complexes **4** and **5**.

direction of a reaction through the mononuclear palladacycle in the presence of pyridine at high oxidation potentials has been shown. It is possible to control the selectivity of introduction of a phosphorus-containing substituent, giving the diethyl arylphosphonate ArP(O)(OEt)$_2$ with a yield of up to 90% or the aryl phosphinic acid Ar−O−P(O)(H)(OH) with a yield of up to 82% depending on the reaction conditions. The reaction conditions (presence or absence or pyridine base and ligand, anode potential) determine the palladium intermediates through which electrolysis will go and the general synthetic results.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00247.

> Experimental procedures for all experiments and characterization, X-ray, electrochemical, and NMR data (PDF)

Accession Codes

CCDC 1994142−1994144 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing 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.

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Notes

The authors declare no competing financial interest.

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