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Oxidatively Resistant Ligands for Palladium-Catalyzed Aerobic Alcohol Oxidation

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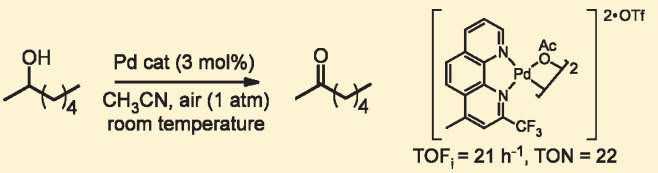
Supporting Information

ABSTRACT: The complex $[(\text{neocuproine})\text{Pd}(\text{OAc})]_2[\text{OTf}]_2$ (**1**) catalyzes the aerobic oxidation of 2-heptanol at room temperature, but competitive ligand oxidation leads to low catalyst lifetimes. In an effort to mitigate the oxidative degradation of the ligand, a variety of Pd complexes ligated by fluorinated phenanthrolines (bis-2,9-(trifluoromethyl)-1,10-phenanthroline (btfm-phen), 4-methyl-2-(trifluoromethyl)-1,10-phenanthroline (tfmm-phen), and 2-(*o*-difluorophenyl)-1,10-phenanthroline (odfp-phen)) were prepared and tested. Active catalyst precursors were generated by in situ conproportionation of (N−N)Pd(OAc)$_2$ and $[(\text{N}-\text{N})\text{Pd}(\text{NCCH}_3)_2[\text{OTf}]_2$. Pd complexes derived from tfmm-phen catalyzed the aerobic oxidation of 2-heptanol at room temperature with up to 22 turnovers, nearly double that of **1**.



INTRODUCTION

Palladium-catalyzed aerobic alcohol oxidation[1−6] has advanced considerably since the initial report in 1977.[7] More than a decade later, it was discovered that coordinating solvents such as DMSO or pyridine could effectively stabilize Pd(0) intermediates and facilitate their reoxidation by oxygen before Pd black formation occurs.[8−11] Subsequently, other ligands were used to similar effect, and well-defined complexes of palladium with sparteine,[12−14] phenanthroline,[15−19] and N-heterocyclic carbene (NHC)[2,20−23] scaffolds have been reported for aerobic alcohol oxidation. Frequently these systems rely on acetate counterions due to their ability to facilitate deprotonation of coordinated alcohols; while other coordinating anions are tolerated, they typically require additional base for catalysis.[2,24,25]

We previously reported that the 2,9-dimethyl-1,10-phenanthroline (neocuproine) complex $[(\text{neocuproine})\text{Pd}(\text{OAc})]_2[\text{OTf}]_2$ (**1**) is active for the aerobic oxidation of 2-heptanol at room temperature.[26] Complex **1** exhibits a high initial turnover rate (∼78 $\text{Pd}^{-1}\ \text{h}^{-1}$), but degrades rapidly due to competitive oxidation of the ligand by partially reduced oxygen species (Scheme 1). Stahl and co-workers[27] reported similar ligand oxidation after partial reduction of oxygen by Pd, yielding a reactive Pd(II)-hydroperoxo species. The use of other oxidants, such as benzoquinone, can mitigate this destructive side reaction, but the synthetic utility of oxygen as a terminal oxidant remains attractive.[28] Herein we document efforts to develop more oxidatively resistant phenanthroline ligands to mitigate competitive ligand oxidation pathways in the aerobic oxidation of alcohols.

RESULTS AND DISCUSSION

Synthesis of Oxidatively Resistant Ligands. Four phenanthroline derivatives were targeted as potential ligands: 1,10-phenanthroline (phen), bis-2,9-(trifluoromethyl)-1,10-phenanthroline (btfm-phen), 4-methyl-2-(trifluoromethyl)-1,10-phenanthroline (tfmm-phen), and 2-(*o*-difluorophenyl)-1,10-phenanthroline (odfp-phen). Of these, phen is commercially available and btfm-phen can be synthesized by radical chlorination of neocuproine[29] followed by halogen exchange with SbF_3/SbF_5.[30]

Several 4,5-disubstituted 2-(trifluoromethyl)-1,10-phenanthrolines are known,[31,32] but 2-(trifluoromethyl)-1,10-phenanthroline (tfm-phen) has not been reported. We initially attempted the synthesis of tfm-phen by a Skraup−Doebner−Von Miller reaction using α,β-unsaturated carbonyl **4** (Scheme 2) and 8-aminoquinoline.[33,34] However, isolation of the aldehyde **4** from Et_2O proved difficult due its high volatility.[35] The less volatile ketone derivative **5**[36] was easier to purify, and condensation of **5** with 8-aminoquinoline yielded the desired trifluoromethyl-substituted phenanthroline **6**.[33]

Fluorinated aryl phenanthrolines have been proposed as oxidatively resistant ligands as reported by Sadighi et al.[37] in Cu-mediated transfer of nitrenes. Related 2-polyfluoroaryl-phenanthrolines have also been reported by Deacon et al.[38,39] We adapted a synthetic route to 2-phenyl-1,10-phenanthroline reported by Thummel and co-workers (Scheme 3).[40] Substitution of 2′,6′-difluoroacetophenone for acetophenone in the final step yielded **7** in 58% yield from 8-amino-7-quinolinecarbaldehyde. Despite being five steps, this strategy provides an expeditious route to **7**, requiring no purification steps until the penultimate step. Attempts to synthesize this compound through Sauvage-type conditions[41] using 2,6-difluorophenyl lithium[42] and phenanthroline provided low yields of **7**, which could not readily be purified.

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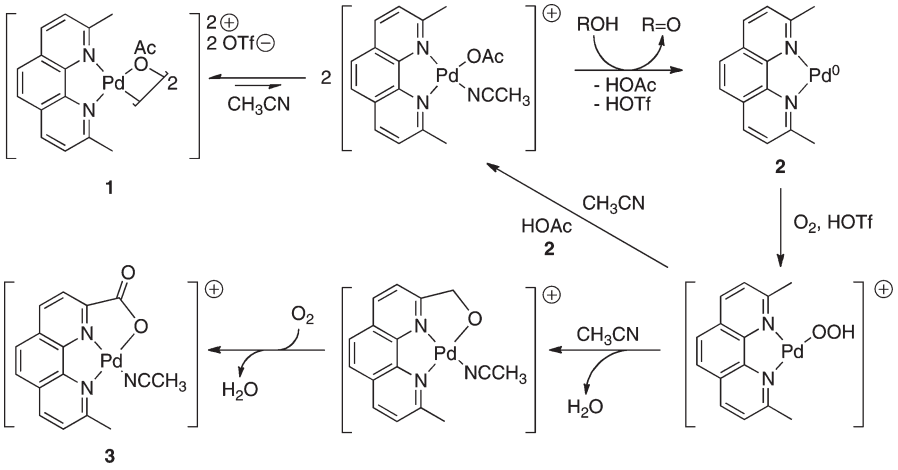
Scheme 1. Ligand Oxidation Resulting from Oxygen Reduction in Aerobic Alcohol Oxidation



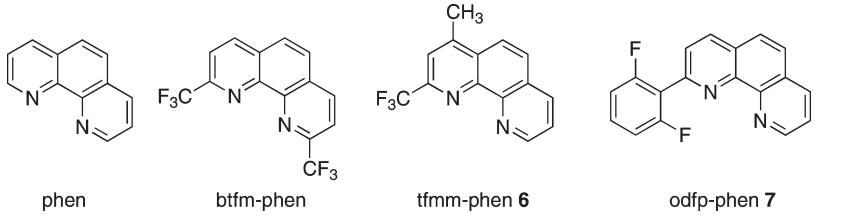
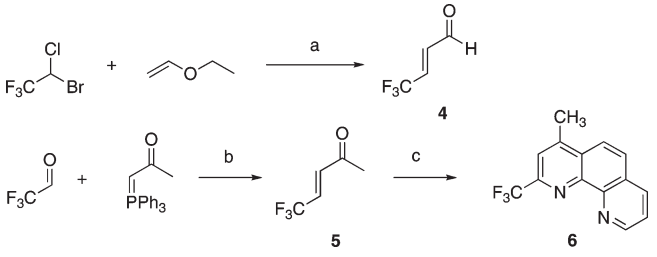


Figure 1. Substituted phenanthroline ligands.

Scheme 2. Synthesis of 4-Methyl-2-(trifluoromethyl)-1,10-phenanthroline (6)[a]



[a] Conditions: (a) $Na_2S_2O_4$, $NaHCO_3$, CH_3CN, H_2O, 10 °C, 1 h.; (b) Et_2O, polyphosphoric acid, rt, 2 h (63%); and (c) 8-aminoquinoline, NaI (1 mol %), H_2SO_4, 110 °C, 5 h (21%).

Synthesis of Phenanthroline Palladium Complexes. The synthesis of cationic (N−N)Pd acetate complexes was carried out by conproportionation of a 1:1 mixture of the diacetate (N−N)Pd$(OAc)_2$ (**A**) and ditriflate [(N−N)Pd$(NCCH_3)_2$]-[OTf]$_2$ (**B**) complexes by a procedure previously described (Scheme 4).[26]

For the phenanthroline complexes, the diacetate complex (phen)Pd$(OAc)_2$ was synthesized as previously reported.[43] Our attempts to generate the ditriflate complex [(phen)Pd$(CH_3CN)_2$][OTf]$_2$ by reaction of (phen)$PdCl_2$ with AgOTf in acetonitrile[44] were unsuccessful and yielded at least two species by ^{1}H NMR. Attempted ligation of phenanthroline with $(CH_3CN)_4Pd(OTf)_2$ also yielded multiple unidentified species, as determined by ^{1}H NMR. However, treatment of (phen)Pd$(OAc)_2$ with triflic acid followed by two recrystallizations from CH_3CN and Et_2O generated [(phen)Pd$(CH_3CN)_2$][OTf]$_2$ as a single species. The observed ^{1}H NMR chemical shifts were consistent with that previously reported.[44]

Addition of [(phen)Pd$(CH_3CN)_2$][OTf]$_2$ to (phen)Pd$(OAc)_2$ in CD_3CN yielded a complex ^{1}H NMR spectrum that was consistent with the formation of several new species. Removal of the solvent under vacuum yielded an orange solid, characterized as the dimeric [(phen)Pd$(OAc)]_2$[OTf]$_2$, **8**. X-ray quality crystals of **8** were obtained by slow diffusion of diethyl ether into a saturated acetonitrile solution of a 1:1 mixture of [(phen)Pd$(CH_3CN)_2$][OTf]$_2$ and (phen)Pd$(OAc)_2$.

The structure of [(phen)Pd$(OAc)]_2$[OTf]$_2$ (**8**, Figure 2) is similar to that previously reported for its neocuproine analogue **1**[26] and other palladium phen dimers.[45−47] A comparison of selected bond lengths and angles of **8** with the neocuproine analogue **1** is provided in the Supporting Information. Due to the absence of flanking methyl groups, the Pd−N bond lengths of the dimeric phen complex **8** are shorter than those for the neocuproine dimer **1**. The O−Pd−O bond angles in **8** (91.26(15) and 90.67(18) Å) are closer to the ideal 90° for a square-planar geometry than those found in **1** (84.17(9) and 81.85(8) Å), and the Pd−Pd distance in **8** (2.8548(9) Å) is shorter than that of **1** by 0.1 Å and in the range of that proposed for weak Pd−Pd interactions.[47−50]

Despite a previous report describing (btfm-phen)Pd$(OAc)_2$ as an effective alcohol oxidation catalyst at 80 °C in DMSO/water,[18] our attempts to prepare (btfm-phen)Pd$(OAc)_2$ were unsuccessful; we were unable to observe complexation of this ligand to Pd$(OAc)_2$ in either CH_3CN or toluene/CH_2Cl_2 (see Supporting Information).

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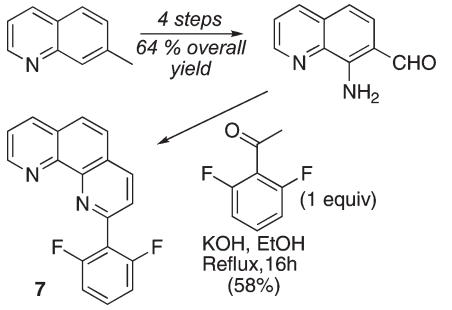
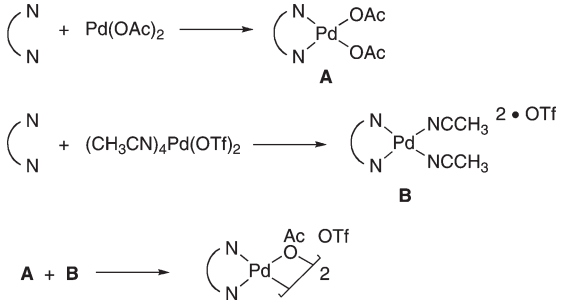
Scheme 3. Abridged Synthetic Route to odfp-phen 7



Scheme 4. General Procedure for the Formation of Cationic Palladium Complexes in situ



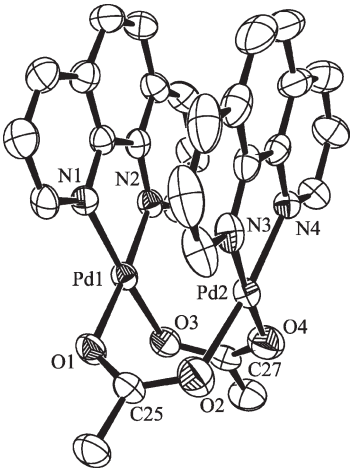
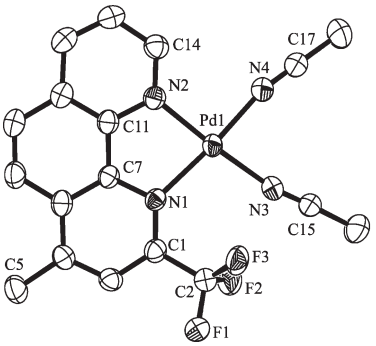


Figure 2. X-ray crystal structure of $[(phen)Pd(OAc)]_2[OTf]_2$ (**8**) with ellipsoids drawn at 50% probability. The unit cell contains two dimeric complexes. An interdimer Pd−Pd distance of 3.0996(11) Å was observed. The second dimeric unit, hydrogen atoms, triflate counterions, and solvent molecules have been omitted for clarity. Select bond lengths (Å) and angles (deg): Pd1−Pd2, 2.8548(9); Pd1−O1, 2.007(3); Pd1−O3, 2.021(4); Pd1−N1, 2.014(4); Pd1−N2, 2.000(4); Pd2−O2, 2.013(4); Pd2−O4, 2.016(4); Pd2−N3, 2.034(4); Pd2−N4, 2.032(4); O3−C27, 1.286(7); C27−O4, 1.299(7); O1−C25, 1.282(6); C25−O2, 1.308(7); O1−Pd1−O3, 91.26(15); O2−Pd2−O4, 90.67(18); O1−Pd1−N1, 93.38(16); and N1−Pd1−N2, 82.21(16).

The less sterically demanding 2-(trifluoromethyl)-4-methyl-1,10-phenanthroline (tfmm-phen) **6** could be readily complexed to palladium by stirring an equimolar solution of **6** and $Pd(OAc)_2$ in toluene/CH_2Cl_2 to yield $(tfmm\text{-}phen)Pd(OAc)_2$ (**9**) as a red solid. Complex **9** is only sparingly soluble in chloroform, dichloromethane, and acetonitrile, but exhibits higher solubility in 1,1,2,2-tetrachloroethane (TCE). ^1H NMR spectroscopy in d_2-TCE showed a single species with two inequivalent acetate ions.



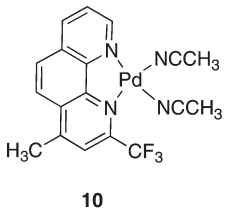


Figure 3. X-ray crystal structure of $[(tfmm\text{-}phen)Pd(CH_3CN)]_2[OTf]_2$ (**10**) with ellipsoids drawn at 50% probability. Hydrogen atoms and triflate counterions are omitted for clarity. Select bond lengths (Å) and angles (deg): Pd(1)−N(1), 2.073(3); Pd(1)−N(2), 1.984(3); Pd(1)−N(3), 2.000(3); Pd(1)−N(4), 1.992(3); N(2)−Pd(1)−N(4), 93.48(11); N(2)−Pd(1)−N(3), 175.77(11); N(4)−Pd(1)−N(3), 82.58(11); N(2)−Pd(1)−N(1), 81.70(10); C(1)−N(1)−Pd(1), 133.6(2); and C(14)−N(2)−Pd(1), 127.2(2).

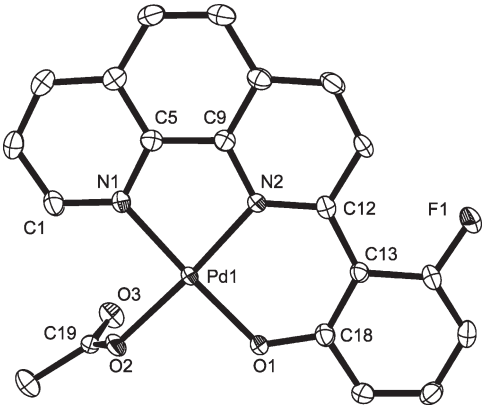


Figure 4. X-ray crystal structure of **12** with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Select bond lengths (Å) and angles (deg): Pd(1)−N(2), 1.987(2); Pd(1)−N(1), 1.998(2); Pd(1)−O(1), 1.9521(19); Pd(1)−O(2), 2.0340(19); N(2)−Pd(1)−N(1), 84.05(9); O(1)−Pd(1)−N(2), 92.99(8); O(1)−Pd(1)−O(2), 91.36(8); N(1)−Pd(1)−O(2), 91.48(9); O(1)−Pd(1)−N(1), 176.45(9); N(2)−Pd(1)−O(2), 174.49(8); O(1)−C(18)−C(13), 127.0(2); O(1)−C(18)−C(17), 113.7(2); and Pd(1)−O(1)−C(18)−C(13), 4.1(4).

The dicationic analogue $[(tfmm\text{-}phen)Pd(NCCH_3)_2][OTf]_2$ (**10**) was prepared by addition of $[(CH_3CN)_4Pd][OTf]_2$ to **6**; preparation by addition of triflic acid to **9** did not yield **10** cleanly. Slow diffusion of Et_2O into a solution of **10** in acetonitrile yielded crystals suitable for X-ray diffraction (Figure 3). The Pd−N1 bond (2.073(3) Å) is elongated compared to Pd−N2 (1.984(3) Å), and it is also slightly longer than previously observed Pd−N bond lengths in analogous dicationic phenanthroline-based systems.[26,44]

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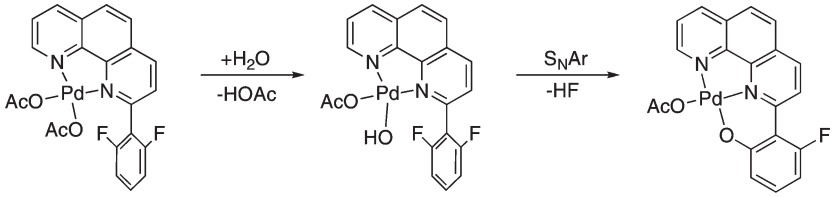
Scheme 5. Proposed Mechanism for Palladium-Mediated Fluoride Substitution by Adventitious Water



Conproportionation of **9** and **10** in a 1:1 molar ratio produced a complex ^{1}H NMR spectrum consistent with the generation of several new cationic species; no residual **9** or **10** was detectable after mixing. The complexity in the ^{1}H NMR spectrum is likely a consequence of monomer−dimer equilibria[26] of a variety of stereoisomeric dimers of the asymmetric phenanthroline Pd complexes.

The $Pd(OAc)_2$ complex of *o*-difluorophenyl-phenanthroline (odfp-phen) was prepared by mixing $Pd(OAc)_2$ with odfp-phen in dry toluene/CH_2Cl_2 to yield (odfp-phen)$Pd(OAc)_2$ (**11**) as a yellow solid. A half-equivalent of CH_2Cl_2 remained even after long periods under high vacuum, but the identity of **11** was established by ^{1}H and ^{13}C NMR spectroscopy and combustion analysis (as the CH_2Cl_2 solvate).

The diacetate complex **11** was crystallized over several days from a saturated acetonitrile solution, and analysis of the X-ray structure revealed that the new phenoxide complex **12** had formed (Figure 4). Complex **12** was fully characterized by ^{1}H and ^{13}C NMR spectroscopy, both of which were consistent with substitution of one of the fluorine atoms with oxygen. Solutions of **11** in rigorously dried acetonitrile did not convert to **12**, suggesting that the substituted oxygen in **12** arises from adventitious water.

The formation of **12** by hydrolysis of **11** was confirmed by the addition of water to a dry acetonitrile solution of **11**. After three days, crystals of **12** could be isolated in 36% yield. We propose that adventitious water displaces one of the acetate ligands to generate the Pd-hydroxo complex **13**, which undergoes intramolecular nucleophilic aromatic substitution of fluoride, yielding **12** (Scheme 5). Alternatively, reversible dissociation of one of the acetates could generate a cationic Pd complex, which could activate one of the ortho-fluorines toward *inter*molecular S_NAr by hydroxide. We currently disfavor the second hypothesis, as similar substitution by methoxide was not observed when methanol was used as a solvent. The transformation of **11** to **12** may have implications for carbon−fluorine bond activation, such as those reported for Pt(II)[51−53] and Ni(0)[54−58] complexes, and is similar to substitution reactions observed by Usòn et al.[59]

Initial attempts to prepare the palladium ditriflate complex of odfp-phen (**14**) from a mixture of $(CH_3CN)_2PdCl_2$ and 2 equiv of AgOTf in acetonitrile led to the cationic Pd chloride complex [(odfp-phen)$Pd(NCCH_3)Cl$][OTf] (**15**) in 10−20% yield (Scheme 6). Crystallization of **15** from acetonitrile afforded crystals suitable for X-ray analysis (Figure 5). The asymmetrically substituted complex **15** exists as a single isomer in the solid state. The coordinated chloride is *trans* to the nitrogen bearing the *o*-difluorophenyl substituent. The *o*-difluorophenyl substituent lies out of plane of the phenanthroline ligand by 58.8(5)°, as evidenced by the N2−C12−C13−C18 torsion angle.

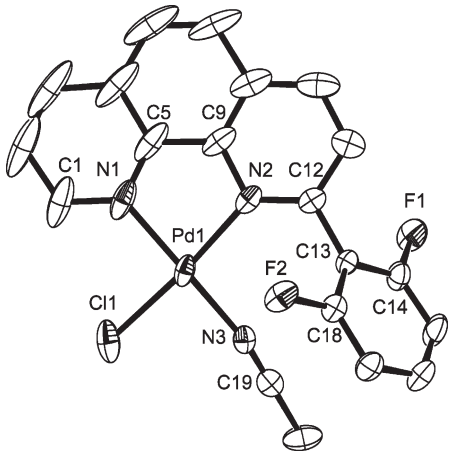


Figure 5. X-ray crystal structure of **15** with ellipsoids drawn at 50% probability. Hydrogen atoms and a triflate counterion have been omitted for clarity.

In contrast to **11**, the monocationic complex **15** did not hydrolyze in wet CD_3CN and showed no sign of fluoride displacement, even after heating to 70 °C for 7 days. The higher hydrolytic stability of **15** relative to **11** suggests that the presence of the ancillary acetate ligand in **11** facilitates the displacement of the fluoride to give **12**.

Treatment of **15** with excess AgOTf in refluxing acetonitrile for several days afforded the dicationic bis-acetonitrile complex **14** (Scheme 6). The dicationic **14** was less hydrolytically stable than **15**, and over the course of several days in wet acetonitrile, the complex degraded into several unidentifiable species.

Combination of **11** and **14** in a 1:1 molar ratio in dry CD_3CN yielded several new species. Analysis of the ^{1}H NMR spectrum was complicated by the increased number of possible stereoisomers combined with the known solution equilibria;[26] analogous to the mixing of **9** and **10**, no residual peaks attributable to **11** or **14** were observed after mixing.

Catalytic Aerobic Alcohol Oxidation. To assess the influence of the ligands on the activity of the Pd complexes for aerobic alcohol oxidation, we investigated the oxidation of 2-heptanol in acetonitrile in air at room temperature, as previously described (Figure 6 and Table 1).[26] For these experiments, the cationic Pd complexes were either generated in situ (from **9**/**10** and **11**/**14**) or introduced as the isolated Pd dimers (complexes **1** and **8**) at a Pd concentration of 1.5 mM (3 mol % relative to 2-heptanol).

As previously reported, the dimeric complex **1** exhibits a fast initial rate (Figure 6, Table 1), but the activity drops off rapidly and the maximum conversion under these conditions is only

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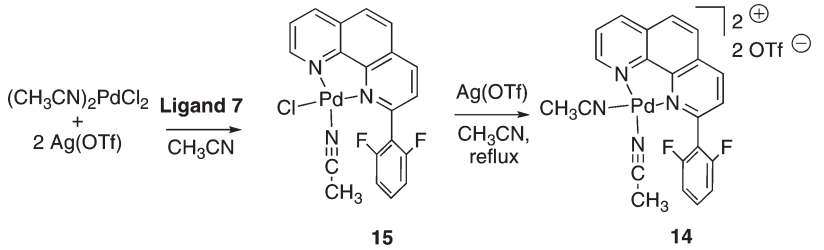
Scheme 6. Synthesis of 14 and 15



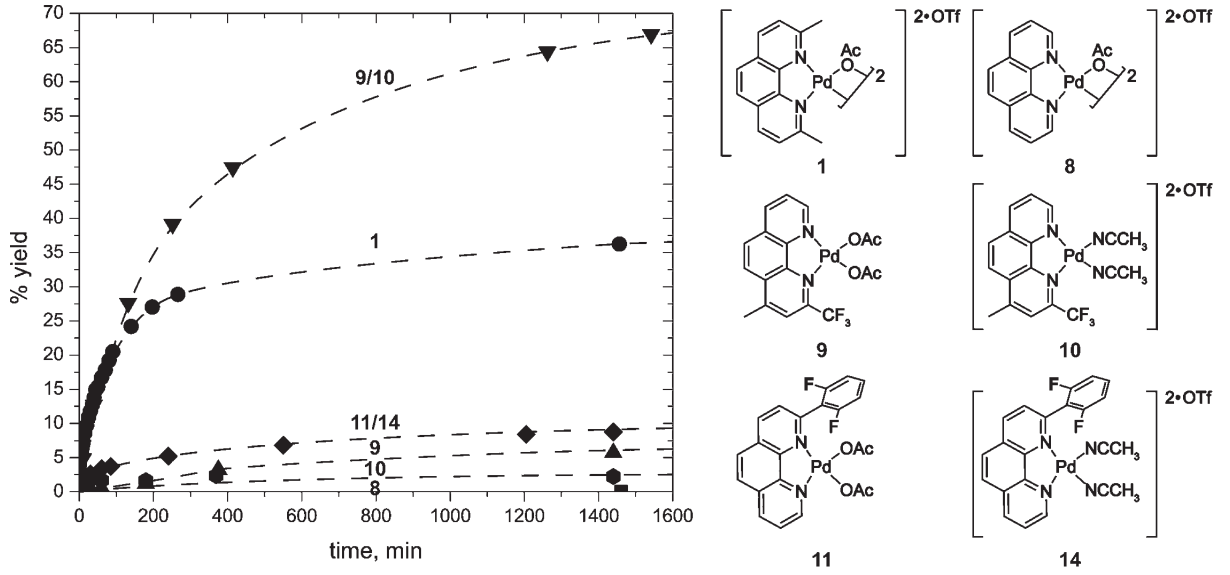
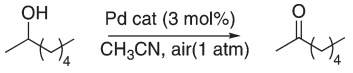


Figure 6. Reaction progress for the palladium-catalyzed aerobic oxidation of 2-heptanol to 2-heptanone using **1** (●), **8** (■), **9** (▲), **10** (⬢), **9/10** (▼), and **11/14** (♦) at room temperature in acetonitrile; in all cases, 3 mol % of Pd was employed. Dashed lines are included only to serve as guides for the eye.

Table 1. Efficiency of Various Cationic Palladium Complexes for the Aerobic Oxidation of 2-Heptanol at Room Temperature



entry	complex	yield (%)[a]	TON[b]	TOF_i (h^{-1})[c]
1	**1**	36	12	78
2	**8**	trace		
3	**9/10**	67	22	21
4	**11/14**	8	2.5	60

[a] After 24 h reaction time. [b] TON = moles ketone/mol Pd. [c] Initial turnover frequency (mol ketone/(mol Pd·h)).

36%.[26] As previously discussed, this behavior was attributed to competitive ligand oxidation, generating the inactive carboxylate **3** (Scheme 1).

The cationic phenanthroline dimer **8**, lacking oxidizable methyl groups, was completely inactive under these conditions (Table 1, entry 2). We attribute the lack of activity to the formation of the stable of μ-hydroxo-bridged dimer **16**.[26,60] Addition of water to dimer **8** leads to the formation of **16** (identified by ^{1}H NMR and independent synthesis[60]) along with several other unidentified species. Complexes analogous to **16** have been proposed as resting states by Sheldon and co-workers[16,18] in aerobic alcohol oxidations carried out at higher temperatures. It has been previously observed that increased steric bulk or higher temperatures are required with (phen)Pd(OAc)$_2$ to destabilize the μ-hydroxo intermediates and achieve greater alcohol-oxidation activity.[18] This hypothesis provides a rationale for the poor activity of **8**; if the μ-hydroxo-bridged dimer **16** is formed in the course of the catalytic cycle, this dimer would likely be inactive at the low temperatures investigated here. These results imply that substitution at the 2- and/or 9-positions of phenanthroline is important to retain activity at low temperature, but these substituents must also resist competitive oxidation.[26]

The introduction of a single trifluoromethyl group to the 2-position of phenanthroline was expected to destabilize dimers analogous to **16** while preventing the harmful degradation pathways caused during oxygen reduction. A 1:1 mixture of complexes **9** and **10** catalyzed the oxidation of 2-heptanol at room temperature to afford 2-heptanone in 67% yield after 24 h (entry 3). In accordance with our previous observations,[26] the diacetate complex **9** or ditriflate complex **10** under identical conditions provided only 6% and 3% conversion, respectively, after 24 h.

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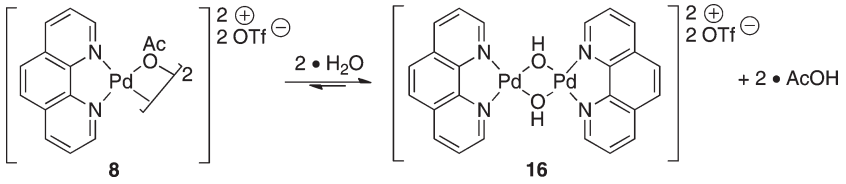
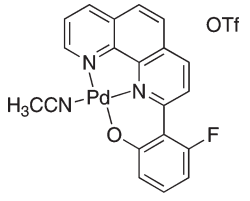
Scheme 7. Formation of μ-Hydroxo-Bridged Dimers



8 16

Catalysts derived from a mixture of **9**/**10** reached a turnover number of 22 after 24 h, which is nearly twice that previously observed with **1**. Full conversion of 2-heptanol at 3 mol % catalyst loading was not obtained even at extended reaction times. Though a substoichiometric amount of palladium black was observed after 24 h of reaction, a sharp decrease in the rate of alcohol oxidation preceded Pd precipitation by several hours, indicating that Pd-black formation in itself may not be responsible for the observed loss in activity. Analysis of the reaction mixture after 24 h by ESI-MS yielded the expected mass of the ligand with no evidence of ligand oxidation. Attempts to prolong catalyst lifetime by introducing additional ligand into the reaction mixture (0.5 equiv relative to Pd) resulted in slower TOFs but similar levels of conversion (61% yield at 72 h). Thus, while the activity and longevity of catalysts derived from the tfmm-phen ligand **6** are superior to that of catalyst **1** derived from neocuproine, the modest turnover numbers observed implicate additional catalyst deactivation pathways and highlight the need for a better understanding of catalyst inactivation processes to enable further optimization.

Investigation of a 1:1 mixture of **11** and **14** for the aerobic oxidation of 2-heptanol in dry acetonitrile (entry 4) revealed initial rates of alcohol oxidation comparable to **1**, but the reaction rate quickly dropped off (Figure 6, diamonds), and only 2.5 turnovers were achieved after 24 h. Precipitation of the resulting palladium complex was accomplished by addition of diethyl ether, and the ^{1}H NMR spectrum of the precipitate exhibited splitting consistent with the formation of a chelated phenoxide complex, analogous to **12**. Two resonances were observed by ^{19}F NMR, consistent with the presence of a triflate counterion and a single fluoride on the ligand, suggesting the catalyst degradation product is the cationic complex **17**. It is worth noting that fluorine substitution by 2-heptanol was not observed. The formation of tridentate complex **17** inactivates the Pd in a manner that is reminiscent of the inactivation of **1** by intramolecular ligand oxidation to tridentate complex **3**,[26] which exhibited negligible activity compared to its bidentate precursor. Addition of molecular sieves to the 2-heptanol-oxidation reaction mixture catalyzed by **11**/**14** increased the TON of the catalyst to 4.5, suggesting that water produced during oxygen reduction can be scavenged competitively with fluoride displacement.



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CONCLUSION

Cationic Pd-acetate complexes ligated by neocuproine or 2-substituted phenanthroline ligands are active for the aerobic oxidation of secondary alcohols under mild conditions (room temperature, 1 atm air). The dimeric complex [(neocuproine)Pd(OAc)]$_2$[OTf]$_2$ (**1**) exhibits high initial turnover frequency for the aerobic oxidation of 2-heptanol; however, oxidative degradation of the ligand leads to rapid deactivation and low turnover numbers.[26] The synthesis of two new phenanthroline ligands, bearing CF_3 or 1,5-difluorophenyl substituents, was carried out in an effort to generate more oxidatively robust Pd catalysts. Pd complexes derived from these ligands were structurally characterized, and their activity in the aerobic oxidation of 2-heptanol was compared to that of complex **1**. The inactivity of the [(phen)Pd(OAc)]$_2$[OTf]$_2$ (**8**) implies that substituents at the 2- and/or 9- positions of the phen ligand are important for catalytic activity. The higher catalyst lifetimes of Pd complexes bearing the 2-CF_3-substituted ligand 4-methyl-2-(trifluoromethyl)-1,10-phenanthroline (tfmm-phen) reveal that inhibiting ligand oxidation can lead to more robust catalysts for aerobic alcohol oxidation. Nevertheless, the modest turnover numbers observed (22 mol ketone/mol Pd) are less than those observed with Pd carbene complexes (approximately 100 TO).[21] While we observe no evidence for ligand oxidation, other decomposition pathways may limit the lifetimes of catalysts derived from tfmm-phen. Pd complexes derived from the 2-(*o*-difluorophenyl)-1,10-phenanthroline (odfp-phen) ligand exhibit poor catalyst lifetimes as a consequence of facile substitution of the ortho-fluoro substituent by water (a byproduct of the reaction). These results provide insights into the structure/property relationships of Pd oxidation catalysts that may guide future design of oxidatively robust catalysts for the aerobic oxidation of alcohols.

EXPERIMENTAL SECTION

Materials. Unless otherwise stated, solvents were purchased from Sigma-Aldrich or Fisher Chemical and used as received. Deuterated solvents were purchased from Cambridge Isotopes and used as received. 7-Methylquinoline was purchased from TCI America and used without further purification. 8-Aminoquinoline was purchased from Sigma-Aldrich and used without further purification. (1,10-Phenanthroline)Pd(OAc)$_2$,[43] **1**,[26] **4**,[35] and **5**[36] were prepared as previously described. [(CH$_3$CN)$_4$Pd][OTf]$_2$ was prepared in analogy to [(CH$_3$CN)$_4$Pd][BF$_4$]$_2$[61] and was used in situ. 8-Amino-7-quinolinecarbaldehyde was prepared by the route established by Thummel and co-workers.[40] All NMR spectra were acquired on Varian Inova 300, Mercury 400, or Inova 500 MHz spectrometers. ^{1}H and ^{13}C NMR spectra are referenced to the solvent residual peaks. ^{19}F NMR spectra are referenced to CF_3CO_2H (−76.55 ppm) or free triflate anion (−77.6 ppm). For splitting patterns, "s" refers to singlet, "d" refers to doublet, "t" refers to triplet, and "q" refers to quartet.

2-(Trifluoromethyl)-4-methyl-1,10-phenanthroline (6). Enone **5**[36] (6.86 g, 49 mmol) was added over 5 h to a stirred solution of 8-aminoquinoline (4.24 g, 29 mmol) and sodium iodide (0.043 g, 0.28 mmol) in 70% sulfuric acid (10.6 mL) at 110 °C. The reaction was allowed to continue for an additional hour and was then cooled to room temperature. The dark orange-red mixture was poured into 1 M Na_2CO_3 (123 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organics were extracted with 12 M HCl (5 × 50 mL). The aqueous, acidic layer was neutralized using 3 M NaOH/1 M Na_2CO_3 and extracted with CH_2Cl_2 (3 × 100 mL). The compound was purified by silica gel column chromatography (CH_2Cl_2/MeOH; polarity was slowly increased until product eluted), yielding **6** (1.6 g, 21%) in reasonable purity as a brown solid. Further purification can be achieved by crystallization ($CHCl_3$/hexanes) or by column chromatography (acetone/hexanes, 1:4), affording **6** as a white solid. ^{1}H NMR ($CDCl_3$) δ: 9.29 (dd, J = 1.7, 4.6 Hz, 1H), 8.30 (dd, J = 1.7, 8.0 Hz, 1H), 8.07 (d, J = 9.2 Hz, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.84 (s, 1H), 7.69 (dd, J = 4.6, 8.0 Hz, 1H), 2.90 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 151.3, 147.4 (q, $^2J_{CF}$ = 34.4 Hz), 146.9, 146.2, 145.4, 136.2, 129.5 (q, $^4J_{CF}$ = 1.0 Hz), 128.8, 128.5, 123.6, 122.0, 121.8 (obsd d, $^1J_{CF}$ = 275.5 Hz), 120.19 (q, $^3J_{CF}$ = 2.2 Hz), 19.6. ^{19}F NMR ($CDCl_3$) δ: −65.5 (s) Anal. Calcd for $C_{14}H_9F_3N_2$: C, 64.12; H, 3.46; N, 10.68. Found: C, 62.88; H, 3.10; N, 10.36. HRMS-(ES+): calcd for $C_{14}H_{10}F_3N_2$ [M + H] 263.0796, found 263.0795.

2-(2′,6′-Difluorophenyl)-1,10-phenanthroline (7). This compound was prepared by adaptation of the procedure reported by Thummel and co-workers[40] for the synthesis of 2-phenyl-1,10-phenanthroline. A saturated solution of ethanolic potassium hydroxide (0.5 mL) was added dropwise to a solution of 8-amino-7-quinolinecarbaldehyde (0.231 g, 1.34 mmol) and 2′,6′-difluoroacetophenone (0.209 g, 1.34 mmol) in absolute ethanol (15 mL) under an atmosphere of N_2, and the mixture was refluxed for 15 h. The solution was diluted with water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with H_2O (2 × 20 mL) and dried ($MgSO_4$). Flash chromatography on alumina using CH_2Cl_2 as the eluent and subsequent recrystallization with EtOAc/hexane provided the title compound as an off-white solid (0.228 g, 58%). ^{1}H NMR ($CDCl_3$) δ: 9.22 (dd, J = 1.3, 3.8 Hz, 1H, H_9), 8.34 (d,, J = 7.6 Hz, 1H, H_4), 8.25(dd, J = 1.3, 7.2 Hz, 1H, H_7), 7.84 (s, 2H, H_{5-6}), 7.79 (d, J = 7.6 Hz, 1H, H_3), 7.63 (dd, J = 3.8, 7.2 Hz, 1H, H_8), 7.38 (m, J = 1.8, 6.7, 6.3 Hz, 1H, *p*-Ph), 7.04 (m, J = 4.0, 6.5 Hz, 2H, *m*-Ph). ^{13}C NMR ($CDCl_3$) δ: 161.0 (dd, $^1J_{CF}$ = 250.5 Hz, $^3J_{CF}$ = 7.1 Hz), 150.8, 150.1, 146.4, 146.4, 136.3, 136.1, 130.3 (t, $^3J_{CF}$ = 10.3 Hz), 129.0, 127.9, 127.2, 126.3, 125.4, 123.1, 119.0 (t, $^2J_{CF}$ =19.2 Hz), 111.8 (m, $^2J_{CF}$ = 24.2 Hz). ^{19}F NMR ($CDCl_3$) δ: −113.0 (t, J = 6.5 Hz). ESI-MS (+): 293 [M + H]. Anal. Calcd for $C_{18}H_{10}F_2N_2$: C, 73.97; H, 3.45; N, 9.58. Found: C, 73.71; H, 3.38; N 9.39.

[(1,10-Phenanthroline)Pd(NCCH$_3$)$_2$][OTf]$_2$. Triflic acid (1.5 mL, 0.33 M, 2 equiv) was added dropwise to a stirred solution of (phen)$Pd(OAc)_2$ (100 mg, 0.247 mmol) in dry acetonitrile (10 mL). Dry diethyl ether was added to induce precipitation of the resulting complex, which was recrystallized three times from CH_3CN/Et_2O to achieve the desired compound in high purity (22 mg, 0.033 mmol, 13%). While this compound has been previously reported,[44] the ^{1}H NMR shifts reported were suggestive of two species in a 1:1 mixture. We have isolated a single species that matches one set of signals from the previously reported spectrum. ^{1}H NMR (CD_3CN) δ: 8.96 (dd, J = 1.2, 8.4 Hz, 2H), 8.85 (dd, J = 1.2, 5.5 Hz, 2H), 8.24 (s, 2H), 8.04 (dd, J = 5.5, 8.4 Hz, 2H). (signal due to bound CH_3CN could not be resolved from residual water and solvent resonances). ^{13}C NMR (CD_3CN) δ: 153.2, 148.3, 143.5, 132.5, 129.1, 127.4, 122.0 (q, $^1J_{CF}$ = 320.7 Hz). Anal. Calcd for $C_{18}H_{14}F_6N_4O_6PdS_2$: C, 32.42; H, 2.12; N, 8.40. Found: C, 32.31; H, 1.88; N, 8.22.

[(1,10-Phenanthroline)Pd(OAc)]$_2$[OTf]$_2$ (8). To a solution of (phen)$Pd(OAc)_2$ (10.7 mg, 0.026 mmol) in acetonitrile (2 mL) was added [(phen)$Pd(NCCH_3)_2$][OTf]$_2$ (17.7 mg, 0.026 mmol), and the solution was stirred for 15 min. Removal of solvent under vacuum afforded **8** quantitatively. Anal. Calcd for $C_{30}H_{22}F_6N_4O_{10}Pd_2S_2$: C, 36.42; H, 2.24; N, 5.66. Found: C, 35.87; H, 1.56; N, 6.09. X-ray quality crystals of **8** were obtained by slow diffusion of diethyl ether into a saturated acetonitrile solution of a 1:1 mixture of [(phen)$Pd(CH_3CN)_2$][OTf]$_2$ and (phen)$Pd(OAc)_2$.

(4-Methyl-2-(trifluoromethyl)-1,10-phenanthroline)Pd(OAc)$_2$ (9). $Pd(OAc)_2$ (0.0856 g, 0.38 mmol) was added to a stirred solution of **6** (0.100 g, 0.38 mmol) in acetone (10 mL). The solution was allowed to stir overnight, during which time a fine, dark red precipitate formed. The red solid was isolated by vacuum filtration, rinsed repeatedly with acetone and Et_2O, and finally dried under high vacuum to give **9** (0.138 g, 74%). ^{1}H NMR ($Cl_2CDCDCl_2$) δ: 8.62 (d, J = 6.8 Hz, 2H, H_7 + H_9), 8.16 (d, J = 9.1 Hz, 1H, H_5), 8.11 (d, J = 9.1 Hz, 1H, H_6), 8.07 (s, 1H, H_3), 7.90 (m, 1H, H_8), 2.98 (s, 3H, Me), 2.17 (s, 3H, OAc), 1.99 (s, 3H, OAc). ^{13}C NMR ($Cl_2CDCDCl_2$) δ: 178.8, 178.0, 152.4, 150.2, 147.2, 146.82, 146.78, 138.8, 130.7, 130.3, 128.7, 125.5, 124.2, 123.5, 23.2, 23.1, 19.7. ^{19}F NMR ($Cl_2CDCDCl_2$) δ: −61.2, −61.4, −62.2, −65.5. Anal. Calcd for $C_{18}H_{15}F_3N_2O_4Pd\cdot(H_2O)$: C, 42.83; H, 3.39; N, 5.55. Found: C, 42.54; H, 2.88; N, 5.88. HRMS (ES+): calcd for $C_{16}H_{12}N_2O_2F_3Pd$ [M − OAc] 426.9886, found 426.9887.

[(4-Methyl-2-(trifluoromethyl)-1,10-phenanthroline)Pd(NCCH$_3$)$_2$][OTf]$_2$ (10). Trifluoromethyl ligand **6** (0.109 g, 0.42 mmol) was added to a stirred solution of $[CH_3CN)_4Pd][OTf]_2$ (0.580 g, 1.02 mmol) in acetonitrile (4 mL), during which time the solution became orange. The solution was filtered, and Et_2O was carefully layered onto the filtrate (i.e., without mixing) to induce crystallization. The resulting needlelike crystals were recrystallized two times from acetonitrile/Et_2O, yielding pure **10** (0.11 g, 35%). The mother liquor from the two previous recrystallizations was concentrated and treated with Et_2O to yield an additional 0.045 g (49% combined yield) of the title compound. ^{1}H NMR (CD_3CN) δ: 9.48 (dd, J = 1.2, 5.6 Hz, 1H), 8.86 (dd, J = 1.2, 8.4 Hz, 1H), 8.37 (d J = 9.0 Hz, 1H), 8.36 (m, 1H), 8.28 (d, J = 9.0 Hz, 1H), 8.01 (dd, J = 5.6, 8.4 Hz, 1H), 3.04 (s, 3H). ^{13}C NMR (CD_3CN) δ: 156.9, 153.6, 142.7, 133.0, 132.8, 130.3, 127.1, 125.8, 125.4, 123.2, 121.9, 120.6, 119.7, 19.9. ^{19}F NMR (CD_3CN) δ: −59.83, −77.47. ESI-MS (+): 665 [M − 2CH_3CN], 517 [M − 2CH_3CN − OTf]. Anal. Calcd for $C_{20}H_{15}F_9N_4O_6PdS_2$: C, 32.08; H, 2.02; N, 7.48. Found: C, 31.95; H, 1.76; N, 6.51. HRMS (ES+): calcd for $C_{14}H_{12}N_2F_3Pd$ [LPdH$^+$] 368.9831, found 368.9838.

Conproportionation of 9 and 10. Equal molar amounts of the diacetate **9** and the ditriflate **10** complexes were combined in acetonitrile to generate a mixture of stereoisomers (Figure S17). A similar spectrum is obtained upon addition of one equivalent of triflic acid to the diacetate complex **9** in acetonitrile. The resulting solution exhibits similar catalytic activity to that of an equal molar solution prepared by the conproportionation method; the initial rate of oxidation using **9**/triflic acid is slightly retarded, but the final conversion is equal to that obtained by conproportionation within the limits of experimental uncertainty. The complexity associated with the solution speciation upon mixing **9** and **10** is highlighted in Figure S17, which shows the aromatic regions of the ^{1}H NMR spectra of **9**, **10**, and their mixture.

(2-(2′,6′-*o*-Difluorophenyl)-1,10-phenanthroline)Pd(OAc)$_2$ (11). A solution of palladium diacetate (0.076 g, 0.342 mmol) in CH_2Cl_2 (1.2 mL) was added to a stirred solution of ligand **7** (0.100 g, 0.342 mmol) in toluene (6.2 mL). The solution was allowed to stir for 24 h at room temperature, during which time a yellow solid formed. The mixture was poured into petroleum ether (5 mL) to induce further precipitation, and the yellow precipitate was isolated by vacuum filtration and dried under high vacuum (0.168 g, 82%). When complex **12** is prepared by this method, it contains half of an equivalent of CH_2Cl_2 even after extensive drying, as observed by ^{1}H NMR spectroscopy. Due to its low solubility in $CDCl_3$, chemical shifts are also reported in anhydrous CD_3CN. ^{1}H NMR ($CDCl_3$) δ: 8.67 (dd, J = 1.2, 5.3 Hz, 1H),

8.66 (d, J = 9.2 Hz, 1H), 8.57 (dd, J = 1.2, 8.2 Hz, 1H), 8.48 (d, J = 9.2 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.85 (dd, J = 5.3, 8.2 Hz, 1H), 7.25−7.11 (m, 2H), 6.48 (ddd, J = 1.5, 7.6, 14.4 Hz, 1H). ^{1}H NMR (CD_3CN) δ: 8.68 (dd, J = 1.3, 8.3 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H), 8.28 (dd, J = 1.3, 5.3 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.76 (dt, J = 1.0, 8.5 Hz, 1H), 7.73 (dd, J = 5.3, 8.2 Hz, 1H), 7.75 (m, 1H), 7.15 (t, J = 8.2 Hz, 2H), 1.99 (2, 3H), 1.28 (s, 3H). ^{13}C NMR (CD_3CN) δ: 177.5 (OAc), 177.4 (OAc), 161.0 (dd, $^1J_{CF}$ = 249.5 Hz, $^3J_{CF}$ = 6.23 Hz), 154.4, 150.7, 148.3, 147.3, 140.6, 140.5, 133.7 (t, $^3J_{CF}$ = 10.7 Hz), 131.3, 130.57, 130.5, 128.75, 128.3, 126.2, 115 (t, $^2J_{CF}$ = 19.2 Hz), 112.5 (m, $^2J_{CF}$ = 22.7 Hz), 23.2 (OAc), 22.1 (OAc). ^{19}F NMR (CD_3CN): −111.6 (t, J = 7.1 Hz). ESI-MS(+): 398.9 [M − 2OAc + H], 442.9 [M − 2OAc + O_2CH], 456.9 [M − OAc]. Anal. Calcd for $C_{22}H_{16}F_2N_2O_4Pd \cdot 1/2(CH_2Cl_2)$: C, 48.32; H, 3.06; N, 5.01. Found: C, 48.06; H, 3.33; N, 4.80.

Synthesis of Phenoxide Complex 12. Diacetate **11** (20 mg, 0.038 mmol) was dissolved in acetonitrile (5 mL). The solution was filtered into a 20 mL vial through a plug of glass fiber to remove any undissolved material. Two drops of water were added to the solution, and the vial was capped, shaken, and allowed to sit at room temperature for 3 days. Crystals became visible after 24 h but continued to grow when allowed to sit for additional time. X-ray-quality, needle-shaped crystals were isolated by removal of the mother liquor with a pipet and repeated washing of the crystals with Et_2O. Upon drying under high vacuum, complex **12** was obtained in 36% yield (6.3 mg). Additional crystals were obtained by concentration of the mother liquor. Complex **12** is nearly insoluble in acetonitrile and DMSO but is sparingly soluble in chloroform. ^{1}H NMR ($CDCl_3$) δ: 8.74 (d, J = 5.4 Hz, 1H, H_9), 8.61 (d, J = 9.1 Hz, 1H, H_4), 8.55 (d, J = 8.2 Hz, 1H, H_7), 8.49 (d, J = 9.1 Hz, 1H, H_3), 8.00 (d, J = 8.7 Hz, 1H, H_5), 7.88 (d, J = 8.7 Hz, 1H, H_6), 7.84 (dd, J = 5.4, 8.2 Hz, 1H, H_8), 7.20 (m, 1H, H_{Ar}), 7.11(d, J = 8.7 Hz, 1H, H_{Ar}), 6.46 (dd, J = 7.8, 14.3 Hz, 1H, H_{Ar}), 2.30 (s, 3H, OAc). ^{1}H NMR (d_6-DMSO) δ: 8.99 (dd, J = 1.4, 8.3 Hz, 1H), 8.91 (d, J = 9.2 Hz, 1H), 8.66 (dd, J = 1.8, 9.2 Hz, 1H), 8.62 (dd, J = 1.4, 5.2 Hz, 1H), 8.28 (d, J = 8.6 Hz, 1H), 8.24 (d, J = 8.6 Hz, 1H), 8.11 (dd, J = 5.2, 8.3 Hz, 1H), 7.29 (dd, J = 8.0, 15.5 Hz, 1H), 6.90 (d, J = 8.7 Hz, 1H), 6.60 (dd, J = 8.0, 14.2 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 179.1 (OAc), 166.6, 162.5 (d, $^1J_{CF}$ = 251.5 Hz), 150.9, 149.6, 146.3, 145.7, 138.4, 136.0, 132.3 (d, $^2J_{CF}$ =14.8 Hz), 129.3, 127.2, 126.7, 126.5, 126.0, 124.7, 119.4, 102.7 (d, $^2J_{CF}$ = 26.0 Hz), 24.08 (OAc). ^{19}F NMR ($CDCl_3$) δ: −107.9 (dd, J_{HF} = 14.3, 6.5 Hz). ESI-MS(+): 394.8 [M − OAc], 412.8 [M − OAc + H_2O], 792.8 [2M − 2OAc + H], 836.8 [2M − OAc]. Anal. Calcd for $C_{20}H_{13}FN_2O_3Pd$: C, 52.82; H, 2.88; N, 6.16. Found: C, 52.47; H, 2.55; N, 5.90.

[(2-(2′,6′-*o*-Difluorophenyl)-1,10-phenanthroline)Pd(CH_3CN)$_2$][OTf]$_2$ (14). In a flame-dried flask equipped with a reflux condenser was added $PdCl_2$ (57 mg, 0.32 mmol, 1.1 equiv) and odfp-phen **7** (87 mg, 0.30 mmol, 1.0 equiv). Dry acetonitrile (5 mL) was added to the solids, and the solution was refluxed overnight under N_2 atmosphere, during which time a yellow solid was formed. The suspension containing the yellow solid was treated with AgOTf (206 mg, 0.80 mmol, 2.7 equiv) and was refluxed in the dark for 2 days. Additional AgOTf (103 mg, 0.40 mmol) was added to the reaction mixture, and refluxing was continued in the dark for 1 day. At this time, the reaction flask contained a mixture of **15** and **14** in a 2:1 ratio as observed by ^{1}H NMR spectroscopy. The solvent was evaporated to dryness, dissolved in dry acetonitrile (5 mL), and filtered to remove residual AgCl, and AgOTf (106 mg, 0.41 mmol, 1.4 equiv) was added to the solution. The reaction mixture was heated an additional 4 days in the dark at 60 °C. The solvent-evaporation/dissolution/filtration process was repeated two more times, and in this manner, the ratio of **15** to **14** changed to 1:10. Finally, the solvent was evaporated to dryness, dry acetonitrile was added, and the solution was filtered through Celite. Diethyl ether was added to the solution until it became slightly turbid, and then the solution was cooled to −25 °C. Yellow crystals formed overnight, which were isolated by cannula filtration and dried under high vacuum, yielding **14** (44 mg, 19%). ^{1}H NMR (CD_3CN) δ: 9.03 (d, J = 8.4 Hz, 1H, H_4), 8.99(dd, J = 1.1, 8.3 Hz, 1H, H_9), 8.85 (dd, J = 1.1, 5.5 Hz, 1H, H_7), 8.28 (s, 2H, H_{5-6}), 8.10 (d, J = 8.4 Hz, 1H, H_3), 8.04 (dd, J = 5.5, 8.3 Hz, 1H, H_8), 7.78 (m, 1H, Ar_p), 7.35 (m, 2H, Ar_m). ^{13}C NMR (CD_3CN) δ: 160.8 (dd, $^1J_{CF}$ = 251.4 Hz, $^3J_{CF}$ = 5.6 Hz), 154.4, 154.1, 149.6, 148.8, 143.8, 143.7, 136.3 (t, $^3J_{CF}$ = 10.8 Hz),132.8, 132.1, 130.8, 129.5, 129.0, 127.3, 122.0 (q, $^1J_{CF}$ = 321.2 Hz), 116.2 (t, $^2J_{CF}$ = 18.6 Hz), 113.5 (m, $^2J_{CF}$ = 20.5 Hz). ^{19}F NMR (CD_3CN) δ: −77.6, −110.7 (t, J = 7.5 Hz). Exposure to high vacuum for prolonged periods of time resulted in partial loss of coordinated acetonitrile. Anal. Calcd for $C_{24}H_{16}F_8N_4O_6PdS_2$: C, 37.01; H, 2.07; N, 7.19. Found: C, 36.60; H, 1.83; N, 6.68. Anal. Calcd for $C_{22}H_{13}F_8N_3O_6PdS_2$: C, 35.81; H, 1.78; N, 5.69. Found: C, 35.56; H, 1.82; N, 6.10.

[(2-(2′,6′-*o*-Difluorophenyl)-1,10-phenanthroline)Pd(CH_3CN)Cl][OTf] (15). Cationic-palladium precursor $(CH_3CN)_4Pd(OTf)_2$ (320 mg, 0.564 mmol) was prepared in situ by addition of $(CH_3CN)_2PdCl_2$ (0.1 g, 0.564 mmol) to AgOTf (0.289 g, 1.128 mmol) by analogy to previous reports.[61] After removing AgCl by filtration, the precursor solution was added to a stirred solution of odfp-phen (148 mg, 0.508 mmol, 0.9 equiv) in acetonitrile and allowed to stir 2 h, after which time the reaction mixture was concentrated and precipitated with Et_2O. The resulting solid (0.161 g) contained an acetonitrile-insoluble portion (we attribute this to additional AgCl), which was removed by redissolving the precipitate in acetonitrile and filtering. The filtrate was evaporated to dryness, and the complex was recrystallized twice by slow addition of Et_2O to acetonitrile, producing complex **15** in 10% yield (0.043 g). ^{1}H NMR (CD_3CN) δ: 9.43 (dd, J = 1.3 5.6 Hz, 1H, H_9), 8.95 (d, J = 8.4 Hz, 1H, H_4), 8.86 (dd, J = 1.3, 8.2 Hz, 1H, H_7), 8.23 (d, J = 1.5 Hz, 2H, H_{5-6}), 8.08 (d, J = 8.4 Hz, 1H, H_3), 7.99 (dd, J = 5.6, 8.2 Hz, 1H, H_8), 7.73 (m, 1H, Ar_p), 7.32 (m, 2H, Ar_m). ^{13}C NMR (CD_3CN) δ: 160.9 (dd, $^1J_{CF}$ = 250.6 Hz, $^3J_{CF}$ = 5.8 Hz), 153.1, 149.4, 148.5, 143.8, 143.6,142.4, 135.6 (t, $^3J_{CF}$ = 10.4 Hz) 132.4, 131.5, 130.5, 129.3, 128.6, 126.6, 122.0 (q, $^1J_{CF}$ = 320.9 Hz), 116.6 (t, $^2J_{CF}$ = 18.6 Hz), 113.41 (m, $^2J_{CF}$ = 23.1 Hz). ^{19}F NMR (CD_3CN) δ: −77.6, −111.2 (t, J = 7.2 Hz). Anal. Calcd for $C_{21}H_{13}ClF_5N_3O_3PdS$: C, 40.40; H, 2.10; Cl, 5.68; N, 6.73. Found: C, 40.29; H, 1.71; Cl, 6.07; N, 6.53.

Conproportionation of 11 and 14. An equal molar quantity of the ditriflate complex **14** (20 mg, 0.0257 mmol) and the diacetate complex **11** (13 mg, 0.0257 mmol) were combined in acetonitrile until all solids were dissolved. Figure S36 shows the aromatic regions of the ^{1}H NMR spectra of **11**, **14**, and their mixture.

Phenoxide Complex 17. The diacetate complex **11** (8.07 mg, 0.015 mmol) was added to a flame-dried flask with anhydrous CH_3CN (1 mL), and the flask was capped with a rubber septum. To this was added a stock solution of ditriflate complex **14** (11.68 mg, 0.015 mmol) in CH_3CN (0.5 mL), and the reaction mixture was stirred. Upon complete dissolution of all solids, a stock solution of 2-heptanol (0.5 mL, 0.2 M) was added through the septum and the solution was stirred at room temperature under a balloon full of air for 24 h. The reaction mixture was filtered, and Et_2O was added to effect precipitation of **17**. The solid was collected by centrifugation, washed with Et_2O, and dried briefly under high vacuum. ^{1}H NMR (CD_3CN) δ: 8.76 (d, J = 8.2 Hz, 1H), 8.64 (d, J = 5.2 Hz, 1H), 8.51 (dd, J = 15.7, 9.2 Hz, 1H), 8.01 (dd, J = 11.6, 8.7 Hz, 2H), 7.89 (dd, J = 5.2, 8.2 Hz, 1H), 7.18 (dd, J = 14.9, 8.1 Hz, 1H), 6.66 (d, J = 8.6 Hz, 1H), 6.50 (dd, J = 7.8, 14.5 Hz, 1H). ^{19}F NMR (CD_3CN) δ: −77.6, −105.9 (dd, J = 14.4, 6.2 Hz)

General Method for Aerobic Oxidation of 2-Heptanol Using Cationic Palladium Complexes. A solution of 2-heptanol (146 μL, 1.00 mmol) and decane (100 μL, 0.538 mmol) in acetonitrile (1.5 mL) was stirred under a balloon of air for 5 min. At t = 0, the palladium catalyst (3 mol %) was added either as a solid or as a solution in acetonitrile; in either case, the reaction mixture was adjusted such that it contained a total acetonitrile volume of 2 mL. The mixture was stirred

at room temperature, and aliquots were taken periodically and subjected to analysis by GC. Initial turnover frequencies (TOF_i) were calculated on the basis of the conversion of 2-heptanol to 2-heptanone after 1 min of reaction time. 2-Heptanone was confirmed by co-injection with an authentic sample.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H, ^{13}C, and ^{19}F NMR spectra of new compounds, experimental procedures for complexation studies with btfm-phen, CIF files giving crystal data for compounds **8**, **10**, **12**, and **15**, and a comparison of the bond lengths of **8** and **1**.This material is available free of charge via the Internet at http://pubs.acs.org.

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