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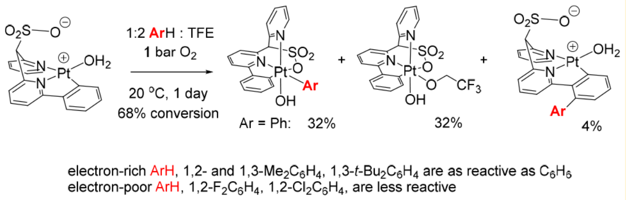
Consecutive C−H and O_2 Activation at a Pt(II) Center To Produce Pt(IV) Aryls

David Watts, Peter Y. Zavalij, and Andrei N. Vedernikov*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States

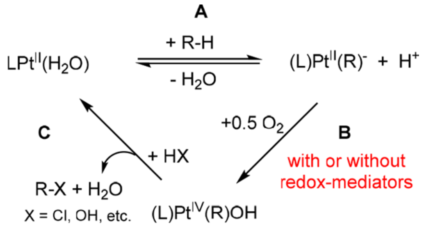
Supporting Information

ABSTRACT: Aerobic C−H functionalization of benzene and a series of electron-rich and electron-poor arenes has been demonstrated using a Pt(II) aqua complex supported by a sulfonated CNN-chelating pincer ligand in wet 2,2,2-trifluoroethanol (TFE) solutions at 20 °C and ambient pressure of air or O_2. The reaction results in Pt(IV) aryl hydroxo complexes and a Pt(IV) trifluoroethoxo complex as two major products, in a 1:1 molar ratio, along with minor Pt(II) products of the arene and pincer ligand oxidative C−C coupling.



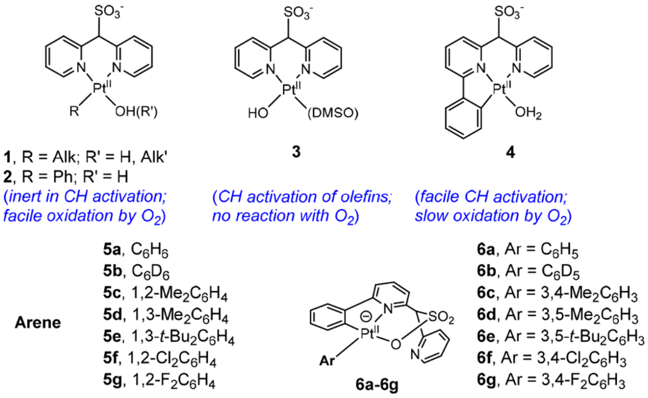
Selective oxidative functionalization of hydrocarbon C−H bonds using O_2, an inexpensive and environmentally benign reagent, is an attractive and challenging practical goal.[1] Soluble platinum complexes may be good candidates to serve as catalysts in such reactions potentially incorporating the three major steps A−C shown in Scheme 1.[2−13] Previous successful attempts have relied exclusively on the use of redox mediators such as heteropolyacids,[3,14,15] $CuCl_2$,[15,16] or $FeCl_3$,[15] with the mediator being responsible for O_2 activation (Scheme 1B). Notably, all the known systems are marked with low (<60%) selectivity with respect to the product RX due to concurrent CH activation of RX[4] and the ability of some mediators to oxidize RX.[3,14] The latter can be avoided in mediator-free systems. For example, the di(pyridine)methanesulfonate (dpms) ligand enables direct O_2 activation at a Pt(II) center in complexes **1** and **2** (Chart 1) in hydroxylic solvents[13,17] and the Pt(IV) alkyls resulting from oxidation of **1** undergo highly selective C(sp^3)−O reductive elimination. Nevertheless, Pt^{II} complexes of the dpms series have not been used in the catalytic fashion outlined in Scheme 1. Complexes **1** and **2** are inert in CH activation, whereas complex **3**, which breaks allylic CH bonds in olefinic substrates,[18] does not allow for subsequent O_2 activation.

Scheme 1. Aerobic CH Functionalization by $LPt^{II}(H_2O)$



To overcome the above limitations, a series of Pt(II) complexes such as **4** (Chart 1) were introduced recently.[19,20]

Chart 1. Sulfonated Dipyridine Pt(II) Complexes for CH and O_2 Activation along with Arenes 5 Studied in This Work



Complex **4** is a metallacyclic analogue of the phenyl complex **2** but, in contrast to **2**, **4** is an efficient catalyst for the H/D exchange between (deuterio-) poly(methyl)benzenes and 2,2,2-trifluoroethanol (TFE) or TFE-*d* at 20−80 °C (eq 1).

$$C_6H_6 + nCF_3CH_2OD \rightarrow C_6H_{6-n}D_n + nCF_3CH_2OH \qquad (1)$$

In this work we demonstrate that CH activation of benzene and aromatic substrates **5c−g** by **4** can be followed by O_2 activation with the derived anionic Pt(II) aryl intermediates, such as **6**, likely responsible for the latter step. The reaction leads to two types of major isolable Pt(IV) products, arene-derived hydroxo complexes **7** and the trifluoroethoxo hydroxo complex **8**. A minor Pt(II) species **9** also forms, resulting from oxidative C−C coupling of the arene and **4** (Scheme 2; C_6H_6 as the substrate). Since the aryl hydroxo Pt(IV) complexes **7**

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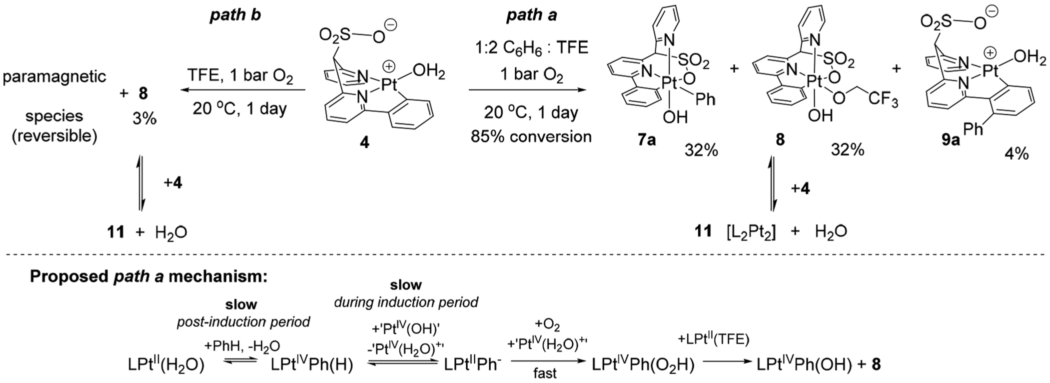
Scheme 2. Oxidation of C_6H_6 and Complex 4 by O_2 in TFE Solutions[23]



are inert toward C−O reductive elimination, similarly to all other known Pt(IV) aryl hydroxo complexes,[17,21] step C in Scheme 1 could not be completed.

Earlier we found that the phenyl complex **2** can be quantitatively oxidized to Pt(IV) phenyl hydroxo derivatives when its aqueous or methanol solutions are exposed to O_2 for 40−48 h at 20 °C.[17] If we consider the analogy between **2** and **4**, if **4** is to serve as a catalyst in aerobic oxidations, this type of reaction would be undesirable. To probe the reactivity of **4** toward O_2, we exposed a dry TFE solution of **4** to O_2 gas at 21 °C and 1 atm. About 50% of **4** was consumed after 3 h; however, the Pt(IV) complex **8** had not formed; the main reaction product(s) were purple NMR-silent species (Figures S7 and S8).[22,23] The formation of the purple species could be reversed by introducing 500 mM of water (Figures S9 and S10). The Pt(IV) complex **8** appeared in our reaction mixtures, either dry or wet, only after about 24 h in a low 3% yield (Scheme 2, *path b*). Altogether, these observations suggest a much lower reactivity of **4** toward O_2, in comparison to **2**, with a possible involvement of paramagnetic Pt intermediates.[7] To simplify analysis of our reaction mixtures by means of ^{1}H NMR spectroscopy, wet TFE solutions containing 0.150 M of water were used in our subsequent experiments.

Having demonstrated the ability of **4** to activate both CH bonds of benzene and O_2, we set up benzene oxidation. Stirring a solution of **4** in a 1/2 (v/v) mixture of C_6H_6 and TFE for 24 h under 1 atm of O_2 at 22 °C, under ambient light or in the dark, resulted in $\sim$85% conversion of **4** and formation of a 1/1 mixture of two Pt(IV) hydroxo complexes: the phenyl complex **7a** (32% yield), a product of benzene activation, and its trifluoroethoxo analogue **8** (32% yield)[23] (Scheme 2, *path a*). Formation of **9a**, a product of oxidative C−C coupling of benzene and **4**, was also observed in a low 4% yield. Notably, Pt(IV) complexes **8** and **7a** were both produced at a more than 1 order of magnitude faster average rate (*path a*) in comparison to the formation of **8** in the absence of benzene (*path b*) (Figure S6a,b), thus supporting the notion that not **4** but rather benzene-derived electron-richer species such as **6a** may be responsible for O_2 activation.

The identity of the new complex **7a** as well as **10a**, a PPh_3 derivative of **9a**, was confirmed by single-crystal X-ray diffraction (Figure 1). The major product **7a**, similar to **8**, features a meridional CNO coordination of the pincer ligand, whereas in **10a** and, as we assume, in **9a**, the ligand coordination mode is CNN.

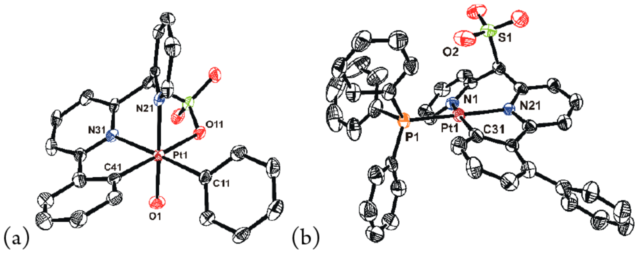


Figure 1. ORTEP drawing (50% probability ellipsoids) for (a) **7a** and (b) **10a**,[24] a PPh_3 derivative of **9a**. Hydrogen atoms and cocrystallized solvent are omitted for clarity.

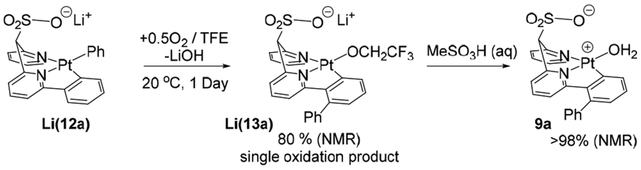
With these results on hand, we wanted to explore the mechanism of the oxidation with O_2 of solutions of **4** in a wet 1/2 C_6D_6/TFE mixture. The reaction showed complex kinetics with an induction period in the beginning (Figure S6b) and inhibition by its product **8** but not **7** (Figures S6d, S27, and S28). Next, we have found that the induction period can be eliminated in the presence of either of **8** or **7b** (Figure S6c,d). These Pt(IV) hydroxo species may be acting as weak Brønsted bases[12] responsible for the formation of anionic Pt(II) aryls such as **6b**. In turn, the induction period increases to >24 h in the presence of 0.3 equiv of CF_3CO_2H (Figure S31). Hence, we speculate that the induction period is needed to raise the basicity of the reaction mixture by producing a sufficient concentration of Pt(IV) hydroxo species. In turn, the reaction inhibition by **8** is related to the ability of **8**, but not **7b**, to form with **4** the 1/1 adduct **11**, as confirmed independently (equilibrium constant $K = 95 \pm 10$ calculated as $K = [\mathbf{11}][D_2O]/[\mathbf{4}][\mathbf{8}]$).

We next found the rate law for the formation of **7b** by measuring initial rates of accumulation of **7b** observed after the reaction induction period. The rate law implies first order in $[C_6D_6]$ and $[\mathbf{4}]$ but zero order in $[O_2]$. By comparing the observed reaction rate constants for C_6H_6/CF_3CH_2OH and C_6D_6/CF_3CH_2OH systems, we found the deuterium kinetic isotope effect of the reaction, $k_H/k_D = 1.6 \pm 0.1$, which is the same as in the H/D exchange reaction (1) catalyzed by **4**.[19]

Next, by using additives able to affect the rates of some radical reactions, we found that accumulation of the reaction products **7b** and **8** is not inhibited by 10 equiv of 2,6-di-*tert*-butyl-4-methylphenol (BHT) but is about 1 order of magnitude slower in the presence of 0.5 equiv of *p*-hydroquinone. Remarkably, while BHT does not change the reaction selectivity, *p*-hydroquinone additives caused the **7b**/**8** ratio to increase from 1/1 to 5/1. Formation of benzoquinone was also detected in the latter test. Reactions of Pt(II) complexes such as $[LPt^{II}Ph]^-$ with O_2 in protic media typically produce the hydroperoxo Pt(IV) intermediates $LPt^{IV}Ph(O_2H)$[4,7−10] (Scheme 2, bottom). The latter may transfer one oxygen atom from the peroxo ligand to a Pt(II) complex to form 2 equiv of $LPt^{IV}Ph(OH)$ (reaction with $[LPt^{II}Ph]^-$) or 1 equiv each of $LPt^{IV}Ph(OH)$ and $LPt^{IV}(OCH_2CF_3)(OH)$ (reaction with TFE-derived $[LPt^{II}(OCH_2CF_3)]^-$). When *p*-hydroquinone is present, we speculate that it efficiently intercepts the reactive species $LPt^{IV}Ph(O_2H)$ to produce 1 equiv of $LPt^{IV}Ph(OH)$ and benzoquinone (*path b*), thus suppressing the formation of a second equivalent of Pt(IV) products. If O_2 activation were done by $[LPt^{II}(OCH_2CF_3)]^-$, in the presence of *p*-hydroquinone the intermediate Pt(IV) peroxo species $LPt^{IV}(OCH_2CF_3)(O_2H)$ would be selectively reduced to **8** (*path b*), leading to **7b**/**8** ratios of less than 1/1, which does not match our experimental observations. Hence, on the basis of these observations, we propose that O_2 activation is carried out predominantly by phenyl Pt(II) intermediates such as **6b**.

We next wanted to probe the identity of the Pt(II) phenyl species responsible for O_2 activation in the oxidation reaction in Scheme 2, *path a*. Assuming that the *mer*-CNO-coordinated **7a** results from oxidation of the CNO-coordinated **6a**, we wanted to check if the minor reaction product, CNN-coordinated **9a**, may result from oxidation of **12a**, a CNN-coordinated isomer of **6a** (Scheme 3). Complex **12a** as a lithium salt has been prepared independently and submitted to aerobic oxidation in TFE. At 1 atm of O_2 and 20 °C, Li(**12a**) is consumed with a half-life of ∼2 h, reaching >95% conversion after 1 day and producing the C−C coupled Pt(II) complex Li[**13a**] in 80% yield.[25] The latter, upon acidic workup, could be converted quantitatively to **9a**. Since **13a** is the only oxidation product of **12a**, we assume that the CNN-coordinated Pt(II) phenyl species **12a** is not likely to be the reaction intermediate leading to **7a** and that **6a** instead may be responsible for the formation of **7a**.

Scheme 3. Oxidation with O_2 of Pt(II) Phenyl Complex 12a in TFE



A plausible mechanism for reaction of $LPt^{II}(H_2O)$ (**4**) with benzene and O_2 is shown in Scheme 2 (bottom). During the induction period the Pt(IV) hydroxo complex **8** is forming slowly according to Scheme 2 (*path b*) and then, additionally, in the reaction with benzene (Scheme 2, *path a*). When the concentration of **8** is high enough, in the postinduction period, CH activation of the arene to form a transient $LPt^{IV}Ph(H)$ is,[19] most likely, the reaction rate determining step. It is followed by "$Pt^{IV}(OH)$"-assisted formation of $LPt^{II}Ph^-$ (**6a**) and subsequent fast O_2 activation by **6a** leading to a Pt^{IV} hydroperoxide.[9] The latter transfers one of its peroxo oxygen atoms to a TFE analogue[19] of **4** to produce **7a** and **8** in a 1/1 ratio.

The reaction in Scheme 2 is not limited to a single arene. We explored aerobic oxidation of solutions of **4** in TFE containing electron-rich and electron-poor disubstituted benzenes using their 1/2 (v/v) mixtures (Chart 1). In addition to **8**, selective (≥90%) formation of a single Pt(IV) aryl complex **7c−f** was observed.[26] The reaction was equally fast for benzene and *o*- and *m*-xylenes (**5c,d**) but noticeably slower for *m*-di-*tert*-butylbenzene (**5e**), which has limited solubility in TFE (Table S1). Even slower reaction rates were observed for electron-poor *o*-dichlorobenzene (**5f**) and *o*-difluorobenzene (**5g**). Another difference between electron-rich and electron-poor substrates is their Pt(IV) product ratio, **8**/**7**, which is greater than 1/1 for the electron-poor Pt(IV) aryl complexes **7f,g**. We assume that **7f,g** form at a slower rate in comparison to **8** because the background oxidation of **4** to **8** (Scheme 2, *path b*) becomes competitive with the arene activation (Scheme 2, *path a*). Formation of C−C coupled products **9** could not be detected in these slow oxidation reactions.

Overall, in this work we have demonstrated, for the first time, the feasibility of consecutive activation of CH bonds of various arenes at a Pt(II) center and O_2 activation by the resulting Pt(II) aryl intermediates, leading to Pt(IV) aryl hydroxo derivatives. Although the latter could not be engaged in reductive C−O coupling in this system, our work may be important in directing the future design and development of catalytic systems for selective hydrocarbon CH functionalization utilizing O_2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00662.

Complete experimental details and crystallographic information for **7a** and **10a** (PDF)

Accession Codes

CCDC 1862275−1862276 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for A.N.V.: avederni@umd.edu.

ORCID

Andrei N. Vedernikov: 0000-0002-7371-793X

Notes

The authors declare no competing financial interest.

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(22) Our attempts at EPR characterization of these solutions were not successful.

(23) [**7**] and [**8**] were determined upon removal of TFE using DMSO-d_6, which destroys adduct **11** responsible for the difference between the conversion of **4** and the combined yield of **7**−**9**.

(24) CCDC 1862275−1862276 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Center.

(25) The remaining 20% is Li[(C_6H_4-dpms)Pt(OCH_2CF_3)], as confirmed via independent synthesis by reacting **2** with 1 equiv of $NaOCH_2CF_3$. Li[(C_6H_4-dpms)Pt(OCH_2CF_3)], presumably, results from protonoloysis of the Pt−Ph bond in **10a** by TFE solvent. Indeed, solutions of **10a** that are left for extended periods in TFE in the absence of O_2 are completely converted to Li[(C_6H_4-dpms)Pt(OCH_2CF_3)].

(26) Formation of two isomeric $LPt^{IV}Ar(OH)$ species in a 2/1 ratio, with Ar = 3,4-difluorophenyl (isolated) and, presumably, Ar = 2,3-difluorophenyl (not isolated), respectively, was apparent for *o*-difluorobenzene as a substrate.

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