Platinum Model Studies for Palladium-Catalyzed Oxidative Functionalization of C−H Bonds

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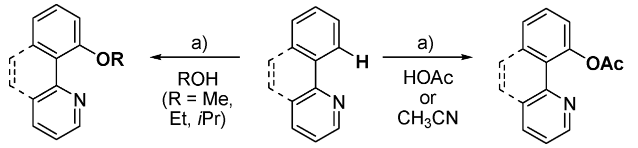
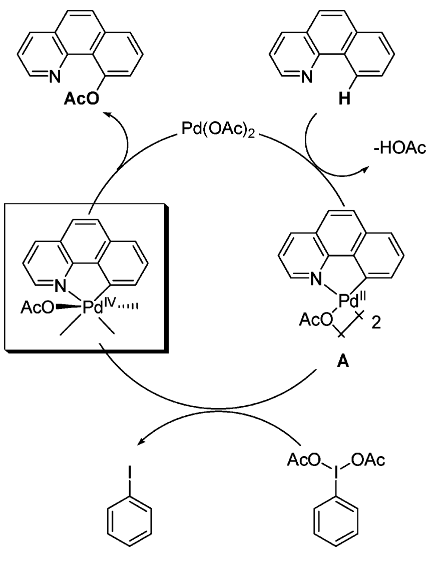
Summary: The synthesis of (CN)Pt^{II}(acac) complexes (CN = benzo[h]quinoline, 8-methylquinoline) and their oxidation with PhI(OAc)$_2$ are reported as a model system for palladium-catalyzed C−H bond functionalization. Dimeric Pt^{III}−Pt^{III} complexes containing a bridging acetate ligand are obtained in HOAc, and monomeric Pt^{IV} complexes incorporating alkoxide and acetate ligands are obtained in MeOH, EtOH, and iPrOH. The implications of these results for the mechanism of analogous Pd-catalyzed reactions is discussed.

Scheme 1. Catalytic Oxygenation of Organic Substrates[a]



[a] Legend: (a) 1−5% Pd(OAc), 1−2 equiv PhI(OAc)$_2$, 75−100 °C.

Scheme 2. Proposed Catalytic Cycle for Palladium-Catalyzed Acetoxylation of Benzo[*h*]quinoline



Palladium-catalyzed C−H activation/functionalization reactions are of great utility in synthetic chemistry, as they enable the direct replacement of carbon−hydrogen bonds with new functionality.[1] The use of organic substrates with appropriate chelate-directing groups allows such transformations to proceed under mild conditions and with extremely high levels of regioselectivity.[2] Our group has been particularly interested in developing *oxidative* chelate-directed C−H activation/functionalization reactions, and we have recently reported that Pd(OAc)$_2$ catalyzes the oxygenation of a wide variety of organic substrates in the presence of PhI(OAc)$_2$ as a stoichiometric oxidant.[3] This versatile reaction can be utilized for the oxidation of both arene[3b] and alkane[3a] C−H bonds. Furthermore, changing the reaction solvent from AcOH (or MeCN) to an alcohol (ROH) allows the installation of either an acetoxy (OAc) or an ether (OR) group, respectively (Scheme 1).

Preliminary mechanistic investigations[3b] have suggested that these reactions proceed through cyclometalated Pd^{IV} acetate or alkoxide intermediates[4] rather than via a more conventional Pd^{II}/Pd^0 redox cycle (Scheme 2).[5] Organometallic Pd^{IV} intermediates have recently been invoked in several other catalytic reactions;[6] however, they have typically not been isolated or even detected in situ as a result of their high reactivity. In fact, the only organometallic Pd^{IV} complexes successfully characterized to date possess electronic stabilization by a minimum of two strongly electron-donating ligands.[7]

To probe the feasibility, structure, and reactivity of the proposed Pd^{IV} catalytic intermediates, we sought a model system that would yield compounds of greater

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(6) For example, see: (a) Manzoni, M. R.; Zabawa, T. P.; Kasi, D.; Chemler, S. R. *Organometallics* **2004**, *23*, 5618. (b) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (c) Böhm, V. P. W.; Herrmann, W. A. *Chem. Eur. J.* **2001**, *7*, 4191. (d) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (e) Stock, L. M.; Tse, K.; Vorvick, L. J.; Walstrum, S. A. *J. Org. Chem.* **1981**, *46*, 1757. (f) Henry, P. M. *J. Org. Chem.* **1971**, *26*, 1886.

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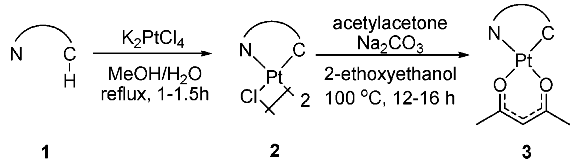
10.1021/om049163c CCC: $30.25

Table 1. Synthesis of (CN)Pt^{II}(acac) Complexes



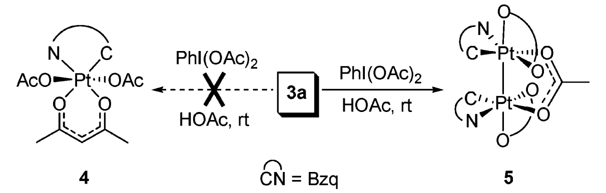
entry	ligand	product	yield, %
1	benzo[*h*]quinoline (**1a**)	(Bzq)Pt(acac) (**3a**)	67
2	8-methylquinoline (**1b**)	(8-MQ)Pt(acac) (**3b**)	52

stability while maintaining similar trends in reactivity. The use of platinum complexes as analogues to the postulated palladium intermediates seemed a reasonable choice because (a) organometallic Pt^{IV} complexes are often stable and isolable,[8,9] and (b) literature precedent suggests similar reactivity to its upper neighbor on the periodic table.[10,11] We communicate herein preliminary studies of the oxidation of cyclometalated Pt^{II} model complexes with PhI(OAc)$_2$ in both acetic acid and alcohol (ROH) solvents. While the reactions in ROH afford monomeric Pt^{IV} alkoxides, oxidation in acetic acid produces an unexpected and novel Pt^{III}−Pt^{III} dimer. The synthesis and characterization of these complexes as well as their implications for the mechanism of palladium-catalyzed oxidations are discussed.

To effectively model the Pd(OAc)$_2$-catalyzed oxidation reactions, we sought stable Pt^{II} complexes with comparable ligand environments to the proposed Pd^{II} intermediate **A** (Scheme 2). Cyclometalated (CN)Pt^{II}(acac) derivatives (acac = acetylacetonate) were selected as viable models as a result of their CNO$_2$ coordination sphere, their high air and moisture stability, and their ready availability. As such, (Bzq)Pt^{II}(acac) (**3a**) and (8-MQ)Pt^{II}(acac) (**3b**) (Bzq = benzo[*h*]quinoline and 8-MQ = 8-methylquinoline) were prepared from K_2PtCl_4 using a modification of the literature procedure (Table 1).[12]

Initial studies focused on the oxidation of **3a** with PhI(OAc)$_2$ in CH_3CN and AcOH—solvents in which our Pd-catalyzed acetoxylation reactions are typically conducted. We anticipated that these transformations would yield octahedral Pt^{IV} products such as **4** (Scheme 3),[13] which serve as analogues to the putative Pd^{IV} catalytic intermediates. While the reaction of **3a** with PhI(OAc)$_2$ in CH_3CN afforded a complex mixture of products, the analogous reaction in HOAc produced a single major Pt-containing species as an air- and moisture-stable orange solid.[14,15] However, ^{1}H NMR spectroscopic analysis revealed that this was *not* the expected bis(acetate) Pt^{IV} product **4**. Instead, the new acetate signal at 2.41 ppm integrated to 1.5 (rather than 6) relative to the aromatic Bzq protons. In addition, one of the aromatic protons appeared at a highly unusual upfield chemical shift of 4.96 ppm, characteristic of strong shielding within the aromatic ring current. An electrospray mass spectrum revealed this complex to be cationic with a mass of 1003.2, consistent with a dimeric structure containing 2 equiv of the starting complex plus an additional −OAc moiety. We also found that only 0.5 equiv of oxidant was required for clean formation of the product, suggesting the occurrence of a *single* two-electron-oxidation event.[16]

Scheme 3. Oxidation of (Bzq)Pt(acac) in HOAc



This product (**5**) was definitively characterized by X-ray crystallography[17] and was found to possess the dimeric structure shown in Figure 1.[18] The bridging acetate of **5** renders the two planar Bzq ligands slightly nonparallel, and the two octahedrons are in a staggered conformation about the Pt−Pt bond, with an aromatic proton of each Bzq projecting directly above the π system of the adjacent ligand. This structure is consistent with all of the solution characterization data described above, and the Pt−Pt bond distance of 2.5647(2) Å is comparable to those in other Pt^{III}−Pt^{III} systems.[19] Notably, the mono(acetate)-bridged structure of **5** appears to be unique for diplatinum complexes, although similar bimetallic structures containing a single bridging acetate ligand have been observed by van Koten and co-workers for Pt−Hg systems.[20]

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[9] For a review on platinum(IV) chemistry see: Jain, V. K.; Rao, G. S.; Jain, L. *Adv. Organomet. Chem.* **1987**, *27*, 113.

[10] For example, see: (a) Wolowska, J.; Eastham, G. R.; Heaton, B. T.; Iggo, J. A.; Jacob, C.; Whyman, R. *Chem. Commun.* **2002**, 2784. (b) Huang, T.-M.; Chen, J.-T.; Lee, G.-H., Wang, Y. *Organometallics* **1991**, *10*, 175.

[11] For very recent related efforts to use organometallic Pt complexes as models for Pd-catalyzed oxidation reactions, see: Canty, A. J.; Denney, M. C.; van Koten, G.; Skeleton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 5432.

[12] (a) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055. (b) Cockburn, B. N.; Howe, D. V.; Keating, T.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 404.

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[14] Preliminary results indicate that an analogous dimeric Pt^{III} product is formed upon oxidation of the 8-MQ complex **3b** with PhI(OAc)$_2$ in HOAc.

[15] Preparation of **5**: complex **3a** (154 mg, 0.33 mmol) and PhI(OAc)$_2$ (61 mg, 0.19 mmol) were combined in HOAc (70 mL), and the mixture was stirred at room temperature for 2 h, to afford an orange solution. Evaporation of the solvent yielded an orange residue. Complex **5** (85 mg, 49% assuming $^-$OAc as the counterion) was isolated as a stable orange solid by repeated sonication of the crude residue with benzene followed by removal of the soluble material. The tetrafluoroborate salt (for crystallography) was obtained by stirring **5** with excess $NaBF_4$ (~8 equiv) in THF, evaporation of the solvent, dissolution of the crude material in CH_2Cl_2, and filtration through Celite to remove salts. Analytical data are reported in the Supporting Information.

[16] Notably, this complex is unreactive toward further oxidation and remains unchanged (by ^{1}H NMR spectroscopy) in the presence of up to 10 equiv of PhI(OAc)$_2$.

[17] Crystal data for **5**: $C_{47}H_{41.5}BN_2O_{6.5}F_4Cl_{1.5}Pt_2$, M_r = 1268.49, monoclinic, space group $C2/c$, a = 25.6259(12) Å, b = 18.6076(8) Å, c = 20.7769(9) Å, α = 90°, β = 114.1230(10)°, γ = 90°, V = 9042.0(7) Å^3, T = 123(2) K, Z = 8, D_c = 1.864 Mg m^{-3}, μ(Mo Kα) = 6.339 mm^{-1}, 11 249 independent reflections (R_{int} = 0.0574). Final R1(2σ) = 0.0320, wR2(all data) = 0.0777.

[18] Although the anion initially associated with **5** is presumed to be either AcO$^-$ or HO$^-$, their presence in the crystal lattice was ambiguous. Stirring the isolated complex with $NaBF_4$ in THF exchanged the anions, allowing crystallization of the BF_4^- salt. Further details and alternate views of **5** can be found in the Supporting Information.

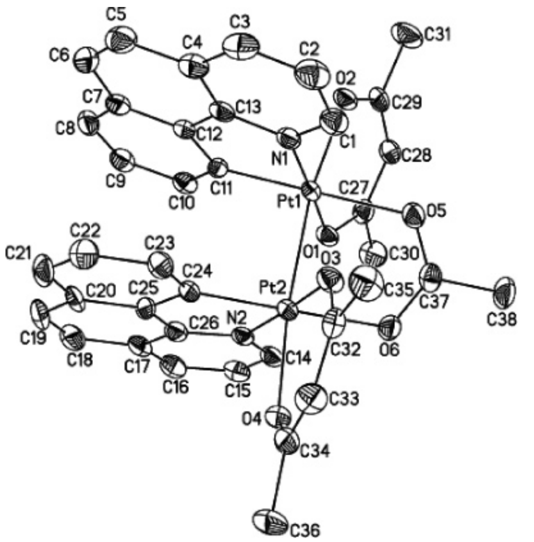
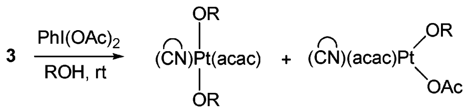


Figure 1. Selected bond distances for **5** (Å): Pt1−N1 = 2.010(4), Pt2−N2 = 2.014(3), Pt1−C11 = 1.993(4), Pt2−C24 = 2.004(4), Pt1−O1 = 2.011(3), Pt2−O3 = 2.008(3), Pt1−O2 = 2.117(3), Pt2−O4 = 2.115(3), Pt1−O5 = 2.129(3), Pt2−O6 = 2.147(3), Pt1−Pt2 = 2.5647(2). Selected bond angles (°): O2−Pt1−P2 = 170.58(8), Pt1−Pt2−O4 = 172.39(9), C11−Pt1−O5 = 179.60(16), N1−Pt1−O1 = 176.64(13), O5−C37−O6 = 125.0(4).

Table 2. Oxidation of (CN)Pt^{II}(acac) in Alcohols



6 **7**

entry	ligand	ROH	**6**:**7**[a]	isolated yield, %
1	Bzq	MeOH	2.0:1 (**6a**:**7a**)	70 (**6a**)
2	Bzq	EtOH	1.6:1 (**6b**:**7b**)	60 (**6b**)
3	Bzq	*i*PrOH	0.4:1 (**6c**:**7c**)	30 (**6c**)
4	8-MQ	MeOH	1:1 (**6d**:**7d**)	nd[b]
5	8-MQ	EtOH	1:4 (**6e**:**7e**)	nd[b]
6	8-MQ	*i*PrOH	single product (**7f**)	92% (**7f**)

[a] Ratios are approximate and were determined by ^{1}H NMR integration of the crude reaction mixture. [b] Inseparable mixture of products.

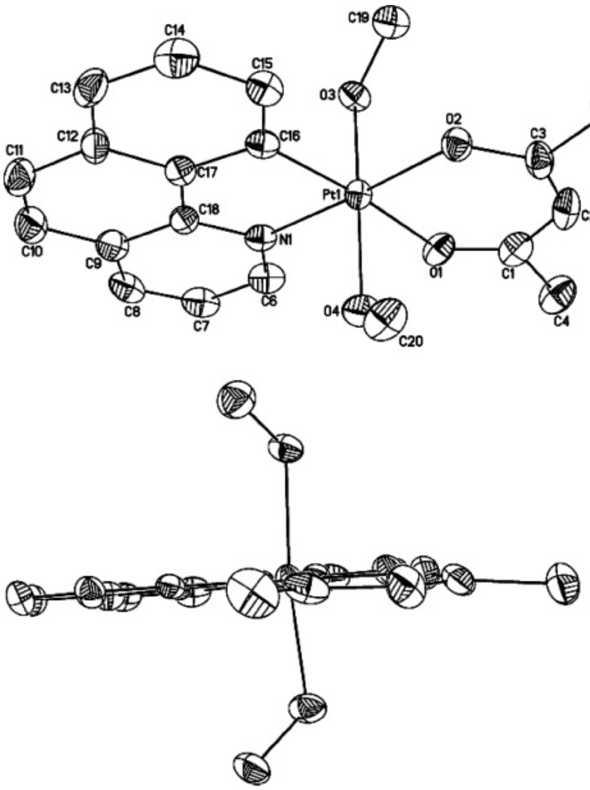


Figure 2. Selected bond distances for **6a** (Å): Pt1−N1 = 2.014(4), Pt1−C16 = 2.001(5), Pt1−O1 = 2.108(3), Pt1−O2 = 1.997(3), Pt1−O3 = 2.014(3), Pt1−O4 = 2.008(3). Selected bond angles (°): O3−Pt1−O4 = 172.59(12), O2−Pt1−N1 = 175.12(14), O1−Pt1−C16 = 173.59(14), C16−Pt1−N1 = 82.54(17), O1−Pt1−O2 = 93.72(13), O3−Pt1−N1 = 87.84(13), O1−Pt1−O4 = 85.38(13).

Investigations next turned to the oxidation of Pt^{II} model complex **3a** in alcohol solvents (conditions under which ethers are formed in Pd(OAc)$_2$-catalyzed reactions). We anticipated that the decreased ability of alkoxide ligands (relative to carboxylates) to bridge two Pt centers would lead to monomeric Pt products in these systems. Indeed, the reaction of 1 equiv of **3a** with 2.5−3.5 equiv of PhI(OAc)$_2$ in MeOH at room temperature cleanly afforded a mixture of Pt^{IV} alkoxides **6a** and **7a** (Table 2). The bis(methoxide) product **6a** was readily purified by chromatography on silica gel,[21] and its structure was confirmed by X-ray crystallography (Figure 2).[22] In general, these metrical parameters are comparable to those of other organometallic Pt^{IV} alkoxides,[8e,23] and deviation from perfect octahedral geometry in this structure is minimal. The mixed methoxide/acetate product **7a** proved difficult to separate cleanly from **6a**, but the stoichiometry of this complex was readily determined by ^{1}H NMR integration, which showed a 1:1 ratio of methoxide and acetate ligands. The cis orientation of the acetate and methoxide in **7a** was established on the basis of ^{1}H NMR NOE studies, which showed enhancement of the methoxide methyl resonance upon irradiation of the acetate methyl group.[24]

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(20) (a) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014. (b) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 469.

(21) Preparation of **6a**: complex **3a** (80 mg, 0.17 mmol) and PhI(OAc)$_2$ (166 mg, 0.51 mmol) were combined in a 100 mL flask, and MeOH (40 mL) was added. The mixture was stirred at room temperature for 5 h, during which time the solution changed color from orange to yellow. After evaporation of the solvent, the crude material was immediately purified by flash chromatography on silica gel (R_f = 0.61 in 20% MeOH in CH$_2$Cl$_2$), with CH$_2$Cl$_2$ to 5% MeOH in CH$_2$Cl$_2$ as eluents. Complex **6a** was isolated as a yellow solid (64 mg, 70%). Analytical data are reported in the Supporting Information.

(22) Crystal data for **6a**: $C_{20}H_{21}NO_4Pt \cdot H_2O$, M_r = 552.48, triclinic, space group $P\bar{1}$, a = 7.3732(12) Å, b = 8.7736(14) Å, c = 15.3642 Å, α = 86.341(3)°, β = 79.228(3)°, γ = 89.303(3)°, V = 974.4(3) Å^3, T = 150(2) K, Z = 2, D_c = 1.883 Mg m^{-3}, μ(Mo Kα) = 7.231 mm^{-1}, 4765 independent reflections (R_{int} = 0.0359). Final R1(2σ) = 0.0309, wR2(all data) = 0.0789.

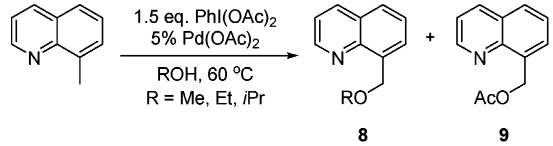
(23) Kapteijn, G. N.; Meijer, M. D.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1997**, *264*, 211.

(24) The cis orientation of the alkoxide and acetate ligands in **7b**−**f** was established via similar NOE experiments (see the Supporting Information for details).

Interestingly, the ratio of products **6** and **7** did not vary significantly with either reaction time or concentration; however, it showed a marked dependence on the alcohol solvent. In general, more of the mixed complex (**7**) was formed as the size of the alcohol increased from MeOH to EtOH to *i*PrOH (Table 2, entries 1−3, respectively), suggesting that the bis(alkoxide) product is disfavored with increasing sterics. The ratio of bis(alkoxide) to mixed alkoxide/acetate product also showed a significant dependence on the cyclometalated ligand; for example, changing from benzo[*h*]quinoline to the less rigidly planar ligand 8-methylquinoline resulted in a significant increase in the ratio of mixed complex **7** to bis(alkoxide) **6** (e.g., Table 2, entries 1 and 4, 2 and 5, 3 and 6).

As described above, the Pt^{II} oxidation reactions were designed to model intermediates in the $Pd(OAc)_2$-catalyzed oxygenation of organic substrates with $PhI(OAc)_2$. Preliminary results suggest that the Pt^{IV} alkoxides **6** and **7** may indeed be relevant to these catalytic intermediates, as trends observed in their formation are closely mirrored in the Pd^{II}-catalyzed reactions. For example, while the catalytic oxidation of benzo[*h*]quinoline in ROH affords only aryl ether products,[3b] analogous reactions of less rigidly planar 8-methylquinoline produce mixtures of benzyl ether **8** and benzyl ester **9** (Scheme 4). Furthermore, the ratio of **8** to **9** in this transformation correlates with the size of the alcohol and decreases significantly (from approximately >50:1 to 22:1 to 4:1) as ROH is changed from MeOH to EtOH to *i*PrOH, respectively.[25,26] These results are consistent with competing C−O bond-forming reductive elimination from Pd^{IV} bis(alkoxide) and mixed alkoxide/acetate intermediates (analogues of **6** and **7**), whose ratio in solution is dictated by steric/electronic factors analogous to those for the Pt^{IV} complexes. By way of contrast, we currently have little evidence concerning the relevance of Pt^{III} dimer **5** to intermediates in the Pd-catalyzed reactions, but this is certainly a previously unforeseen possibility that merits further consideration. The +3 oxidation state is viable for palladium, and Pd^{III} complexes have been reported[27] and/or characterized by EPR spectroscopy[28] and electrochemistry.[29] However, the intermediacy of such species in Pd-catalyzed reactions has not, to our knowledge, been proposed in the literature.

Scheme 4. Catalytic Functionalization of 8-Methylquinoline in Alcohol Solvents



In conclusion, we have demonstrated that cyclometalated Pt^{II}(acac) complexes undergo facile oxidation with $PhI(OAc)_2$. In acetic acid, the reactions produce Pt^{III} dimers, while in alcohol solvents Pt^{IV} alkoxide products are formed. Preliminary evidence suggests that the latter may be analogues to high-oxidation-state intermediates formed during $Pd(OAc)_2$-catalyzed oxygenation reactions. Current efforts aim to further investigate the role of oxidant and cyclometalating ligand on the oxidation of (CN)Pt^{II}(acac) complexes as well as to probe the reactivity of both Pt^{III} and Pt^{IV} products toward C−O bond-forming reductive elimination.[30] In addition, the direct examination of reactive intermediates in Pd-catalyzed C−H bond oxidation reactions is currently in progress. We anticipate that these continuing investigations will provide important mechanistic insights into the palladium-catalyzed reactions.

Acknowledgment. We thank Waseem Anani and Kami Hull for carrying out the $Pd(OAc)_2$-catalyzed oxidation of 8-methylquinoline. In addition, we thank Jim Windak and Paul Lennon for acquiring the mass spectral data. This work was supported by a Camille and Henry Dreyfus Foundation New Faculty Award.

Supporting Information Available: Text, tables, and figures giving procedural and characterization data for all new compounds and complete crystallographic data for **5** and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Control studies have established that the benzyl ether products (**8**) are formed directly, *not* by nucleophilic substitution of **9** with ROH under the catalytic conditions.

[26] The ratio of **8** to **9** for each alcohol solvent was estimated by gas chromatography. These ratios do change upon modification of the reaction conditions (e.g., temperature, equivalents of oxidant). However, a similar trend (that the ratio of **8** to **9** decreased significantly from MeOH to EtOH to *i*PrOH) was observed under all conditions. A full account of this work is forthcoming: Anani, W.; Hull, K. L.; Sanford, M. S. Manuscript in preparation.

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