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Regeneration of an Iridium(III) Complex Active for Alkane Dehydrogenation Using Molecular Oxygen

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Supporting Information

ABSTRACT: $(^{dm}$ Phebox)Ir(OAc)₂(OH₂) (1a) has previously been found to promote stoichiometric alkane dehydrogenation, affording alkene, acetic acid, and the corresponding Ir hydride complex $(^{dm}$ Phebox)Ir(OAc)(H) (2a) in high yield. In this study, we describe the use of oxygen to quantitatively regenerate 1a from 2a and HOAc. Distinct reaction intermediates are observed during the conversion of 2a to 1a, depending upon the presence or absence of 1 equiv of acetic acid, highlighting potential mechanistic implications regarding alkane dehydrogenation catalysis and the use of oxygen as an oxidant in such systems.



Lagging behind the recent remarkable advances in C–H bond functionalization has been the effective use of molecular oxygen as an oxidant in such transformations. For the development of commercially viable large-scale reactions, including selective alkane oxidation, the use of dioxygen or air holds tremendous potential on the basis of thermodynamic, environmental, and economic considerations. Recently, very successful catalysts have been reported for alkane dehydrogenation to alkenes.¹ The efficient production of alkenes is highly attractive, as these molecules are important building blocks in the chemical industry. However, alkane dehydrogenation reactions are typically performed using a sacrificial olefin as an oxidant (A, eq 1). The use of oxygen as the oxidant for alkane dehydrogenation could have dramatic advantages in terms of cost and environmental impact.

$$\bigwedge_{R} + A \xrightarrow{\text{catalyst}} \bigwedge_{R} + AH_2 \qquad (1)$$

Homogeneous alkane dehydrogenation catalysts have primarily been based on low-valent Ir, Pt, and Rh species,² with pincer-ligated iridium catalysts as the most successful reported to date.³ The pincer Ir catalysts have been shown to operate with various olefins as hydrogen acceptors at moderate temperatures or in open systems (acceptorless) at high temperatures.⁴ However, the proposed active catalyst in these systems, a (pincer)Ir^I fragment, reacts with dinitrogen, water, oxygen, or olefin, all inhibiting dehydrogenation.^{3a,b,S} Recently, we reported stoichiometric n-octane dehydrogenation by the Ir^{III} complex (^{dm}Phebox)Ir(OAc)₂OH₂ (1a; ^{dm}Phebox = 2,6bis(4,4-dimethyloxazolinyl)-3,5-dimethylphenyl) to generate $(^{dm}$ Phebox)Ir(OAc)H (2a), HOAc, and octene (eq 2).⁶ This dehydrogenation reaction was not inhibited by the presence of nitrogen, water, or alkene, an important advantage in comparison with (pincer)Ir^I systems in terms of developing practical systems for catalytic dehydrogenation.

In this contribution, we report that the Ir^{III} hydride product of alkane dehydrogenation, **2a**, reacts with oxygen in the







run this system as a continuous catalytic cycle,⁷ the sum of eq 3 and the previously reported eq 2 represents a catalytic transfer of hydrogen from alkane to oxygen to give alkene and water. The chemistry reported herein thus offers a new paradigm for alkane dehydrogenation catalysis wherein an Ir^{III} species activates and dehydrogenates alkane, and oxygen serves as the hydrogen acceptor.

Exposure of a bright orange benzene- d_6 solution of **2a** and 1 equiv of acetic acid to ambient air at room temperature caused the solution to turn yellow within several minutes.⁸ Monitoring the reaction by ¹H NMR spectroscopy revealed quantitative formation of **1a** over the course of 2 h (eq 3). The identity of **1a** was confirmed by spiking the product solution

Received: December 31, 2013 Published: March 11, 2014 with an authentic sample of 1a.⁹ When a benzene- d_6 solution of 2a and 1 equiv of acetic acid was exposed to 3 atm of oxygen (instead of air), 1a formed after 2 h in slightly lower yield (83%). When the same reaction with 3 atm of oxygen was performed with added water (12 equiv), the yield of 1a increased to 96%; this result is consistent with the presence of coordinated water in 1a.

During the reaction of **2a** and acetic acid with oxygen (or air) as described above, an intermediate species (3a) was observed in the ¹H NMR spectrum (Figure 1). After only 10 min, signals characteristic of 3a are quite clear in the alkyl and oxazolinyl regions of the spectrum. Two singlets indicative of inequivalent methyl groups on the oxazoline rings of 3a were observed at 1.24 and 1.48 ppm. In the oxazolinyl region of the ¹H NMR spectrum, two doublets assigned to the methylene protons were observed for 3a at 3.95 and 4.20 ppm consistent with C_s symmetry for the intermediate. During the course of the reaction these doublets shifted downfield to 4.09 and 4.21 ppm (Figure 1, 1 h 30 min). The shift in the signals may represent an additional intermediate or merely a change in chemical shift of the signals of 3a caused by changing reaction conditions. Attempts to grow X-ray-quality crystals of the intermediate(s) at various temperatures, as low as -80 °C, only afforded crystals of the final product complex 1a.

To investigate the generality of the oxygen reaction, analogous Ir^{III} hydride complexes bearing different carboxylate groups, $(^{dm}Phebox)Ir(X)H$ (X = OBz (2b), OPiv (2c)), were prepared and their reactivity with oxygen was examined. Addition of 1 equiv of benzoic acid to 2a in benzene- d_6 resulted in displacement of the acetate ligand with benzoate, generating 2b in quantitative yield by ¹H NMR spectroscopy (eq 4). In the



¹H NMR spectrum of **2b**, the hydride resonance was observed at -33.7 ppm and three signals indicative of the benzoate protons were observed at 7.18 (1H), 7.22 (2H), and 8.55 ppm (2H) consistent with benzoate coordination at the Ir^{III} center.

The pivalate derivative 2c was similarly generated in quantitative yield from the reaction of 2a and 1 equiv of pivalic acid (eq 4). The *tert*-butyl substituent of the pivalate ligand was observed at 1.46 ppm and integrated to nine protons relative to the two singlets, each six protons, assigned to the two unique oxazoline methyl substituents of the ^{dm}Phebox ligand. The hydride signal in the ¹H NMR spectrum of 2c was observed at -33.8 ppm, consistent with the data obtained for 2a,b.

The addition of 1 equiv of benzoic acid to a benzene- d_6 solution of 2b resulted in broadening of the benzoate aromatic signals consistent with exchange between benzoic acid and the coordinated benzoate. This exchange is similar to that observed for 2a with acetic acid.⁸ When the benzene- d_6 solution of 2b and benzoic acid was exposed to air at room temperature, within 10 min an intermediate species (3b) and the product 1bwere both observed in the ¹H NMR spectrum. Similar to the data observed for 3a, the spectral data for 3b were consistent with a $C_{\rm s}$ structure. Complete disappearance of 2b and intermediate 3b was observed after 2.5 h at room temperature, generating complex 1b in 80% yield (by integration against an internal standard). The identity of 1b was confirmed by spiking the final solution with an authentic sample of 1b.¹⁰ In addition, the structure of complex 1b was determined by X-ray crystallography (Figure 2). The $C_{2\nu}$ symmetry noted in solution is also evident in the solid state, as the two benzoate ligands are



Figure 2. ORTEP diagram of $({}^{dm}Phebox)Ir(OBz)_2(OH_2)$ (1b) (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ir(1)-C(1) = 1.935(3), Ir(1)-N(1) = 2.0597(17), Ir(1)-O(2) = 2.0418(15), Ir(1)-O(5) = 2.218(3); N(1)-Ir(1)-N(1) = 158.52(9), C(1)-Ir(1)-O(2) = 88.85(4), C(1)-Ir(1)-O(5) = 170.67(7), C(1)-Ir(1)-N(1) = 79.26(5).



6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7

Figure 1. ¹H NMR spectral data in the aromatic and oxazolinyl regions acquired over the course of the reaction of 2a with acetic acid and air at room temperature in benzene- d_6 .

related by a mirror plane. The water molecule in **1b** is located *trans* to the aryl backbone of the ^{*dm*}Phebox ligand with an Ir–O bond length of 2.218(3) Å. This is very close to the reported Ir–O bond length of 2.206(3) Å for the Ir–OH₂ moiety of **1a**.¹¹ The Ir(1)–O(2) bond length of 2.0418(15) Å is also similar to the Ir–OAc bond lengths reported for **1a** (2.037(3) and 2.058(3) Å).

Upon the addition of 1 equiv of pivalic acid to a benzene- d_6 solution of 2c, exchange between the pivalate ligand and pivalic acid, similar to that observed for 2a,b and their respective acids, was indicated by the presence of a broad signal at 1.25 ppm for the *tert*-butyl groups.⁸ When the solution of 2c and pivalic acid was exposed to air, the reaction proceeded similarly to the reactions of the carboxylate complexes 2a,b described above; formation of an intermediate species 3c and the product 1c was observed by ¹H NMR spectroscopy within 10 min at room temperature (Figure S3). The presence of 3c was indicated by the appearance of two new doublets, integrating in a 1:1 ratio at 3.94 and 4.18 ppm in the oxazolinyl region. Additionally, two singlets at 1.49 and 1.20 ppm were assigned as the oxazoline methyl groups, each integrating to six protons. After 3 h, complex 1c had formed in quantitative yield by ¹H NMR spectroscopy. The identity of 1c was confirmed by independent synthesis of the complex.¹⁰

In an effort to identify the intermediate 3a, the reaction of 2a with oxygen in the absence of acetic acid was performed. Surprisingly, exposure of a benzene- d_6 solution of 2a to 3 atm of oxygen (or 1 atm of air) at room temperature did not result in an immediate reaction by ¹H NMR spectroscopy. Over the course of 3.5 h at room temperature, the solution slowly darkened from bright orange to jungle green. At this time complete consumption of 2a was observed and a new complex (4a), with signals different from those assigned to 3a, was present in the ¹H NMR spectrum (eq 5). The ¹H NMR



spectral data for **4a** were indicative of the formation of a species with C_s symmetry akin to the starting material **2a**; two doublets were present in the oxazolinyl region at 3.84 and 3.91 ppm, each integrating to two protons. Singlets at 1.25 (6H), 1.46 (6H), and 2.66 ppm (6H) were assigned to two different types of methyl substituents on the oxazoline rings and the methyl groups in the ^{dm}Phebox backbone, respectively. A signal attributable to a single coordinated acetate ligand was observed at 1.89 ppm (3H). Integration of the ^{dm}Phebox aryl proton at 6.42 ppm against an internal standard showed that **4a** was formed in 54% yield. No other products were observed in the spectrum, and no precipitate was present in the NMR tube, which suggests that additional paramagnetic Ir species were formed.

To investigate whether 4a was a potential intermediate in the reaction of 2a and acetic acid with oxygen, acetic acid was added to a benzene- d_6 solution of 4a (Scheme 1). Upon the addition of 1 equiv of acetic acid, the mixture did not change color and there was no evidence of reaction by ¹H NMR spectroscopy. The addition of a second equiv of acetic acid also did not result in an



immediate reaction. When the reaction mixture was left at room temperature for 72 h, complex 1a was generated in 83% yield based on the amount of 4a. In the absence of added acetic acid, decomposition of 4a led to the generation of 1a in 23% yield after 72 h. The lack of a rapid reaction when acetic acid was added to 4a is not consistent with this species being an intermediate in the reaction of 2a and acetic acid with oxygen. Moreover, we can conclude that the differences in the ¹H NMR spectra of 3a and 4a are not simply due to differences in the reaction media; these species are indeed different complexes.

In terms of proposing compositions of 3a and 4a, it seemed plausible that at least one of these complexes could be an Ir-OOH species formed by oxygen insertion into the Ir-H bond: e.g., (dmPhebox)Ir(OAc)(OOH). Notably there is literature precedent for oxygen insertion into metal-hydride bonds and for the formation of Ir-OOH complexes.¹²⁻¹⁵ Nocera and co-workers have reported the structural characterization of Ir2^{II,II}(tfepma)2- $(CN^{t}Bu)_{2}Cl_{3}(OOH)$ (tfepma = MeN[P(OCH_{2}CF_{3})_{2}]_{2}), which was generated from the reaction of $Ir_2^{II,II}$ (tfepma)₂(CN^tBu)₂-Cl₃(H) with oxygen in a THF solution.¹³ Insertion of oxygen into an Ir^{III}-H bond to form a Ir^{III}-OOH intermediate was proposed in Rauchfuss' catalytic hydrogenation of oxygen by Cp*IrH(rac-TsDPEN) (TsDPEN = H₂NCHPhCHPhN- $(SO_2C_6H_4CH_3)^{-}$.¹⁴ Ison and co-workers proposed a Cp*Ir-OOH intermediate in the catalytic oxidation of alcohols in toluene using [Cp*IrCl₂]₂ as a precatalyst.¹⁵ If an OOH ligand was present in intermediate species 4a, protonation of 4a should yield hydrogen peroxide. Thus, an assay was performed to detect hydrogen peroxide released upon protonation of 4a.¹⁶ Complex 4a was isolated as a dark green solid by removal of benzene- d_6 in vacuo. Isolated 4a was dissolved in acetonitrile and subjected to an excess of H₂SO₄. The formation of hydrogen peroxide was clearly evident when this mixture was added to an aqueous solution of KMnO4. The reaction between H2O2 and KMnO₄ was monitored by UV-visible spectroscopy.¹⁶ Notably, the Ir dicarboxylate product 1a was found to catalyze the disproportionation of hydrogen peroxide; the addition of 50 equiv of a 30% hydrogen peroxide solution to a benzene solution of 1a resulted in immediate bubbling. After 20 h, gas evolution had ceased and complex 1a was still present in solution without any decomposition to metal black. This disproportionation would complicate using the assay described above for 4a to determine whether intermediate 3a contained a hydroperoxide ligand. If hydrogen peroxide was produced upon protonation of 3a, 1a (which appears even at early reaction times) would promote its disproportionation to oxygen and water.

The formation of different intermediate species in the reactions of 2a with oxygen in the presence or absence of acetic acid implies different mechanisms for the two reactions. In the absence of acetic acid, the reaction with oxygen could form a hydroperoxide intermediate (4a), as shown in Scheme 1. This proposal is consistent with detection of hydrogen peroxide

upon the addition of sulfuric acid to 4a. However, we also have evidence that 4a is not formed when the reaction is carried out in the presence of acetic acid. The reaction of 4a and acetic acid does lead to 1a, but the reaction is too slow for 4a to be considered a kinetically competent intermediate in the formation of 1a from the reaction of 2a with acetic acid and oxygen. It appears that the interaction of 2a with acetic acid allows a faster reaction with oxygen to generate 3a. The intermediate 3a observed in the reaction of 2a and acetic acid with oxygen may also be a hydroperoxide species, but it is not 4a. Several possibilities for 3a-c include protonated hydroperoxo, hydroxo or peracetate complexes.¹⁷

We have previously reported that $(^{dm}Phebox)Ir(OAc)_2(OH_2)$ (1a) reacts with octane to give octene, $({}^{dm}Phebox)Ir(OAc)H$ (2a), acetic acid, and water. In this work we have demonstrated that 2a reacts with oxygen (in the presence of acetic acid and water) to regenerate 1a in high yield. The derivatives $(^{dm}$ Phebox)Ir(X)₂(H) (**2b**,c; X = OBz, OPiv) show similar behavior. These reactions occur at room temperature and proceed through a (^{dm}Phebox)Ir intermediate, possibly an Ir-OOH species. Generation of 1a-c from 2a-c with oxygen represents the key regeneration step needed to achieve aerobic dehydrogenation of alkanes. In contrast, most of the well-known homogeneous alkane dehydrogenation catalysts are incompatible with oxygen. This work involving high-oxidation-state $\mathrm{Ir}^{\mathrm{III}}$ complexes for alkane activation thus suggests a novel approach toward developing alkane functionalization systems that can utilize oxygen as a hydrogen acceptor. Current studies are focused on determining the identities of the intermediate species and the mechanism of this reaction, as well as applying these findings toward the development of a catalytic system.

ASSOCIATED CONTENT

S Supporting Information

Full experimental details including X-ray crystallographic data for **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(7) Catalytic *n*-octane dehydrogenation using **2a** was not observed at 200 °C with air (1 atm). While some oxidation of *n*-octane was observed, similar results in the absence of Ir were noted. An oxygen atmosphere at high temperature may be incompatible with these Ir complexes and/or intermediates, but further studies are needed.

(8) In the absence of oxygen, only degenerate exchange of the acetate ligand and the hydride moiety of **2a** with the added acetic acid was observed. Exchange of the acetate was evidenced by a single broad resonance at 1.87 ppm in the ¹H NMR spectrum that corresponded to the methyl groups of both acetate and acetic acid. In addition, a slower H/D exchange between the hydride ligand and acetic acid- d_4 (3 equiv) occurs under these conditions; 50% deuterium incorporation into the hydride position was observed after 2 h at room temperature.

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