

# An Iridium(IV) Species, [Cp\*Ir(NHC)Cl]<sup>+</sup>, Related to a Water-Oxidation Catalyst

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Received October 26, 2010

The Ir precatalyst (3) contains both a Cp\* and a  $\kappa^2 C^2$ ,  $C^2$ -1,3-diphenylimidazol-2-ylidene ligand, a C-C chelate, where one C donor is the NHC and the other is a cyclometalated N-phenyl wingtip group. The structure of **3** was confirmed by X-ray crystallography. Like our other recently described Cp\*Ir catalysts, this compound is a precursor to a catalyst that can oxidize water to dioxygen. Electrochemical characterization of the new compound shows that it has a stable iridium(IV) oxidation state, [Cp\*Ir<sup>IV</sup>(NHC)Cl]<sup>+</sup>, in contrast with the unstable Ir(IV) state seen in our previous cyclometalated [Cp\*Ir<sup>III</sup>(2-pyridyl-2'-phenyl)Cl] catalyst. The new iridium(IV) species has been characterized by EPR spectroscopy and has a rhombic symmetry, a consequence of the ligand environment. These results both support previous studies which suggest that Cp\*Ir catalysts can be advanced through the relevant catalytic cycle(s) in one-electron steps and help clarify the electrochemical behavior of this class of water-oxidation catalysts.

## Introduction

Rising demand for alternative energy due to geopolitical concerns such as global climate change has led to increased interest in carbon-neutral "green" fuels.<sup>1-3</sup> In order to produce these alternative fuels, an abundant and sustainable source of reducing equivalents must be found. Green plants, algae, and cyanobacteria utilize water as their source of electrons and protons for sustaining life processes and reducing carbon dioxide to carbohydrates. Specifically, generation of protons and electrons out of water is accomplished by the enzyme-cofactor complex Photosystem II (PSII).<sup>4-6</sup> In PSII, a manganese-calcium cluster is sequentially oxidized and ultimately releases four protons, four electrons, and dioxygen from two water molecules (eq 1).

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2$$
 (1)

Many artificial photosynthesis and solar-fuel production schemes, inspired by natural photosynthesis, propose using water as a source of reducing equivalents for reduction of

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protons to hydrogen or carbon-containing molecules to other fuels.<sup>7–13</sup> Homogeneous water oxidation catalysts, which have well-defined structures and mechanisms of action, are a key component of many of these proposed systems.<sup>14</sup> The so-called "blue dimer", the first homogeneous water-oxidation catalyst, was described in 1982 by Meyer and co-workers.15 Since then, binuclear ruthenium-based wateroxidation catalysts have been studied in great detail.<sup>16-20</sup> More recently, mononuclear ruthenium water oxidation catalysts have emerged as attractive systems for catalytic water oxidation, due to their efficacy and simplicity.<sup>21,22</sup> Mechanistic investigations of both mononuclear and binuclear ruthenium catalysts

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Published on Web 02/08/2011

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Figure 1. Cp\*Ir water oxidation catalysts and precatalysts.<sup>28,29</sup>

have led to a consensus view of the requirement for high-valent ruthenium intermediates which arise by oxidation via protoncoupled electron transfer.<sup>20</sup> In these mechanistic proposals, oxidation from lower valent ruthenium occurs along with deprotonation of water bound to the metal center. Eventually, a sufficiently oxidizing intermediate is reached (usually a ruthenium(V) oxo species) which is susceptible to either nucleophilic attack from substrate water or accomplishes O–O bond formation by oxo-oxo coupling.<sup>18</sup> Such high-valent intermediates have also found use in oxidative transformations of organic molecules.<sup>23–26</sup>

Iridium catalysts also oxidize water. In 2008, Bernhard and co-workers showed that, upon addition of cationic iridium(III) bis(solvento) bis(2-pyridyl-2'-phenyl) complexes to solutions of cerium(IV) ammonium nitrate, oxygen is evolved.<sup>27</sup> More recently, we have investigated a series of Cp\*Ir oxidation catalysts which are capable of water oxidation at high rates.<sup>28,29</sup> Among these catalysts, 1 and 2, which bear the cyclometalated phenylpyridine (ppy) ligand (Figure 1), are among the most active, achieving turnover numbers for oxygen evolution of 10 turnovers min<sup>-1</sup> when driven with cerium(IV) at pH 0.89. Catalyst 1 also has been shown to mediate oxidative transformations of organic molecules such as alkane hydroxylation.<sup>26</sup> These oxidations are anticipated to proceed via proton-coupled electron transfer to form high-valent iridium-oxo intermediates. However, no spectroscopic characterization of intermediates has been possible for the Cp\*Ir(ppy)L system, primarily due to its fast rate of oxygen evolution and the consequent short lifetimes of intermediates in solution. Reactions carried out in water or in water/organic solvent mixtures rapidly lead to product formation. DFT calculations have supported the proposed mechanism of sequential one-electron oxidations of the complex occurring via proton-coupled electron transfer.<sup>29</sup> The key intermediate for water oxidation was proposed to be an iridium(V) oxo, which has favorable energetics to undergo attack from nucleophilic water and form the O–O bond.

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Since the isolation of the first stable free N-heterocyclic carbene (NHC) by Arduengo in 1991, NHCs have seen extensive use as ligands in organometallic complexes with catalytic applications and can impart unique activity to catalytic systems.<sup>30–33</sup> NHC ligands are known for binding tightly to metal centers and for their high donor capacity relative to phosphines.<sup>31,34</sup> Additionally, the relatively strong  $\sigma$ -donor power of the ligand assists in stabilizing high-valent metal complexes. Recently, Cp\*Ir catalysts bearing an N-heterocyclic carbene ligand have been shown to be competent for water oxidation.<sup>35,36</sup>

We now report the synthesis of the N-heterocyclic carbene Cp\*Ir complex **3** (Scheme 1), which is a competent catalyst precursor for water oxidation. The stabilizing effect of the NHC ligand on high-valent iridium is clearly seen by comparing the electrochemical behavior of **1** and **3**. By electrochemistry, **1** lacks a stable iridium(IV) form, even in the absence of water. However, **3** shows quasi-reversible formation of an iridium(IV) species. Furthermore, a singly oxidized iridium(IV) species is now experimentally observable by electron paramagnetic resonance (EPR) spectroscopy using  $[Ru^{III}(bpy)_3]^{3+}$  (bpy = 2,2'-bipyridine) as a primary oxidant. This oxidant was chosen because it is sufficiently strong to effect oxidation to Ir(IV) but not so strong as to access the Ir(V) state.

## **Results and Discussion**

Synthesis and Characterization of  $Cp*Ir(\kappa^2 C^2, C^2, NHC)$ -(CI). N, N'-Diphenylimidazolium chloride (4) was synthesized by an adaptation of the standard preparation for N, N'-dimesitylimidazolium chloride.<sup>37</sup> Although 4 was originally synthesized by Wanzlick in the 1960s, its use in organometallic chemistry has been limited, due to its relative instability as a free carbene.<sup>38</sup> For our purposes, the phenyl wingtip groups were anticipated to provide necessary oxidation resistance versus other alkyl or mixed aryl-alkyl NHCs. Treatment of the imidazolium salt 4 with [Cp\*IrCl<sub>2</sub>]<sub>2</sub> in the presence of potassium *tert*-butoxide generates 3 (Scheme 1). Following chromatographic purification (see the Experimental Section), 3 was isolated as an analytically pure yellow powder. Crystals suitable for X-ray analysis were obtained from dichloromethane solution by vapor diffusion of pentane. The solid-state structure is shown in Figure 2. The obtained structure has an Ir-C(11) bond length of 1.998(5) Å and an Ir-C-(15) bond length of 2.047(5) Å, consistent with those observed in similar Cp\*Ir(NHC) complexes.<sup>35,39-41</sup>

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**Figure 2.** ORTEP drawing of the crystal structure of Cp\*Ir-( $\kappa^2 C^2, C^2$ '-NHC)(Cl) (3). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Water Oxidation. Cp\*Ir complexes have been shown to be competent catalysts for a variety of oxidative transformations.<sup>42–46</sup> Using cerium(IV) ammonium nitrate (CAN) as the primary oxidant, 1 has been shown to be competent for water oxidation,<sup>29</sup> epoxidation of cyclooctene, and C–H oxidation of *cis*-decalin to *cis*-decalol.<sup>26</sup>

In the case of the NHC precatalyst 3, two primary oxidants were screened for driving water oxidation. By analogy with previous work with 1 and 2,<sup>28,29</sup> cerium(IV) ammonium nitrate was chosen (78 mM, pH 0.89) and gives a rate of oxygen evolution of 8 turnovers min<sup>-1</sup> at 4.5  $\mu$ M loading of 3. However, under these harsh conditions of very low pH and high salt concentration, oxygen evolution data from a Clarktype electrode show a distinct lag phase, slight consumption of oxygen upon injection, and distinct upwardly concave shape (Figure 3). The lag phase showing consumption of oxygen is unique, not previously observed for other Cp\*Ir systems.<sup>28</sup> It is, however, possible that this corresponds to a slow dissociation of  $Cl^{-36}$  followed by oxidation to  $OCl^{-}$  or higher oxyanions. Though kinetically slow under ambient conditions, it is thermodynamically possible for oxygen to oxidize Cl<sup>-</sup> to OCl<sup>-</sup>. In the presence of cerium(IV) and highvalent iridium, this reaction may be kinetically accessible. It is also possible, as noted below, that this oxygen consumption corresponds to a ligand oxidation or ligand loss. The dependence of the oxygen-evolution rate on precatalyst loading

shows that 3 gives faster rates of oxygen evolution at higher loadings, suggesting multimolecular mechanisms of oxygen evolution. A traditional log-log plot of the same data gives an order of reaction in 3 of 1.85. By analogy with previously studied Cp\*Ir complexes,  $^{28,47}$  this suggests that the NHC ligand may be lost under the harsh catalytic conditions, though not under electrochemical conditions (vide infra), to give a  $[Cp*Ir(H_2O)_3]^{2+}$  fragment which contributes to catalysis (see the Supporting Information). Catalysts 1 and 2 exhibit much more unexceptional oxygen evolution traces when exposed to water in the presence of cerium(IV) (Figure 3).<sup>28,29</sup> Thus, with cerium(IV), 3 exhibits activity distinct from that of previously studied iridium half-sandwich compounds, suggesting a different mode of precatalyst activation<sup>28</sup> and the possibility of heterogeneous catalysis. Overall, although 3 has been shown to be a competent precatalyst, complex 1 exhibits superior rates of reaction.

As Ce(IV) oxidations require low pH which can contribute to catalyst deactivation, we thus also screened sodium periodate as the primary oxidant for oxygen evolution, as it can function near neutral pH. Under our chosen conditions (5 mM, pH ca. 5), periodate gives rates of 12-16 turnovers min<sup>-1</sup>. **3** shows deactivation at higher oxidant loadings, suggesting a multimolecular deactivation pathway. Interestingly, the oxygen evolution traces themselves appear more as expected at low micromolar precatalyst loadings, with a linear oxygen evolution trace, diminished lag phase, and no initial oxygen consumption. This supports the hypothesis that oxygen consumption is a product of the harsh conditions required when using Ce(IV) as oxidant. However, a log-log plot of the rate dependence gives an order of 0.67 in 3, suggesting complicated kinetics (see Supporting Information). This complication may arise from the fact that periodate can function as a one- or two-electron oxidant.48 A more detailed study of the mechanism of periodate-driven water oxidation is underway so as to allow direct comparison of this result to a wide range of water oxidation catalysts.

**Electrochemical Studies.** Electrochemical studies allow us to carefully examine the oxidation behavior of our complexes without the complications that come from the presence of our primary oxidants, cerium(IV) and periodate. Compounds 1-3 are soluble in acetonitrile and a 50/50 acetonitrile/water mixture and were investigated in these solvents by cyclic voltammetry with a basal plane graphite working electrode in a standard three-electrode configuration (see the Experimental Section for details). As reported previously, compound 1 displays three dominant irreversible waves in electrochemical studies in organic solvent (Figure 4).<sup>29</sup> The first oxidation, which occurs near 1.1 V

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Figure 3. Oxygen evolution traces in 5 mL H<sub>2</sub>O using 78 mM cerium(IV) as the terminal oxidant: (left) complex 1 (10  $\mu$ M loading); (right) complex 3 (15  $\mu$ M loading).



Figure 4. Cyclic voltammograms of compounds 1 (bottom) and 2 (top) in acetonitrile with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Conditions: ca. 3 mM catalyst, scan rate 100 mV/s.

vs NHE, is totally irreversible. Upon removal of the chloride ligand and substitution to form the triflate complex 2, this first oxidation completely disappears. In both complexes 1 and 2, there are two higher potential, irreversible oxidations which occur near 1.6 and 2 V. In the case of complex 1, there is an additional irreversible feature appearing as a shoulder on the 1.6 V oxidation. Cyclic voltammograms collected on

acetonitrile solutions containing tetrabutylammonium chloride show this oxidation corresponds to free chloride oxidation (presumably to chlorine) at the basal plane graphite electrode, as observed in similar cases by other groups.<sup>49</sup>

On the basis of the results in Figure 4, the 1.1 V oxidation wave peak arises from oxidation of the chloride-bound Cp\*Ir(ppy)Cl (1). This oxidation is followed at higher potentials by completely irreversible oxidation of the analogous [Cp\*Ir(ppy)MeCN]<sup>+</sup> adduct. The cationic solvento complex is thus significantly more difficult to oxidize than the neutral, chloride-bound complex. This is consistent with the complete loss of the 1.1 V irreversible oxidation when the chloride ligand in 1 is substituted for triflate in 2. In the case of this solvento complex, the 1.6 V oxidation wave does not appear to change potential in comparison with 1. However, the 2 V oxidation observed in the case of 1 does seem to change in appearance: this could be due to the formation of different species in solution. However, two factors complicate further analysis of these oxidation waves. First, they are both completely irreversible, which is likely a result of high instability in solution in the oxidized form. Furthermore, the very high potential required for observation of the ca. 2 V oxidation (and in the case of 1, the presence of chloride) makes identification of even the exact peak potential uncertain.

Supporting this model of the electrochemical data, upon titration of chloride into solutions containing 2, the first irreversible oxidation in 1 can be seen to reappear (see the Supporting Information). This strongly supports the idea that the first oxidation of 1 in Figure 4 is associated with the chloride-bound complex. Additionally, the equilibrium between chloride-bound and solvent species can be shifted by chloride addition so as to favor chloride-bound species; the resulting 1.1 V oxidation wave plateaus in intensity after addition of ca. 8-10 equiv of chloride per metal center.

Compound **3** has different redox behavior compared with compounds **1** and **2**. A wide scan from ca. 0.2 V to nearly 2.0 V vs NHE shows several oxidation waves (Figure 5, upper panel). The first oxidation wave is quasi-reversible on a full-width scan and occurs at  $E_{1/2} = 0.9$  V. This appears to be analogous to the irreversible oxidation wave which appears at 1.1 V in the case of compound **1** (vide infra). The second oxidation is fully irreversible and occurs at approximately 1.5 V; this is a slightly less oxidizing potential than that which is required for the oxidation wave near 1.6 V in the case of

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Figure 5. Cyclic voltammograms: (top) 3 (solid line) and 1 (dashed line) in acetonitrile solution with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte; (bottom) compound 3, centered on the lowest potential, quasi-reversible redox process. Conditions: ca. 3 mM complex, scan rate 100 mV/s.

compounds 1 and 2. Computational analysis using density functional theory (DFT) supports these data, confirming the lower iridium(III)/iridium(IV) oxidation potential of complex 3 in comparison to complex 1 (see the Supporting Information for details).

Narrowing the scan window to contain only the quasireversible feature at 0.9 V results in an improvement of the electrochemical reversibility for the oxidation-reduction process taking place (Figure 5, bottom panel). Examination of the behavior of the peak confirms that the process is nearly reversible, as judged by electrochemical theory.<sup>50</sup> The peak separation ( $\Delta E_p$ ) is 76 mV, only slightly larger than the ideal 59 mV. Furthermore, the ratio of peak currents ( $i_{p,c}/i_{p,a}$ ), expected to be unity for an ideal reversible process, is found experimentally to be 0.90. With this result, we expected that the quasi-reversible process taking place was the one-electron oxidation-reduction of the Cp\*Ir<sup>III</sup>(NHC)Cl complex with chloride in the inner coordination sphere.

Addition of water to solutions containing 1-3 in acetonitrile with electrolyte results in a complete change in the electrochemical response (Figure 6). For complex 3 in a 50/



**Figure 6.** Cyclic voltammograms: (top) **3** in acetonitrile (ca. 3 mM) containing electrolyte; (bottom) **3** in a 50/50 acetonitrile/ water mixture (ca. 2 mM, bold line) and background (dashed line). The scan rate was 100 mV/s.

50 water/acetonitrile mix, the reversible oxidation peak centered at 0.9 V disappears entirely, consistent with displacement of all inner-sphere chloride for inner-sphere aqua ligands. Furthermore, at ca. 1.4 V, there is onset of a completely irreversible, catalytic oxidation process, indicative of conversion of bound water into dioxygen. The potential of this catalytic process is consistent with assignment of the ca. 1.5 V process for 3 in MeCN as irreversible oxidation of the acetonitrile-bound species. In the case of water ligation, a redox-leveling effect due to proton-coupled electron transfer processes is expected to result in nearly isoenergetic oxidation couples leading to catalytic water oxidation (i.e.,  $Ir^{III}$ -OH<sub>2</sub>/ $Ir^{IV}$ -OH,  $Ir^{IV}$ -OH/ $Ir^{V}$ =O).<sup>28,51</sup> Similar changes in voltammetric response are seen in the case of 2 in water/acetonitrile mixtures. In 50/50 acetonitrile/ water, 2 shows only a catalytic wave (Figure 7). In neither case are deposition or decomposition processes evident from the voltammetry. This suggests that ligand loss does not occur under these conditions, since loss of ligand to form a fragment such as [Cp\*Ir(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> would lead to alternative catalytic processes that we have reported elsewhere.<sup>47</sup>

**EPR Observation of Iridium**(IV) **Species.** The electrochemical results shown above imply that the iridium(IV) species

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**Figure 7.** Cyclic voltammograms: (top) **2** in acetonitrile (ca. 3 mM) containing electrolyte; (bottom) **2** in a 50/50 acetonitrile/ water mixture (ca. 3 mM). The scan rate was 100 mV/s.

obtained upon oxidation of 3 is stable at room temperature, but on a limited time scale. Due to this limited stability, a bulk electrolysis experiment to stoichiometrically prepare the iridium(IV) species seemed unlikely to succeed. Thus, we turned to the well-known chemical oxidant  $[Ru^{III}(bpy)_3]^{3+}$  for rapid preparation of the oxidation product. [Ru<sup>III</sup>(bpy)<sub>3</sub>]<sup>3+</sup> has a standard redox potential, E°, of 1.25 V vs NHE in MeCN, depending on the exact conditions.<sup>52</sup> Thus, it is poised to afford the product of the observed quasi-reversible electrochemical wave which occurs at 0.9 V while not subsequently oxidizing the complex to the product of the irreversible feature observed at 1.4 V. Also, oxidation with  $[Ru^{III}(bpy)_3]^{3+}$  should oxidize the iridium complex quickly, affording time to rapidly freeze the sample before disproportionation or decomposition of the oxidized iridium species. The sample could then be analyzed by EPR spectroscopy.

 $[Ru(bpy)_3](PF_6)_3$  was prepared from  $[Ru(bpy)_3](Cl)_2$  by oxidation with PbO<sub>2</sub> and precipitation from acid solution by KPF<sub>6</sub>, according to Drago and co-workers,<sup>53</sup> and stored under vacuum in a freezer to minimize decomposition. In a glovebox under a nitrogen atmosphere, **3** and  $[Ru(bpy)_3]$ 



**Figure 8.** X-band EPR spectra: (solid line) **3** oxidized by 0.75 equiv of  $[Ru^{III}(bpy)_3]^{3+}$ ; (dashed line)  $[Ru^{III}(bpy)_3]^{3+}$  control.

 $(PF_6)_3$  were each dissolved in a 1/1 acetonitrile/toluene solvent mixture (this mixture forms a glass and is suitable for EPR studies). Solutions were cold when mixed, having been chilled in the glovebox cold well by liquid nitrogen; the final solution was removed at low temperature from the glovebox and immediately frozen in liquid nitrogen for EPR analysis. The results of the EPR experiments are summarized in Figure 8.

The oxidized iridium complex (solid line in Figure 8) gives a rhombic signal with a center crossing point at g = 2.17. Initially, **3** is a low-spin iridium(III) complex with a d<sup>6</sup> configuration and S = 0. The ruthenium(III) oxidant is lowspin d<sup>5</sup>,  $S = \frac{1}{2}$ , and gives the EPR signal shown as the dashed line in Figure 8. This spectrum (axial with  $g_{\parallel}$  omitted for clarity) obtained for [Ru<sup>III</sup>(bpy)<sub>3</sub>]<sup>3+</sup> is consistent with literature data.<sup>53</sup> Upon treatment of **3** with [Ru<sup>III</sup>(bpy)<sub>3</sub>]<sup>3+</sup>, the resulting iridium-(IV) complex is apparently low-spin d<sup>5</sup> with  $S = \frac{1}{2}$ . Upon reduction by the iridium, the ruthenium oxidant is EPR silent with S = 0. Thus, the spectrum in Figure 8 is consistent with generation of [Cp\*Ir<sup>IV</sup>(NHC)CI]<sup>+</sup>.

Few examples of  $Cp^*Ir^{IV}$  complexes have been observed by EPR, and most of those previously described bear at least two identical strong donor ligands, such as methyl groups.<sup>54–56</sup> In this case, we have prepared a Cp\*Ir complex bearing a chelating, nonsymmetrical NHC ligand. In the previously characterized Cp\*Ir<sup>IV</sup> species, the presence of identical ligands induces higher symmetry, as is evident in their axial EPR spectra. We know of no prior case in which a Cp\*Ir<sup>IV</sup> species gives rise to a spectrum with rhombic symmetry, which is consistent with the presence of three different ligands in our Cp\*Ir<sup>IV</sup> species. Spin–orbit coupling between the different energy levels leads to well-resolved  $g_x$ ,

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Figure 9. Calculated SOMO for  $[Cp*Ir^{IV}(NHC)Cl]^+$  (left) and drawing rotated clockwise 90° about the vertical axis (right). Hydrogen atoms are omitted for clarity.

 $g_y$ , and  $g_z$  components (2.53, 2.17, and 1.85, respectively). No hyperfine coupling is observed, all iridium isotopes having  $I = {}^{3}/_{2}$ , consistent with little s character in the SOMO. Near g = 2, a very weak signal corresponding to an organic radical is visible, possibly arising from partial decomposition of the ruthenium oxidant during preparation and storage. DFT analysis of the iridium(IV) SOMO that would arise from one-electron oxidation of complex **3** further supports the assignment of the observed EPR signal to iridium(IV). The SOMO (Figure 9) shows a largely metal-centered orbital with little s character. This is consistent with the rhombic spectrum observed experimentally.

After the initial EPR spectrum was obtained, the sample was warmed to room temperature under argon. After 3 min, the sample was refrozen and another EPR spectrum recorded. The newly acquired spectrum showed the same features as previously observed with essentially no loss in intensity, indicating that on a minute time scale, the iridium-(IV) species is stable under an inert atmosphere. However, repeating the same procedure and allowing the sample to incubate at room temperature for 30 min caused the signal to disappear; no other peaks are seen, and so any decomposition products are not EPR active. This result is consistent with the electrochemistry results, which suggest limited stability of the iridium(IV) species at room temperature.

A sample was similarly prepared for <sup>1</sup>H NMR analysis containing a 1/1 mixture of complex 3 and  $[Ru(bpy)_3]^{3+}$ . Room-temperature spectra with a scan time of 3 s showed diamagnetic peaks consistent with the presence of [Ru<sup>II</sup>  $(bpy)_3]^{2+}$ , as verified by measurements on a pure sample. Weak signals in the aromatic region indicate the presence of an iridium(III) or a diamagnetic Ir(V) species. However, these peaks are not well resolved and are overwhelmed by the signal from  $[Ru^{II}(bpy)_3]^{2+}$  (Figure 10). Given that there are essentially no substrates present in the reaction mixture other than the bound chloride that could undergo oxidization, it is possible that the iridium(IV) species either directly oxidizes chloride or disproportionates to iridium(III) and iridium(V) before reaction or decomposition. This would give a wide array of potential iridium-containing products and could explain the poorly resolved spectrum.

In an attempt to observe iridium(IV) species directly by <sup>1</sup>H NMR, paramagnetic <sup>1</sup>H NMR spectra were recorded at -35 °C. Unfortunately, even with a scan time of 30 ms, no new signal was observed and the resulting NMR spectra only contain the previously described diamagnetic signals. The paramagnetic iridium(IV) species visible by EPR presumably relaxes too rapidly to be observed by NMR. It is noteworthy that no signal is observed that can be attributed to  $[Ru^{III}(bpy)_3]^{3+}$  (Figure 10). The spectrum obtained of



**Figure 10.** 500 MHz <sup>1</sup>H NMR spectra in 1/1 toluene/acetonitrile: (A) diamagnetic spectrum of 1/1  $3/[Ru^{III}(bpy)_3]^{3+}$ ,  $\delta 6.0-10.0$  ppm; (B) paramagnetic spectrum of 1/1  $3/[Ru^{III}(bpy)_3]^{3+}$ ,  $\delta -50$  to +50 ppm; (C) paramagnetic spectrum of  $[Ru^{III}(bpy)_3]^{3+}$ ,  $\delta -50$  to +50 ppm. Peaks are referenced to toluene solvent.

pure  $[Ru^{III}(bpy)_3]^{3+}$  under identical conditions matches the literature data, thus validating the parameters used for

observing paramagnetic species.<sup>53</sup> Furthermore, lack of a ruthenium(III) signal in the mixed sample indicates total reduction to ruthenium(II), confirming the data observed by EPR spectroscopy and further affirming that the observed EPR signal must arise from [Cp\*Ir<sup>IV</sup>(NHC)Cl]<sup>+</sup>.

An analogous EPR experiment was run on catalyst 1. A small signal, barely distinguishable from the noise, was observed possibly due to an analogous iridium(IV) species. As seen for complex 3, consumption of  $[Ru^{III}(bpy)_3]^{3+}$  was complete, as observed by EPR. Consistent with the irreversible oxidation observed in electrochemical studies (vide supra), the iridium(IV) species generated upon one-electron oxidation of 1 leads to rapid reaction, possibly via oxidation of chloride. It is thus evident that the NHC ligand in complex 3 imparts greater stability to the high-valent intermediate  $[Cp^*Ir^{IV}(NHC)CI]^+$  than the much weaker donor ppy ligand present in complex 1.

This conclusion is also consistent with the observed higher turnover frequency for 1 as compared to 3 for water oxidation. Both results indicate that a comparatively less stable, and more reactive, iridium(IV) species is obtained from oxidation of the active form of 1 in comparison to the active form of 3. While  $[Cp*Ir^{IV}(NHC)Cl]^+$  is likely not an active participant in the catalytic cycle for water oxidation, a reactive Ir(IV) species, as predicted by DFT,<sup>29</sup> is shown to be a plausible class of intermediate, as demonstrated by the observation of the analogous example studied here.

#### Conclusions

A newly synthesized Cp\*Ir compound, 3, bearing a cyclometalated N,N'-diphenylimidazolyl ligand, Cp\*Ir( $\kappa^2 C^2, C^2$ -NHC)(Cl), has been synthesized and fully characterized by spectroscopy and X-ray crystallography. This complex was shown to be analogous to the Cp\*Ir(ppy)Cl complex, 1, previously described by us as a catalyst precursor for water oxidation. The highly electron donating N-heterocyclic carbene ligand stabilizes a higher valent form of the compound, [Cp\*Ir<sup>IV</sup>(NHC)Cl]<sup>+</sup>, which can be prepared by electrochemical and chemical oxidation. This oxidized form of 3 can be observed using EPR spectroscopy and has rhombic symmetry. The existence of this transient species is consistent with a mechanism for water-oxidation catalysis involving a series of sequential, one-electron oxidations, as proposed previously for the related compounds 1 and 2. This work suggests that further tuning of the electronic properties of ligands on the Cp\*Ir scaffold may afford catalysts with useful reactivity and spectroscopic signatures.

#### **Experimental Section**

[Cp\*IrCl<sub>2</sub>]<sub>2</sub> and [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> were prepared according to literature procedures.<sup>53,57</sup> *N*,*N'*-Diphenylimidazolium chloride was synthesized from aniline, glyoxal, and paraformaldehyde using an adaptation of a known method.<sup>37</sup> CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN were dried on a Grubbs-type solvent purification system.<sup>58</sup> All other reagents and materials were commercially available and used without further purification. Diamagnetic NMR spectra were recorded at room temperature on a 400 or 500 MHz Bruker spectrometer and referenced to the residual solvent peak ( $\delta$  in

ppm, J in Hz). Paramagnetic NMR spectra were obtained on a 500 MHz Bruker spectrometer at -35 °C with a scan time of 30 ms. EPR spectra were recorded on an X-band Bruker ELEXSYS E500 spectrometer equipped with an Oxford ESR-900 cryostat. The nominal temperature for experiments was 8.5 K. The modulation amplitude was set to 2 G and the microwave frequency to 9.388 GHz. Experiments were recorded with a time constant of 41 ms. Elemental analysis was performed by Atlantic Microlabs Inc. (Norcross, GA).

Chloro(1,2,3,4,5-pentamethylcylopentadienyl)( $\kappa^2 C^2, C^2$ -1,3diphenylimidazol-2-vlidene)iridium(III) (3). In a Schlenk flask, 343 mg of imidazolium salt 4 (1.34 mmol, 2 equiv), 535 mg of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (0.67 mmol, 1 equiv), and 300 mg of KO<sup>t</sup>Bu (2.67 mmol, 4 equiv) were combined. Dry dichloromethane (25 mL) was then added, and the reaction mixture was stirred under nitrogen at room temperature for 12 h. The resulting orange solution was filtered through Celite and the solvent removed under reduced pressure. Analytically pure product was obtained using neutral alumina column chromatography with dichloromethane as the eluent. The product elutes as a yellow band with an R<sub>f</sub> value near zero and is isolated as a yellow powder. Crystals for X-ray analysis were obtained by vapor diffusion of pentane into dichloromethane. Isolated yield: 96 mg (10.9%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.42 (s, 15H), δ7.00 (m, 2H), 7.22 (m, 1H), 7.26 (d, J = 2.2, 1H), 7.45 (m, 1H), 7.54 (m, 3H), 7.69 (m, 1H), 7.97 (d, J = 7.6, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 9.18, 91.98, 110.75, 115.50, 122.30, 122.36, 126.08, 126.28, 128.44, 129.84, 137.82, 140.78, 143.93, 146.49, 164.60. Anal. Calcd for C<sub>25</sub>H<sub>27</sub>ClIrN<sub>2</sub>: C, 51.49; H, 4.67; N, 4.80. Found, C, 51.22; H, 4.55; N, 4.79.

**X-ray Diffraction Study of Compound 3.** Crystal samples were mounted in a polyimide MiTeGen loop with immersion oil. All measurements were made on a Rigaku SCXMini diffractometer with filtered Mo K $\alpha$  radiation at a temperature of 223 K. Two  $\omega$ scans consisting of 180 data frames each were collected. The data frames were processed and scaled using the Rigaku CrystalClear program.<sup>59</sup> The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.<sup>60</sup> The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. The final cycles of full-matrix least-squares refinement<sup>61</sup> on  $F^2$  were applied until convergence of unweighted and weighted factors of  $R = \sum_{i=1}^{i} ||F_{oi}| - |F_{ci}|/\sum_{i=1}^{i} |F_{oi}|$  and  $R_w =$  $\{\sum_{i=1}^{i} ||W(F_o^2 - F_c^2)^2]/\sum_{i=1}^{i} [W(F_o^2)^2]\}^{1/2}$ . Crystal data and experimental details are included in the Supporting Information.

Procedure for Sample Preparation for EPR and NMR Analysis. In a glovebox, 1.3 mg of 3 (0.0022 mmol) was dissolved in 500  $\mu$ L of 1:1  $d_3$ -MeCN/ $d_8$ -toluene. Separately, 1.6 mg of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> (0.0022 mmol) was dissolved in 500  $\mu$ L of  $d_3$ -MeCN/ $d_8$ -toluene. The solutions were combined in a cold well and removed from the glovebox at low temperature. Samples were frozen immediately upon removal from the glovebox. Thermal stability was examined by warming the frozen sample to room temperature under a constant flow of argon. Samples were kept at room temperature for 3 min before refreezing and analysis. Samples were then warmed to room temperature and held under argon for 30 min before refreezing for analysis.

**Electrochemical Studies.** Electrochemical measurements were made on a Princeton Applied Research Versastat 4-400 potentiostat/galvanostat using a standard three-electrode configuration. A basal plane graphite electrode (surface area 0.09 cm<sup>2</sup>) was used as the working electrode to reduce background oxidation. The electrode consisted of a brass cylinder, sheathed in a Teflon tube. At the tip of the brass, a two-part silver conducting epoxy (Alfa Aesar) was used to firmly attach the basal plane

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carbon electrode surface to the brass. Finally, the tip was sealed with the organic solvent resistant, electrically insulating, twopart epoxy Tra-bond 2151 (Emerson and Cuming, Canton, MA). Immediately prior to experiments, the working electrode was polished with 1  $\mu$ m alumina paste, washed with copious amounts of water, and allowed to dry completely. Then, the surface of the working electrode was resurfaced with tape to restore the gray, basal surface.

For nonaqueous electrochemical studies, a platinum wire was used as the counter electrode, and a silver wire was used as the pseudoreference electrode. Ferrocene was used as an external standard to calibrate the reference electrode versus NHE (Fc/Fc<sup>+</sup>: +0.690 V vs NHE in MeCN). Experiments were carried out in a dry acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate (Fluka, electrochemical grade) as the supporting electrolyte. For mixed solvent system studies, water was added to the acetonitrile electrolyte solutions in the indicated proportions.

**Kinetic Studies of Oxygen Evolution.** Measurements of the initial oxygen evolution rate were made with a YSI 5300A Biological Oxygen Monitor. Prior to the start of each set of experiments, the gas-permeable membrane was replaced to ensure a high-quality response. The electrode, secured in a Teflon tube, was inserted into a tight-fitting water-jacketed glass vessel. The system was kept at a constant temperature of 25 °C. In a typical experiment, a freshly prepared cerium(IV)

solution in Milli-Q water (5 mL, 78 mM; pH 0.89) was allowed to equilibrate with stirring for 7 min. Data collection over 5–7 min showed equilibration of the system, and when a steady baseline was achieved, 10  $\mu$ L of catalyst solution was injected. Oxygen evolution commenced immediately and typically exceeded the maximum value for the system within 10 min of injection.

**Computational Details.** Density functional theory calculations were carried out using Gaussian 09 Revision A.02.<sup>62</sup> Calculations were performed using the B3LYP functional and the LANL2DZ basis set for iridium and the 6-31G\*\* basis set for all other atoms. The LANL2DZ pseudopotential was used for iridium. Initial geometries were obtained using the coordinates from X-ray structures, and all optimized structures were verified using frequency calculations to check that they did not contain any imaginary frequencies.

Acknowledgment. This material is based in part upon work supported as part of the Argonne-Northwestern Solar Energy Research (ANSER) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-PS02-08ER15944 (G.W.B., R.H.C., J.D.B., and T.P.B.) and the Center for Catalytic Hydrocarbon Functionalization, CCHF under Award Number DE-SC0001298 (R.H.C.) and a catalysis grant from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through grant DE-FG02-84ER13297 (N.D.S.). J.D.B. and T.P.B. thank Gözde Ulas and Ravi Pokhrel for assistance in collecting the EPR spectra. T.P.B. also thanks Meng Zhou and Graham Dobereiner for insightful discussions.

**Supporting Information Available:** Text, tables, figures, and a CIF file giving NMR spectra, supplemental electrochemistry, oxygen evolution data, *xyz* coordinates for calculated structures, and crystallographic information for **3**. This material is available free of charge via the Internet at http://pubs. acs.org.

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