ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Electrochemical Ortho Functionalization of 2-Phenylpyridine with Perfluorocarboxylic Acids Catalyzed by Palladium in Higher Oxidation States

Yulia B. Dudkina,[†] Dmitry Y. Mikhaylov,[†] Tatyana V. Gryaznova,[†] Artem I. Tufatullin,[†] Olga N. Kataeva,[†,‡] David A. Vicic,[§] and Yulia H. Budnikova*[,†]

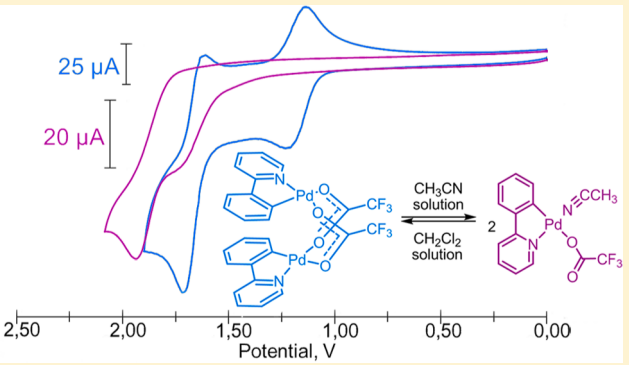
[†]A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of Russian Academy of Sciences, 8 Arbuzov str., Kazan 420088, Russian Federation

[‡]Kazan Federal University, 18 Kremlevskaya str., Kazan 420008, Russian Federation

[§]Department of Chemistry, Lehigh University, 6 East Packer Avenue, Bethlehem, Pennsylvania 18015, United States

Supporting Information

ABSTRACT: The electochemical oxidation of palladium acetate or palladium perfluoroacetate in the presence of 2-phenylpyridine promotes catalytic ortho C−H substitution reactions. As possible intermediates, Pd(II) metallacycles with Pd-bound acetate, perfluoroacetate, and perfluoroheptanoate substituents have been isolated and characterized: binuclear $[(PhPy)Pd(\mu\text{-}OAc)]_2$ and $[(PhPy)Pd(\mu\text{-}TFA)]_2$ and mononuclear $[(PhPy)Pd(TFA)](CH_3CN)$, $[(PhPy)Pd(TFA)](PhPy)$, and $[(PhPy)Pd(PFH)](PhPy)$. The fluorinated derivatives were found to exist in solvent-dependent equilibria between mononuclear and binuclear forms. Cyclic voltammetry was used to elucidate redox properties of the palladacycles and the oxidation route to the final products.



INTRODUCTION

Transformation of C−H bonds into diverse functional groups is a highly attractive strategy in organic synthesis. Mild and selective, it is relevant in all chemical fields, including the synthesis of pharmaceuticals, natural products, agrochemicals, polymers, and other different chemicals. Over the past decade, the field of transition-metal-catalyzed C−H bond functionalizations has developed rapidly, providing new synthetic methods and detailed mechanistic studies.[1−3] Due to the functional group tolerance of palladium and the ability to install many different types of bonds (C−O, C−Hal, C−N, C−S, C−C) palladium complexes are particularly applicable catalysts for such transformations,[1−3] with palladium acetate being the most commonly used. The chemically similar palladium trifluoroacetate (TFA) is less commonly utilized, though it is known to be an efficient catalyst and cocatalyst in rearrangements involving C−H bond activation.[4,5] Moreover, in some cases trifluoroacetic acid additive was found to be critical in achieving a high efficiency of C−H functionalization[6] and the trifluoroacetate ligand was used to improve the solubilities and catalytic activities of transition-metal complexes.[7]

The catalitic cycles of Pd-catalyzed reactions are generally based on Pd^{II}/Pd^{0} shuttles which have been extensively investigated for the past decades,[2,8−12] including the known contribution of electrochemistry to the mechanistic study.[13] However, a variety of Pd-catalyzed ligand-directed C−H oxidative functionalization reactions involve palladium(III)[14−16] and palladium(IV)[17−19] intermediates that makes chemistry of palladium in higher oxidation states a challenging and advanced field. Understanding the properties of Pd^{II}, Pd^{III}, and Pd^{IV} complexes should prove useful for the development of novel catalysts in these types of transformations.

With regard to new methods involving high-valent palladium catalysts, one of the major problems is that the co-oxidants used mostly require stoichiometric transition-metal or organic oxidants, such as Ag salts, organic peroxides, and electrophilic fluorine reagents, which are often either expensive to purchase or difficult to separate from the product mixture.[1,10,18] Moreover, every time a new ligand or substrate or reaction condition is used, extensive screenings are necessary in order to identify the optimal oxidant. Potential-controlled electrolysis under mild conditions is a feasible alternative to the classical methods that have been demonstrated by Kakiuchi[20] in the effective electrochemical halogenation of arylpyridine derivatives.

Recently, we discovered a one-step catalytic method for ortho fluoroalkylation of 2-phenylpyridine that employs higher oxidation states of nickel or palladium by electro-oxidation of stable M^{II} precursors.[21]The aim of this work is to further

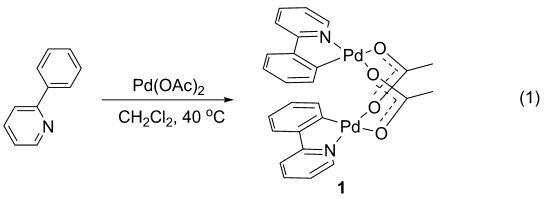
Received: May 30, 2013

   dx.doi.org/10.1021/om400492g | *Organometallics* XXXX, XXX, XXX−XXX

develop that methodology toward alternative approaches to directed perfluorocarboxylation of C−H bonds of aromatic compounds, to characterize fluorinated palladacyclic intermediates, and to investigate the effect of changing acetate to trifluoroacetate ligand for catalytic efficiency.

RESULTS AND DISCUSSION

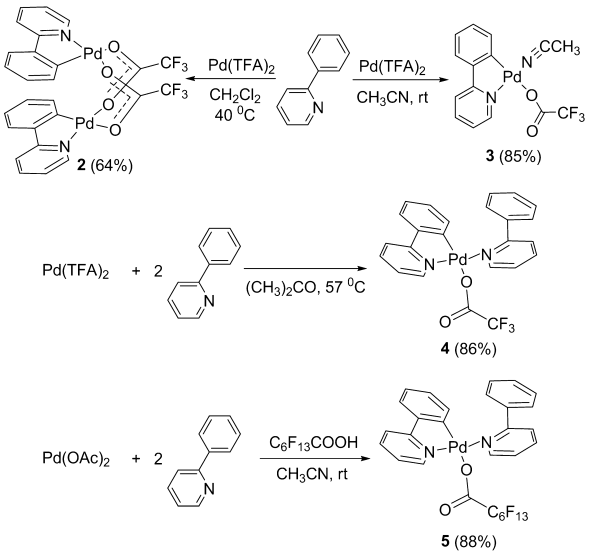
Acetic acid, trifluoroacetic acid, and longer chain perfluoroalkyl carboxylic acids can be used as substrates for the substitution and functionalization of C−H bonds.[1,14,21] We therefore set out to investigate the differences in the nature and electrochemical properties of acetate- and perfluoroacetate-bridged palladacycles that would be competent as reaction intermediates in the functionalization of a C−H bond of phenylpyridine using CH_3COOH and CF_3COOH. The palladium acetate dimer **1** is already known and was synthesized using the method described by Ritter and co-workers (eq 1).[14]



(1)

We found that synthesis of the palladium trifluoroacetate (TFA) derivatives was not as straightforward as the preparation of the nonfluorinated analogues. Treatment of palladium trifluoroacetate with 2-phenylpyridine (PhPy) yields, depending on the solvent employed, either the dimeric or monomeric palladacycles as described in Scheme 1. If dichloromethane is used as solvent, the previously reported dinuclear complex **2**[22] is produced in 64% yield. However, if acetonitrile or acetone is used as the reaction medium, the dimer formation is suppressed and mononuclear **3** or **4** could be produced in 85 and 86% yields, respectively. Complex **5**, which has a structure similar to that of **4** but with a longer fluoroalkyl chain, can be obtained as a product of 2-phenylpyridine treatment with perfluoroheptanoic (PFH) acid in acetonitrile (88% yield).

Scheme 1. Solvent-Dependent Reactivity of Palladium(II) Trifluoroacetate with 2-Phenylpyridine



We were unable to isolate nonfluorinated counterparts of complex **3** and **4** using the same procedures. However, nonfluorinated mononuclear palladacycles similar to **3** and **4** were recently proposed as intermediates in $Pd(OAc)_2$-catalyzed C−H activation reactions.[23]

Crystals of complexes **3**−**5** were grown, and the results of the X-ray diffraction studies are provided in Figures 1−3. The

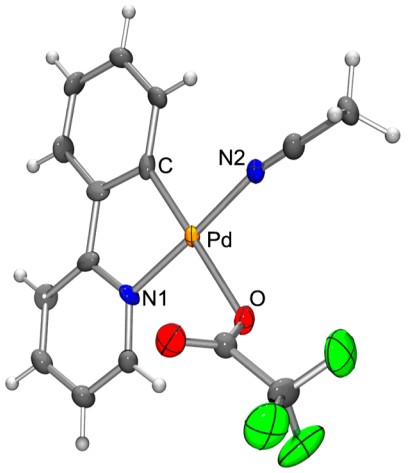


Figure 1. ORTEP representation of the molecular complex [(PhPy)-Pd(TFA)](CH_3CN) (**3**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Pd−C = 1.928; Pd−N1 = 1.995; Pd−O = 2.147; Pd−N2 = 2.015.

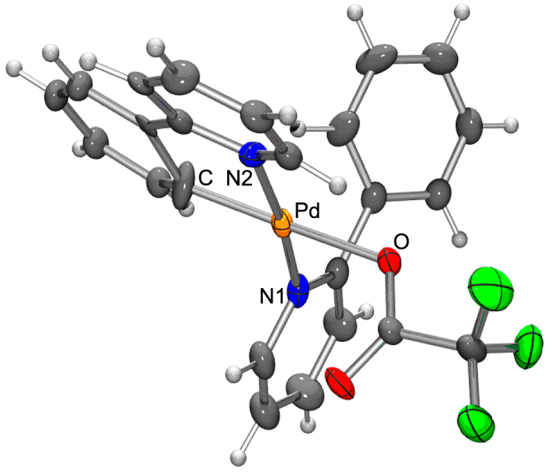


Figure 2. ORTEP representation of the molecular complex [(PhPy)-Pd(TFA)](PhPy) (**4**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Pd−C = 1.970; Pd−N1 = 2.055; Pd−O = 2.141; Pd−N2 = 2.012.

palladium centers in **3**−**5** all adopt a square-planar geometry, with the two nitrogen ligands bound trans to each other. The trifluoroacetate was always found to be bound trans to the carbon of the aryl ligand.

Bimetallic palladium complexes are known to occur in temperature -dependent equilibrium with mononuclear species in the presence of nitrogenous ligands. The equilibrium was first reported in 1987 by Ryabov[24] in terms of bridge-splitting equilibria between chlorine- or acetate-bridged cyclopalladated complexes and free N donor ligands. Subsequently it was shown that the dinuclear palladium complex is favored and exhibits redox synergy in oxidative catalysis.[25,26] We found that

dx.doi.org/10.1021/om400492g | Organometallics XXXX, XXX, XXX−XXX

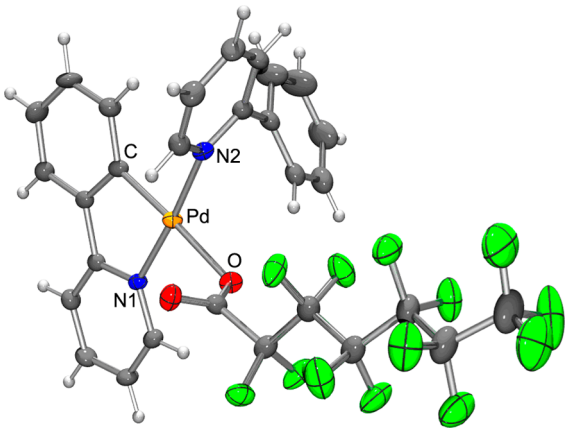
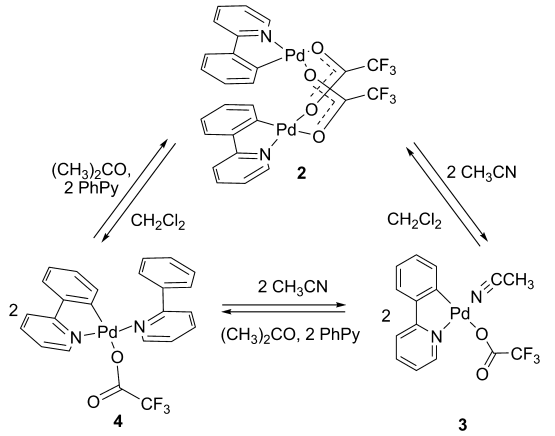


Figure 3. ORTEP representation of the molecular complex [(PhPy)-Pd(PFH)](PhPy) (**5**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Pd−C = 1.973; Pd−N1 = 2.017; Pd−O = 2.141; Pd−N2 = 2.041.

monomer−dimer equilibria for trifluoroacetate derivatives exhibit strong solvent dependence. Thus, the solvent governs the formation of various palladium complexes and the substitution of reaction media involves a change in the environment (Scheme 2). Evidence is obtained for these

Scheme 2. Solvent-Dependent Monomer−Dimer Equilibrium of 2-Phenylpyridyl Palladium(II) Trifluoroacetate



interconversions by ^{1}H NMR spectroscopy on the isolated crystalline complexes **2**−**5** in different solvents. For complexes **2** and **3**, fast interconversions are observed. When complex **2** is dissolved in CD_3CN solvent, quantitative conversion to **3** is observed. However, solutions of **3** in CD_2Cl_2 exhibit two groups of signals for both dinuclear **2** and mononuclear **3**, supporting a ratio of 1:0.15 for **2** and **3**. Palladacycles **4** and **5** were found to persist in noncoordinatng solvents such as chloroform and acetone, showing insignificant dimerization. However the NMR spectrum of complex **4** dissolved in CD_3CN reveals broad signals attributed to initial complex **4**, complex **3**, and free 2-phenylpyridine resulting from fast exchange processes in the solution. Such behavior is also observed for compound **5**.

A cyclic voltammetry study performed in dichloromethane or acetonitrile solution containing TBATFB as the supporting electrolyte and Ag/AgCl as the reference electrode reveals the solvent effects to have major consequences for the redox chemistry of the palladium complexes. Figure 4 shows scans of

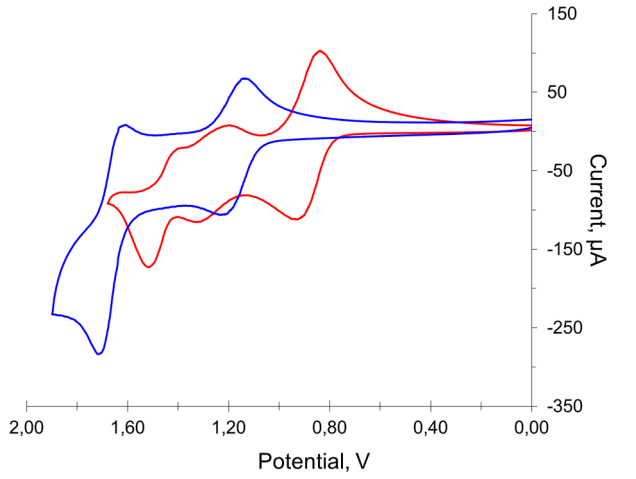


Figure 4. Cyclic voltammograms of [(PhPy)Pd(μ-OAc)] (**1**; red) and [(PhPy)Pd(μ-TFA)]$_2$ (**2**; blue) in CH_2Cl_2.

acetate-bridged **1** and trifluoroacetate-bridged **2** dimers in CH_2Cl_2. Cyclic voltammograms of acetate dimer **1** and trifluoroacetate monomer **3** in acetonitrile solvent are represented in Figure 5. The oxidation potentials of complexes

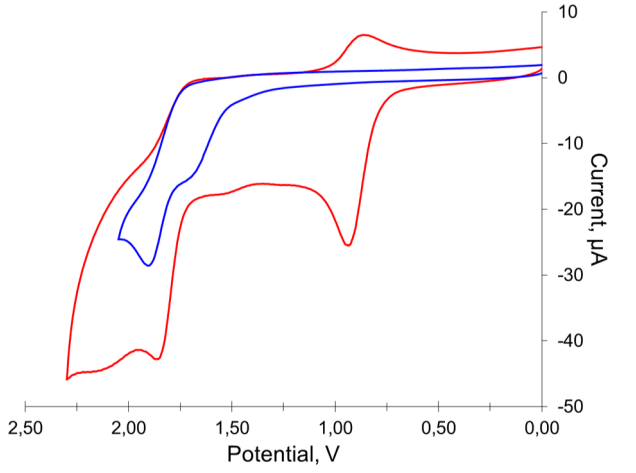


Figure 5. Cyclic voltammograms of [(PhPy)Pd(μ-OAc)]$_2$ (**1**; red) and [(PhPy)Pd(TFA)](CH$_3$CN) (**3**; blue) in CH_3CN.

1−**3** are collected in Table 1. It should be noted that the oxidation potential of free PhPy is 2.15 V in CH_2Cl_2 or 2.08 V in CH_3CN, and no significant peaks for Pd(TFA)$_2$ could be observed under the applied conditions.

The electrochemistry of [(PhPy)Pd(μ-OAc)]$_2$ and [(PhPy)-Pd(μ-TFA)]$_2$ in CH_2Cl_2 and CH_3CN with 0.1 M $TBAPF_6$ as

Table 1. Oxidation Potentials (in V) for Palladacycles 1−3

	CH_2Cl_2 solvent			CH_3CN solvent	
complex	E^1	E^2	E^3	E^1	E^2
1	0.89	1.27	1.46	0.88	1.82[a]
2	1.18	1.67		turns into **3**	
3	turns into **2**			1.72[a]	1.90[a]

[a]For irreversible waves E_{pa} is given.

dx.doi.org/10.1021/om400492g | *Organometallics* XXXX, XXX, XXX−XXX

the supporting electrolyte was described recently.[22] The report shows clearly that acetate-bridged **1** is more easily oxidized than TFA-bridged **2**, which is consistent with our data (Figure 4 and Table 1). However, the shapes and the number of observed peaks in the cyclic voltammograms are somewhat different from those observed under our conditions. In our study, not only do we rationalize the solvent effect behavior but we also derive a different number of electrons for the oxidation stages (see below). The electron number was determined using methods[27] including chronoamperometry and steady-state voltammetry at a microelectrode.

In CH_2Cl_2 solution the acetate derivative **1** (Figure 4, red curve) undergoes three reversible oxidations, which are assigned to $Pd^{II}-Pd^{II}/Pd^{III}-Pd^{III}$, $Pd^{III}-Pd^{III}/Pd^{III}-Pd^{IV}$, and $Pd^{III}-Pd^{IV}/Pd^{IV}-Pd^{IV}$ couples (the absolute value of the number of electrons consumed in the first oxidation step was found to be 2.2). A proposed rationale for the redox behavior of **1** is provided in Scheme 3. In CH_3CN **1** is oxidized successively

Scheme 3. Proposed Mechanism for the Electrooxidation of 1 in CH_2Cl_2

$$Pd^{II}{}_2(PhPy)_2(OAc)_2 - 2e \overset{E^1}{\rightleftharpoons} Pd^{III}{}_2(PhPy)_2(OAc)_2$$

$$Pd^{III}{}_2(PhPy)_2(OAc)_2 + Pd^{II}{}_2(PhPy)_2(OAc)_2 \rightleftharpoons 2\ Pd^{II}(PhPy)Pd^{III}(PhPy)(OAc)_2$$

$$Pd^{III}{}_2(PhPy)_2(OAc)_2 - e \overset{E^2}{\rightleftharpoons} Pd^{VI}(PhPy)Pd^{III}(PhPy)(OAc)_2$$

$$Pd^{VI}(PhPy)Pd^{III}(PhPy)(OAc)_2 - e \overset{E^3}{\rightleftharpoons} Pd^{VI}{}_2(PhPy)_2(OAc)_2$$

in reversible and irreversible steps conforming to $Pd^{II}-Pd^{II}/Pd^{III}-Pd^{III}$ and $Pd^{III}-Pd^{III}/Pd^{IV}-Pd^{IV}$ couples, respectively (Figure 5, red curve). In both solvents **1** exists in a dimeric form.

The cyclic voltammetry data confirm the solvent-dependent nuclearity transformation of the trifluoroacetate derivatives. The voltammogram for dimer **2** features two quasi-reversible two-electron (measured: 2.1) waves, assigned to $Pd^{II}-Pd^{II}/Pd^{III}-Pd^{III}$ and $Pd^{III}-Pd^{III}/Pd^{IV}-Pd^{IV}$ couples (Figure 4, blue curve). The mononuclear complex **3** exhibits two very closely spaced one-electron irreversible oxidations assigned as Pd^{II}/Pd^{III} and Pd^{III}/Pd^{IV} couples (Figure 5, blue curve). Thus, conversion of the dimer into a mononuclear form reveals irreversibility in electrochemical oxidation.

Under spectroelectrochemical conditions, we were able to observe an ESR spectrum of the intermediate at the first oxidation peak of dimer **1** in CH_2Cl_2 (Figure 6). As an ESR spectrum for the $Pd^{III}-Pd^{III}$ dimer could not be obtained due to the fact that the two Pd^{III} centers are strongly antiferromagnetically coupled;[8] the signal (g = 2.14 and ΔH = 40 Hz) was consistent with a paramagnetic mixed-valence $Pd^{II}-Pd^{III}$ state formed in the comproportionation reaction between the initial $Pd^{II}-Pd^{II}$ and final $Pd^{III}-Pd^{III}$ species (Scheme 3). A similar reaction was previously observed under ESR spectroelectrochemical conditions for another two-electron process with $Ni^{II}bpyX_2$ (bpy = 2,2′-bipyridine).[28,29] Our effort to obtain a low-T spectrum of **1** failed because the signal disappeared, the solution being frozen (150 K). The decrease in intensity of the spectrum with decreasing temperature, in contrast with Curie law, is an attribute for dimerization and polymerization processes in the solution.[30]

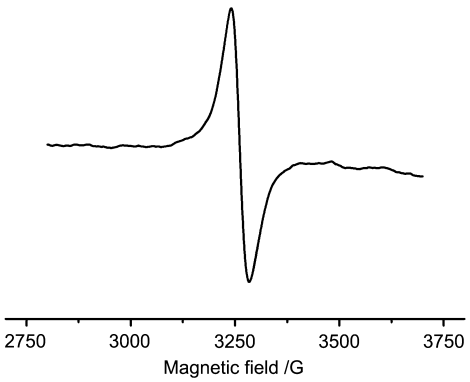
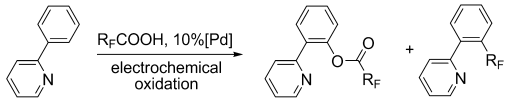


Figure 6. ESR spectrum obtained upon oxidation of [(PhPy)Pd(μ-OAc)]$_2$ (**1**) (CH_2Cl_2 solution, room temperature, 0.9 V vs Ag/AgCl).

Thus, this feature probably indicates one-dimensional Pd^{III} metallacyclic wire formation with oxidation of complex **1**.[31]

The unique feature of trifluoroacetate derivatives to form mono- or dinuclear palladacycles allowed for an investigation of the activity of different catalytic forms. A set of electrochemical oxidative C−H functionalization reactions of 2-phenylpyridine was explored (Table 2).

Table 2. Pd-Catalyzed Functionalization of 2-Phenylpyridine with Perfluoroalkyl Carboxylic Acids



entry	catalyst	solvent	acid	product (yield, %)
1[a]	$Pd(OAc)_2$	CH_3CN	$C_6F_{13}COOH$	**6a** (65)
2[a]	$Pd(TFA)_2$	CH_3CN	$C_6F_{13}COOH$	**6a** (62)
3[b]	$Pd(OAc)_2$	CH_3CN	$C_6F_{13}COOH$	**6a** (15) + **6b** (37)
4[a]	$Pd(OAc)_2$	CH_3CN	HC_4F_8COOH	**7a** (73)
5[a]	$Pd(OAc)_2$	CH_2Cl_2	HC_4F_8COOH	**7a** (14)
6[a]	$Pd(OAc)_2$	CH_2Cl_2	CH_3COOH	**9a** (trace)
7[a]	$Pd(TFA)_2$	CH_3CN	HC_4F_8COOH	**7a** (68)
8[a]	$Pd(OAc)_2$	CH_3CN	CF_3COOH	**8a** (trace)
9[a]	$Pd(TFA)_2$	CH_3CN	CF_3COOH	

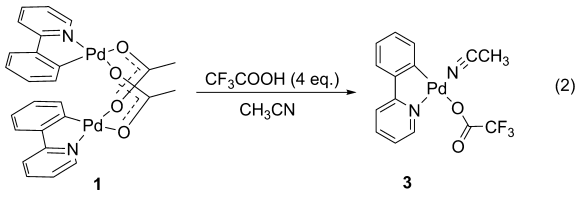
[a]The current strength was 100 mA h^{-1}. 2 F of electricity was passed per PhPy. [b]The current strength was 250 mA h^{-1}. 3 F of electricity was passed per PhPy.

$Pd(OAc)_2$ and $Pd(TFA)_2$ were used as catalysts and dichloromethane or acetonitrile was the reaction medium. Experiments using $Pd(TFA)_2$ in CH_2Cl_2 were not performed, owing to its low solubility. As seen in Table 2, the C−H functionalization products were obtained in good or moderate yields, despite the complete conversion of PhPy. Gratifyingly, we note that the electrochemical oxidations of the palladium complexes indeed lead to perfluorocarboxylate or perfluoroalkyl derivatives as described in Table 2. In the case of long-chain perfluorocarboxylic acids, it is possible to obtain perfluoroalkyl products by increasing the current strength and the amount of passed electricity.

It is noteworthy that both $Pd(OAc)_2$ and $Pd(TFA)_2$ catalysts are equally efficient in CH_3CN. We suggest that functionalization of PhPy with perfluorocarboxylic acids in CH_3CN runs through a mononuclear fluorinated palladium(II) complex formation for both $Pd(OAc)_2$ and $Pd(TFA)_2$ catalysts. In

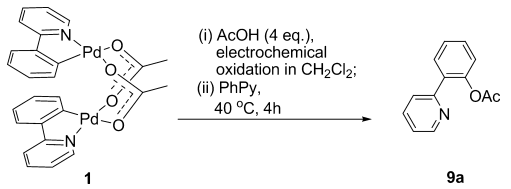
dx.doi.org/10.1021/om400492g | Organometallics XXXX, XXX, XXX−XXX

support of this, the characterized mononuclear complex **3**, resulting from carboxylic acid exchange, was obtained as the product of complete conversion of **1** treated with trifluoroacetic acid in acetonitrile (eq 2).



To get more insight into the monomer−dimer transformations during the C−H functionalization reactions, a sequence of electrochemical oxidation and further stoichiometric reactions with 2-phenylpyridine with $[(PhPy)Pd(\mu\text{-}OAc)]_2$ (**1**) was performed.

Scheme 4. Conversion of 1 into 9a in CH_2Cl_2



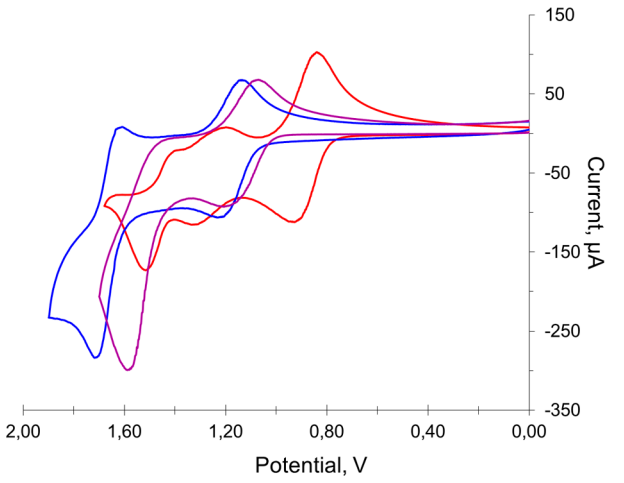


Figure 7. Cyclic voltammograms of $[(PhPy)Pd(\mu\text{-}OAc)]_2$ in the absence (red) and in the presence (6 equiv) of $H(CF_2)_4COOH$ (violet) in CH_2Cl_2 in comparison with $[(PhPy)Pd(\mu\text{-}TFA)]_2$ (blue).

Dimer **1** was electrochemically oxidized in the presence of acetic acid in dichloromethane (Scheme 4). Treatment of this oxidized material with 2-phenylpyridine afforded the product **9a** in 61% yield. During this sequence the reaction mixture changed from yellow to brownish red upon electrochemical oxidation, suggesting binuclear Pd^{III}−Pd^{III} complex formation, and then again to a yellow solution after completion of the reaction. These color changes are consistent with previous studies.[14]

In CH_2Cl_2 solution, complete conversion of acetate-bridged binuclear complex **1** into a perfluorocarboxylate-bridged dimer occurred by treatment with an excess of perfluorocarboxylic acid, as can be seen from the CV experiment (Figure 7).

Addition of perfluoroheptanoic acid to **1** suspended in acetonitrile resulted in a soluble material, suggesting fragmentation of **1** to a mononuclear Pd^{II} complex (Scheme 5). Electrochemical oxidation of this solution presumably leads to a mononuclear Pd^{IV} complex, further treatment of which with phenylpyridine afforded **6a** (67%).

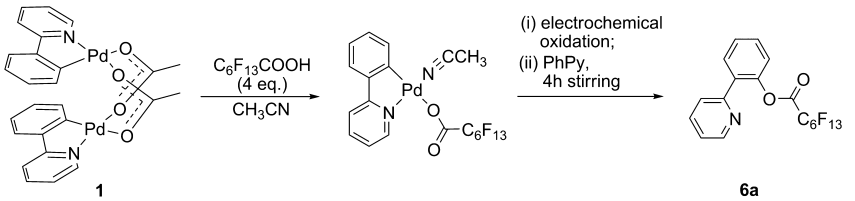
CONCLUSIONS

A convenient approach to C−H substitution products of 2-phenylpyridine using perfluoroalkyl carboxylic acid containing substituents is provided and is based on the electrochemical generation of palladium in high oxidation states. The fluorinated acid substituents make the oxidation of the dimeric palladium cycles more difficult in comparison to nonfluorinated compounds. We have also been able to record a signal in the ESR spectrum during the electro-oxidation of the dimer $[(PhPy)Pd(\mu\text{-}OAc)]_2$ and have tentatively assigned this signal to result from a mixed-valent Pd^{II}−Pd^{III} state. We also report that phenylpyridine palladium(II) trifluoroacetate derivatives were found to exist as mononuclear or binuclear complexes in the presence or absence of nitrogen donor ligands. The NMR and electrochemical data support the notion that C−H functionalization reactions of 2-phenylpyridine with perfluorocarboxylic acids proceed through mononuclear Pd^{II} intermediates in acetonitrile or binuclear fluorinated Pd^{II} intermediates in dichloromethane.

EXPERIMENTAL SECTION

General Considerations. All syntheses were carried out under a dry argon atmosphere. Yields refer to isolated and purified compounds. NMR experiments were carried out with Bruker AVANCE-400 spectrometers (400.1 MHz (^{1}H), 100.6 MHz (^{13}C), 376.5 MHz (^{19}F)). Chemical shifts are reported on the δ (ppm) scale relative to the residual solvent signals for ^{1}H and ^{13}C and to external C_6F_6 (−164.9 ppm) for ^{19}F NMR spectra. NMR data are reported as follows: resonance, multiplicity (singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sext), multiplet (m), broad resonance (br)), coupling constants in Hz, integration. The ESR spectrum was recorded in degassed dichloromethane solution at room temperature on a Bruker EMX spectrometer. The supporting salt Et_4NBF_4 was prepared by mixing an aqueous solution of Et_4NOH (30%) and HBF_4 until a neutral pH value was achieved. The precipitate that formed (Et_4NBF_4) was filtered off, recrystallized from ethanol, and dried in a vacuum desiccator at 100 °C for 48 h. Bu_4NBF_4 was purchased from Aldrich and was used without further purification. Anhydrous solvents were obtained either by distillation over

Scheme 5. Conversion of 1 into 6a in CH_3CN



dx.doi.org/10.1021/om400492g | Organometallics XXXX, XXX, XXX−XXX

phosphoric anhydride (dichloromethane, acetonitrile, ethyl acetate) or by distillation over sodium/benzophenone (ether, pentane, hexane). Trifluoroacetic, perfluoroheptanoic, and 5*H*-perfluoropentanoic acids (purchased from P&M Invest), 2-phenylpyridine (Acros Organics), acetic acid (Acros Organics), and palladium acetate (Alfa Aesar) were used as received.

Electrochemistry. Cyclic voltammograms were recorded with a BASi Epsilon potentiostat (USA) at room temperature in dichloromethane (5×10^{-3} substrate concentration) or acetonitrile (10^{-3} substrate concentration) solution. Bu_4NBF_4 (0.1 M) was used as the supporting electrolyte, and a glassy-carbon electrode was used as the working electrode. The auxiliary electrode was a platinum rod. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 100 mV s^{-1}. Preparative electrolyses were carried out using a B5-49 dc source at a current strength of 100 mA h^{-1} in a 30 mL three-electrode cell. The potential of the working electrode was detected by a V7−27 dc voltmeter in reference to Ag/AgCl electrode. The surface area of the platinum cylindrical anode used as the working electrode was 20.0 cm^2. A ceramic plate with a pore size of 10 μm was used as a membrane. A platinum grid served as a cathode, and the catholyte was a saturated solution of the background used in the anolyte in the corresponding solvent.

Preparation of Palladium Complexes. *Palladium Trifluoroacetate.* The procedure reported by Wilkinson et al. was used, without further modification.[32] $[(PhPy)Pd(\mu\text{-}OAc)]_2$ (**1**) was synthesized utilizing the method described by Ritter.[14] The ^1H and ^{13}C NMR data for **1** matched those reported in the reference.[14]

*$[(PhPy)Pd(\mu\text{-}TFA)]_2$ (**2**).* Palladium trifluoroacetate (1.04 g, 3.1 mmol, 1 equiv) was added to a solution of 2-phenylpyridine (0.48 g, 3.1 mmol, 1 equiv) in CH_2Cl_2 (30 mL). After it was stirred for 4 h at 40 °C, the yellow solution was concentrated in vacuo and the product was precipitated with Et_2O (7 mL). The solid was isolated by filtration, washed with Et_2O (2 × 3 mL), and dried in vacuo to afford 0.99 g of a yellow powder (65% yield). The ^1H and ^{13}C NMR data for **1** matched those reported in ref 22. ^{19}F NMR (376.5 MHz, CD_2Cl_2): δ −74.81.

*$[(PhPy)Pd(TFA)](CH_3CN)$ (**3**).* Palladium trifluoroacetate (1.04 g, 3.1 mmol, 1 equiv) was added to a solution of 2-phenylpyridine (0.48 g, 3.1 mmol, 1.00 equiv) in CH_3CN (30 mL). After it was stirred for 4 h at 21 °C, the yellow solution was concentrated in vacuo and left overnight, and then the colorless crystalline solid was precipitated from the mixture and filtered, and dried in vacuo to afford 1.08 g of the product (84% yield). ^1H NMR (400.0 MHz, CD_3CN): δ 8.30 (br d, J = 5.2 Hz, 1H); 7.96 (ddd, J = 8.1, 7.5, 1.5 Hz, 1H); 7.79 (br d, J = 7.9 Hz, 1H); 7.51 (dd, J = 7.6, 1.3 Hz, 1H); 7.26 (ddd, J = 7.3, 5.7, 1.4 Hz, 1H); 7.19 (br, 1H); 7.16 (td, J = 7.5, 1.1 Hz, 1H); 7.07 (td, J = 7.5, 1.5 Hz); 1.96 (s, 3H). ^{13}C NMR (100.6 MHz, CD_3CN): δ 166.15; 161.06 (q, $^2J_{CF}$ = 34.5 Hz); 150.22; 150.08; 146.40; 141.25; 135.27; 130.40; 126.51; 124.92; 123.99; 120.26; *C*N and solvent peaks overlap; CF_3 peak could not be resolved; 1.68. ^{19}F NMR (376.5 MHz, CD_3CN): δ −75.35.

*[(PhPy)Pd(TFA)](PhPy) (**4**).* Palladium trifluoroacetate (0.50 g, 1.5 mmol, 1 equiv) was added to a solution of 2-phenylpyridine (0.47 g, 3.0 mmol, 2 equiv) in $(CH_3)_2CO$ (50 mL). After it was refluxed for 4 h at 21 °C, the light yellow solution was concentrated in vacuo and the product was precipitated with Et_2O (5 mL), isolated by filtration, and dried in vacuo to afford 0.68 g of a light yellow powder (86% yield). ^1H NMR (400.0 MHz, $CDCl_3$): δ 9.38 (dd, J = 5.7, 0.9 Hz, 1H); 8.40 (dd, J = 5.7, 0.8 Hz, 1H); 8.11−8.08 (m, 2H); 7.96 (td, J = 7.8, 1.6 Hz, 1H); 7.76 (td, J = 7.8, 1.5 Hz, 1H); 7.65 (d, J = 7.8 Hz, 1H); 7.56 (d, J = 8.0 Hz, 1H); 7.44−7.38 (m, 4H); 7.31 (dd, J = 7.7, 1.3 Hz, 1H); 7.10 (ddd, J = 7.2, 5.8, 1.5 Hz, 1H); 7.00 (td, J = 7.5, 1.0 Hz, 1H); 6.83 (td, J = 7.5, 1.4 Hz, 1H); 6.08 (dd, J = 7.8, 0.9 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.00; 161.80 (q, $^2J_{CF}$ = 35.6 Hz); 161.73; 153.91; 150.95; 149.41; 145.30; 140.03; 138.84; 138.56; 133.18; 129.62; 129.20; 128.90 (2C); 128.41 (2C); 126.11; 124.49; 123.22; 123.12; 122.13; 118.30;116.62 (q, $^1J_{CF}$ = 291.6 Hz). ^{19}F NMR (376.5 MHz, $(CD_3)_2CO$): δ −75.46.

*[(PhPy)Pd(PFH)](PhPy) (**5**).* Palladium acetate (0.50 g, 2.2 mmol, 1 equiv), perfluoroheptanoic acid (0.81 g, 2.2 mmol, 1 equiv), and 2-phenylpyridine (0.70 g, 4.5 mmol, 2 equiv) were mixed in 30 mL of CH_3CN. The reaction mixture was stirred for 4 h, washed with water, and dried over $MgSO_4$, and then the solution was concentrated in vacuo to afford 1.53 g of a colorless crystalline solid (88% yield). ^1H NMR (400.0 MHz, $CDCl_3$): δ 9.38 (ddd, J = 5.7, 1.5, 0.9 Hz, 1H); 8.41 (ddd, J = 5.7, 1.5, 0.9 Hz, 1H); 8.10 (dd, J = 7.9, 1.5 Hz, 2H); 7.95 (td, J = 7.8, 1.6 Hz, 1H); 7.76 (td, J = 7.8, 1.6 Hz, 1H); 7.65 (ddd, J = 7.9, 1.2, 0.6 Hz, 1H); 7.56 (br d, J = 7.9 Hz, 1H); 7.44−7.37 (m, 4H); 7.31 (dd, J = 7.7, 1.3 Hz, 1H); 7.09 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H); 6.99 (td, J = 7.5, 1.0 Hz, 1H); 6.81 (td, J = 7.6, 1.4 Hz, 1H); 6.03 (dd, J = 7.8, 0.9 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.01; 161.98 (t, $^2J_{CF}$ = 25.1 Hz); 161.68; 153.97; 150.87; 149.47; 145.30; 140.04; 138.81; 138.45; 133.14; 129.58; 129.17; 128.94; 128.78; 128.74; 128.37; 126.08; 124.46; 123.10; 123.01; 122.09; 118.29; CF_3 and CF_2 groups could not be resolved. ^{19}F NMR (376.5 MHz, $(CD_3)_2CO$): δ −81.69; −116.50; −122.24; −122.90; −123.37; −126.70.

Synthesis of Ortho-Substituted 2-Phenylpyridine. In an electrochemical cell, 7 mmol of 2-phenylpyridine, 14 mmol of substrate acid, and 0.7 mmol of the corresponding Pd salt were dissolved in 20 mL of solvent. Electrolysis was conducted in a divided cell at a platinum anode with the use of Et_4NBF_4 (0.1 M, 0.43 g) or Bu_4NBF_4 (0.1 M, 0.66 g) as background electrolyte in CH_3CN or CH_2Cl_2, respectively, with stirring under a constant stream of argon. At the end of the electrolysis, the reaction mixture was placed in a 50 mL flask, and the solvent was removed on a rotary evaporator. The residue was then washed with water and extracted with benzene (three times with 50 mL). The organic layer was dried over $MgSO_4$, and then the solvent was removed. The product was purified by silica gel column chromatography (ethyl acetate−hexane). Yields of products are provided below.

*Yields of 2-(Pyridin-2′-yl)phenyl Perfluoroheptanoate (**6a**) under Different Reaction Conditions.* Yield: 2.35 g (65%), catalyst $Pd(OAc)_2$, solvent CH_3CN, current strength was 100 mA h^{-1}, 2 F of electricity was passed per PhPy; 2.24 g (62%), catalyst $Pd(TFA)_2$, solvent CH_3CN, current strength was 100 mA h^{-1}, 2 F of electricity was passed per PhPy; 0.54 g (15%), catalyst $Pd(OAc)_2$, solvent CH_3CN, current strength was 250 mA h^{-1}, 3 F of electricity was passed per PhPy. ^1H NMR (400.0 MHz, $CDCl_3$): δ 9.05 (br d, J = 5.1 Hz, 1H); 8.26 (td, J = 7.9, 0.9 Hz, 1H); 7.97 (dd, J = 8.1, 0.8 Hz, 1H); 7.93−7.90 (m, 2H); 7.70−7.67 (m, 1H); 7.59−7.54 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162,08 (t, $^2J_{CF}$ = 25.1 Hz); 154.02; 143.91; 143.63; 132.02; 131.64; 129.38 (2C); 127.90 (2C); 124.41; 124.12; 117.12 (qt, $^1J_{CF}$ = 288.3 Hz, $^2J_{CF}$ = 33.2 Hz); 110.96 (tquin, $^1J_{CF}$ = 270.5 Hz, $^2J_{CF}$ = 33.0 Hz); 110.96 (tquin, $^1J_{CF}$ = 270.5 Hz, $^2J_{CF}$ = 33.0 Hz); 110.41 (tquin, $^1J_{CF}$ = 269.2 Hz, $^2J_{CF}$ = 33.3 Hz); 109.10 (tt, $^1J_{CF}$ = 266.5 Hz, $^2J_{CF}$ = 31.7 Hz); 108.43 (tsext, $^1J_{CF}$ = 273.8 Hz, $^2J_{CF}$ = 35.6 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ −81.22; −117.57; −121.95; −122.71; −123.01; −126.38.

*Yields of 2-(2′-Perfluorohexylphenyl)pyridine (**6b**) under Different Reaction Conditions.* Yield: 1.23 g (37%), catalyst $Pd(OAc)_2$, solvent CH_3CN, current strength was 250 mA h^{-1}, 3 F of electricity was passed per PhPy. ^1H NMR (400.0 MHz, $(CD_3)_2CO$): δ 8.94 (d, J = 4.4 Hz, 1H,); 8.33 (dt, J = 8.1, 1.7 Hz, 1H); 8.21 (br d, J = 8.2 Hz, 1H); 8.13 (m, 2H); 7.75 (ddd, J = 7.5, 5.3, 1.2 Hz, 1H); 7.58 (m, 2H). ^{13}C NMR (100.6 MHz, $(CD_3)_2CO$): δ 160.43 (t, $^2J_{CF}$ = 25.3 Hz); 154.27; 145.24; 142.79; 134.29; 130.83; 129.12; 128.20; 127.76; 124.22; 123.65; 118.66 (tt, $^1J_{CF}$ = 287.3 Hz, $^2J_{CF}$ = 33.4 Hz); 115−105 (m, 4C); 109.93 (qt, $^1J_{CF}$ = 237.6 Hz, $^2J_{CF}$ = 33.7 Hz). ^{19}F NMR (376.5 MHz, $(CD_3)_2CO$): δ −81.57; −117.71; −122.07; −123.89; −123.21; −126.58.

*Yields of 2-(Pyridin-2′-yl)phenyl 5H-Perfluoropentanoate (**7a**) under Different Reaction Conditions.* Yield: 2.04 g (73%), catalyst $Pd(OAc)_2$, solvent CH_3CN, current strength was 100 mA h^{-1}, 2 F of electricity was passed per PhPy; 0.39 g (14%), catalyst $Pd(OAc)_2$, solvent CH_2Cl_2, current strength was 100 mA h^{-1}, 2 F of electricity was passed per PhPy; 1.90 g (68%), catalyst $Pd(TFA)_2$, solvent CH_3CN, current strength was 100 mA h^{-1}, 2 F of electricity was passed per PhPy. ^1H NMR (400.0 MHz, $CDCl_3$): δ 8.90 (br d, J = 3.2 Hz, 1H); 8.27 (t, J = 7.6 Hz, 1H); 7.97 (d, J = 8.0 Hz, 1H); 7.86−7.84 (m, 2H); 7.67 (br t, J = 5.5 Hz, 1H); 7.54−7.47 (m, 2H); 6.25 (tt, J =

dx.doi.org/10.1021/om400492g | *Organometallics* XXXX, XXX, XXX−XXX

52.0, 5.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.43 (t, $^2J_{CF}$ = 25.3 Hz); 153.84; 144.25; 143.31; 131.83; 131.66; 129.46 (2C); 127.91 (2C); 124.57; 124.24; 107.76 (tt, $^1J_{CF}$ = 253.1 Hz, $^2J_{CF}$ = 29.3 Hz); 108.93 (tt, $^1J_{CF}$ = 264.3 Hz, $^2J_{CF}$ = 29.8 Hz); 110.08 (tquin, $^1J_{CF}$ = 263.5 Hz, $^2J_{CF}$ = 30.0 Hz); 110.79 (tquin, $^1J_{CF}$ = 266.5 Hz, $^2J_{CF}$ = 30.5 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ −118.11, −125.83, −130.67, −137.87.

*Yields of 2-(Pyridin-2′-yl)phenyl Trifluoroacetate (**8a**) under Different Reaction Conditions.* The product was observed in traces: catalyst $Pd(OAc)_2$, solvent CH_3CN, current strength was 100 mA h^{-1}, 2 F of electricity was passed per PhPy. ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 8.87 (d, J = 5.1 Hz, 1H); 8.23 (t, J = 7.8 Hz, 1H); 7.94 (d, J = 8.1 Hz, 1H); 7.86−7.83 (m, 2H); 7.63 (t, J = 6.4 Hz, 1H); 7.48−7.46 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 161.41 (q, $^2J_{CF}$ = 36.3 Hz); 153.99; 143.74; 143.66; 132.27; 131.46; 129.34; 127.76; 124.28; 124.04;116.29 (q, $^1J_{CF}$ = 291.1 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ −75.45.

*Yields of 2-(Pyridin-2′-yl)phenyl Acetate (**9a**).* The product was observed in traces: catalyst $Pd(OAc)_2$, solvent CH_2Cl_2, current strength was 100 mA h^{-1}. 2 F of electricity was passed per PhPy. The ^{1}H and ^{13}C NMR data for **9a** matched those reported in ref 14.

Reactions of Phenylpyridyl Palladium Acetate Dimer. *Equation 2.* To a 0.7 mL suspension of **1** (10 mg, 0.016 mmol, 1 equiv) in CD_3CN was added trifluoroacetic acid (7.3 mg, 0.064 mmol, 4 equiv). The reaction mixture immediately changed into a clear colorless solution. ^{1}H NMR data revealed complete conversion of **1** into **3**.

Scheme 4. A 20 mL solution of **1** (0.10 g, 0.16 mmol, 1 equiv), acetic acid (0.05 g, 0.64 mmol, 4 equiv), and Et_4NBF_4 as a supporting salt in CH_2Cl_2 was oxidized in an electrochemical cell (0.9 V vs Ag/AgCl, 2 F of electricity per dimer); the solution changed from bright yellow to brownish red. The reaction mixture was transferred via cannula to a flask with 2-phenylpyridine[33] (0.49 g, 3.1 mmol, 20 equiv) and was heated under reflux for 4 h while the reaction mixture turned clear yellow. According to ^{1}H NMR data versus an internal standard, **9a** was obtained in 61% yield.

Scheme 5. To a clear colorless solution obtained after addition of perfluoroheptanoic acid (0.23 g, 0.64 mmol, 4 equiv) to **1** (0.10 g, 0.16 mmol, 1 equiv) suspended in 20 mL of acetonitrile was added Et_4NBF_4 as a supporting salt. This mixture was electrochemically oxidized (1.80 V vs Ag/AgCl, 2 F of electricity per original dimer). The reaction mixture turned brownish red and was transferred via cannula to a flask with 2-phenylpyridine[33] (0.49 g, 3.1 mmol, 20 equiv) and was heated under reflux for 4 h while the reaction mixture turned clear yellow. According to ^{1}H NMR data versus an internal standard, **6a** was obtained in 67% yield.

Details of X-ray Diffraction Measurements. Single-crystal X-ray diffraction data were collected at 150(2) K with a Bruker AXS Smart APEX diffractometer and Mo Kα radiation (λ = 0.71073 Å). Programs used: data collection, APEX2;[34] data reduction, SAINT;[35] absorption correction, SADABS version 2.10;[36] structure solution, SHELXS97,[37] structure refinement by full-matrix least- squares against F^2 using SHELXL-97[37] and WINGX-97 suite.[38] The figures were generated using ORTEP-3[39] and Mercury CSD 2.0[40] programs.

*Crystal data for **3**:* formula $C_{15}H_{11}F_3N_2O_2Pd$, crystal size 0.52 × 0.22 × 0.13 mm^3, M = 414.66, monoclinic, space group Cc, a = 22.628(7) Å, b = 4.8670(10) Å, c = 13.950(4) Å, β = 98.795(3)°, V = 1518.3(7) Å^3, Z = 4, ρ_{calcd} = 1.814 g cm^{-3}, μ = 1.264 mm^{-1}, θ_{max} = 26°, 4628 reflections collected, 2791 independent (R_{int} = 0.1248) and 2717 observed reflections ($I > 2\sigma(I)$), 209 refined parameters, R1 = 0.0581, wR2 = 0.1518 ($I > 2\sigma(I)$); maximum/minimum residual electron density 2.026/−1.102 e/Å^3 close to the palladium atom, GOF = 1.075.

*Crystal data for **4**.* formula $C_{24}H_{17}F_3N_2O_2Pd$, crystal size 0.34 × 0.31 × 0.21 mm^3, M = 528.80, triclinic, space group $P\bar{1}$, a = 10.0780(10) Å, b = 14.934(2) Å, c = 16.293(2) Å, α = 113.3710(10)°, β = 99.269(2)°, γ = 104.559(2)°, V = 2082.7(4) Å^3, Z = 4, ρ_{calcd} = 1.686 g cm^{-3}, μ = 0.942 mm^{-1}, θ_{max} = 28.55°, 23826 reflections collected, 10239 independent (R_{int} = 0.0346) and 8221 observed reflections ($I > 2\sigma(I)$), 642 refined parameters, R1 = 0.0294, wR2 = 0.0686 ($I > 2\sigma(I)$), maximum/minimum residual electron density 0.763/−0.595 e/Å^3, GOF = 1.026.

*Crystal data for **5**.* formula $C_{29}H_{17}F_{13}N_2O_2Pd$, crystal size 0.31 × 0.24 × 0.18 mm^3, M = 778.85, monoclinic, space group $P2_1/c$, a = 18.167(3) Å, b = 11.479(2) Å, c = 14.622(3) Å, β = 101.087(2)°, V = 2992.3(9) Å^3, Z = 4, ρ_{calcd} = 1.729 g cm^{-3}, μ = 0.732 mm^{-1}, θ_{max} = 26.3°, 30998 reflections collected, 6030 independent (R_{int} = 0.0701) and 4483 observed reflections ($I > 2\sigma(I)$), 424 refined parameters, R1 = 0.0338, wR2 = 0.0690 ($I > 2\sigma(I)$); maximum/minimum residual electron density 0.825/−0.456 e/Å^3, GOF = 0.949.

CCDC 940289−940291 contain supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44(1223)336-033, e-mail deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving X-ray structural information for **3**−**5** and figures giving ^{1}H, ^{13}C, and ^{19}F NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for Y.H.B.: yulia@iopc.ru.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the RFBR grant 11-03-92662-MCXa and by the Russian Ministry of Science and Education, grant number 8446. D.A.V. thanks the U.S. NSF, grant CHE-1124619, for support of this work.

■ REFERENCES

(1) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147−1169.
(2) Negishi, E., *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: Hoboken, NJ, 2002.
(3) Hartwig, J.F., *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: Sausalito, CA, 2010.
(4) Wang, X.; Truesdale, L.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 3648−3649.
(5) Sakai, N.; Ridder, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 8134−8135.
(6) Shan, G.; Yang, X.; Ma, L.; Rao, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 13070−13074.
(7) Yuan, D.; Huynh, H. V. *Organometallics* **2012**, *31*, 405−412.
(8) Mirica, L. M.; Khusnutdinova, J. R. *Coord. Chem. Rev.* **2013**, *257*, 299−314.
(9) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.
(10) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400−3420.
(11) Stoltz, B. M. *Chem. Lett.* **2004**, *33*, 362−367.
(12) Gligorich, K. M.; Sigman, M. S. *Chem. Commun.* **2009**, 3854−3867.
(13) Jutand, A. *Chem. Rev.* **2008**, *108*, 2300−2347.
(14) Powers, D. C.; Geibel, M. A. L.; Klein, J. E. M. N.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 17050−17051.
(15) Powers, D. C.; Ritter, T. *Nat. Chem.* **2009**, *1*, 302−309.
(16) Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2010**, *132*, 7303−7305.
(17) Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824−889.
(18) Canty, A. J. *Dalton Trans.* **2009**, 10409−10417.
(19) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924−1935.

(20) Kakiuchi, F.; Kochi, T.; Mutsutani, H.; Kobayashi, N.; Urano, S.; Sato, M.; Nishiyama, S.; Tanabe, T. *J. Am. Chem. Soc.* **2009**, *131*, 11310−11311.
(21) Dudkina, Y. B.; Mikhaylov, D. Y.; Gryaznova, T. V.; Sinyashin, O. G.; Vicic, D. A.; Budnikova, Y. H. *Eur. J. Org. Chem.* **2012**, 2114−2117.
(22) Bercaw, J. E.; Durrell, A. C.; Gray, H. B.; Green, J. C.; Hazari, N.; Labinger, J. A.; Winkler, J. R. *Inorg. Chem.* **2010**, *49*, 1801−1810.
(23) Canty, A. J.; Ariafard, A.; Sanford, M. S.; Yates, B. F. *Organometallics* **2013**, *32*, 544−555.
(24) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252−1260.
(25) Powers, D. C.; Xiao, D. Y.; Geibel, M. A. L.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 14530−14536.
(26) Powers, D. C.; Ritter, T. *Acc. Chem. Res.* **2012**, *45*, 840−850.
(27) Amatore, C.; Azzabi, M.; Calas, P.; Jutand, A.; Lefrou, C.; Rollin, Y. *J. Electroanal. Chem.* **1990**, *288*, 45−63.
(28) Budnikova, Yu. G.; Yakhvarov, D. G.; Morozov, V. I.; Kargin, Yu. M.; Il'yasov, A. V.; Vyakhireva, Yu. N.; Sinyashin, O. G. *Russ. J. Gen. Chem.* **2002**, *72*, 168−172.
(29) Budnikova, Y. H.; Mikhaylov, D. Y.; Gryaznova, T. V.; Sinyashin, O. G. *ECS Trans.* **2010**, *25*, 66−77.
(30) Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1992**, *114*, 5454−5455.
(31) Campbell, M. G.; Powers, D. C.; Raynaud, J.; Graham, M. J.; Xie, P.; Lee, E.; Ritter, T. *Nat. Chem.* **2011**, *3*, 949−953.
(32) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632−3640.
(33) Excess nitrogenous substrate is necessary for the reductive elimination step.[14]
(34) *APEX2 Software Suite for Crystallographic Programs*, Bruker AXS, Inc., Madison, WI, 2009.
(35) *SMART and SAINT Area Detector Control and Integration Software, Version S.x*; Bruker Analytical X-ray Instruments Inc., Madison, WI, 1996.
(36) Sheldrick, G. M. *SHELX-97: Programs for Crystal Structure Analysis*; University of Göttingen, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1997.
(37) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.
(38) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(39) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565−566.
(40) Macrae, F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466−470.