

Olefin Oxygenation by Water on an Iridium Center

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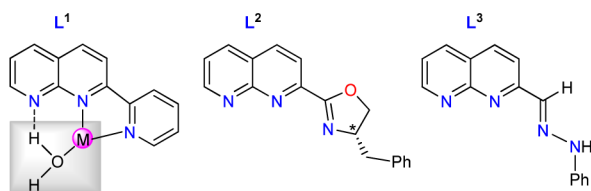
S Supporting Information

ABSTRACT: Oxygenation of 1,5-cyclooctadiene (COD) is achieved on an iridium center using water as a reagent. A hydrogen-bonding interaction with an unbound nitrogen atom of the naphthyridine-based ligand architecture promotes nucleophilic attack of water to the metal-bound COD. Irida-oxetane and oxo-irida-allyl compounds are isolated, products which are normally accessed from reactions with H₂O₂ or O₂. DFT studies support a ligand-assisted water activation mechanism.

The use of water as substrate in metal-catalyzed organic transformations has been limited. A few examples are anti-Markovnikov hydration of alkynes,¹ nitrile hydration,² conversion of cyclic amines to lactams,³ water–gas shift reaction,⁴ and aldehyde–water shift reaction.⁵ Grotjahn et al. reported a variety of bifunctional metal catalysts for alkyne hydration, where pendant basic groups attached to the ligands serve as the internal base for water activation.⁶ Photocatalytic water oxidation in the presence of organometallic complexes is a fundamentally important reaction.⁷ Milstein et al. demonstrated bifunctional water splitting by a dearomatized [Ru–PNN] pincer complex and subsequent light-induced formation of O₂ in a stoichiometric manner.⁸ The water addition proceeds via initial metal coordination followed by proton migration to the cooperating ligand.⁹ Thus, the metal–ligand interplay provides an alternate pathway for water activation that is kinetically more accessible than the direct oxidative addition of water to the metal.¹⁰

The addition of water to a metal is associated with an entropic penalty.¹¹ A hydrogen-bonding interaction in the secondary coordination sphere may compensate for this entropic loss. The 1,8-naphthyridine ligands L¹–L³, shown in Scheme 1, offer the prospect for simultaneous metal coordination and hydrogen-

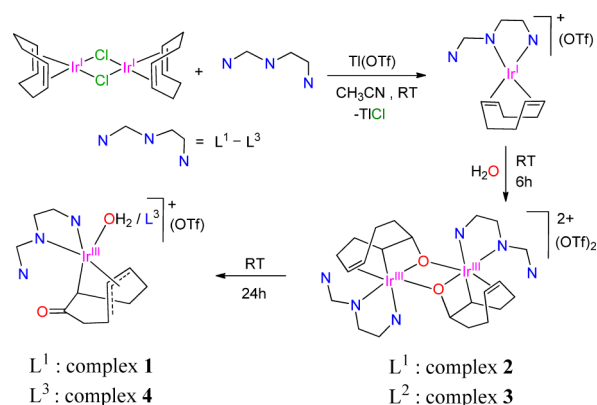
Scheme 1. Naphthyridine-Based Ligands Employed in This Work^a



^aSimultaneous metal coordination and H-bonding interaction of water with ligand scaffold is shown for L¹.

bond interaction with the ligand architecture. Such interactions promote nucleophilic attack of water to a metal-bound substrate and thus favor hydration reactions.^{2a} Water reactions have been largely carried out with Pd, Ru, and Rh, but a parallel chemistry with iridium is not known. Herein we describe the first case of olefin oxygenation by water on an iridium center. A prolonged reaction (24 h) of Ir^I(COD) (where COD = 1,5-cyclooctadiene) with L¹ in the presence of water affords a 5-oxo-6-irida(1,2,3)-allyl compound, **1** (Scheme 2). When the same reaction is

Scheme 2. Syntheses of 2-Irida-oxetane Dimers and 5-Oxo-6-irida(1,2,3)-allyl Compounds in the Water Reactions



performed for 6 h, a 2-irida-oxetane intermediate, **2**, is isolated as a dimer, which readily rearranges to **1** in solution. Use of the L² ligand, with a bulky benzyl substituent at the position *ortho* to the coordinating nitrogen in the oxazoline ring, gives only the oxetane analogue **3**, whereas the L³ ligand, bearing a flexible aniliny group, affords an oxo-irida-allyl analogue, **4**, but the corresponding oxetane compound could not be isolated. Experiments with H₂O¹⁸ unambiguously establish that the source of oxygen in the oxygenated compounds is water and not adventitious oxygen. Density functional theory (DFT) calculations support a ligand-assisted bifunctional water activation pathway as a superior alternative to oxidative addition.

Ir(I) complexes containing COD generally show limited reactivity with molecular O₂ and moisture. Removal of bridging chlorides in [IrCl(COD)]₂ by Ti(OTf) in acetonitrile and subsequent treatment with L¹ afforded a stable complex, [Ir(COD)(L¹)](OTf) (Scheme 2).¹² Subsequent reaction with

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a 10-fold excess of degassed, deionized H₂O at room temperature for 24 h afforded the 5-oxo-6-irida(1,2,3)-allyl compound **1**. The molecular structure of **1**, depicted in Figure 1, shows η^1, η^3 -

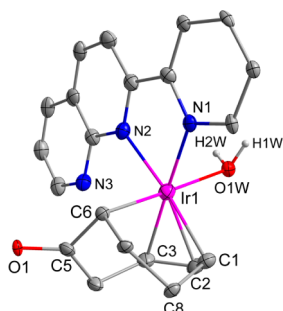


Figure 1. Molecular structure of the cationic unit $[\text{Ir}(\text{C}_8\text{H}_{10}\text{O})(\text{L}^1)(\text{H}_2\text{O})]$ in **1**.

coordination of COD. The C₅ carbon is oxidized to carbonyl, with a C=O distance of 1.217(1) Å. The naphthyridine ligand chelates the metal and is disposed *trans* to the allyl unit (Ir–C = 2.145(8), 2.105(8), and 2.154(8) Å). The Ir–C(alkyl) distance is 2.056(7) Å. Coordination by a water molecule completes octahedral geometry around the metal.

The ¹H NMR spectrum of **1** (Supporting Information (SI), Figure S4) in deuterated acetonitrile is broadly divided into three regions. Nine aromatic protons of the ligand appear in the range between $\delta = 7.77$ and 9.69 ppm. Six methylene protons and one methyne proton of COD appear in the range of $\delta = 1.05$ –2.58 ppm, while three allylic protons show signals farther upfield ($\delta = 4.64$ –5.40 ppm). Signal attributable to metal-coordinated water was not observed, indicating that CD₃CN possibly displaces the water at the metal center. The ¹³C NMR spectrum showed a characteristic signal at $\delta = 220.5$ ppm, assigned to the carbonyl carbon. A strong band at 1666 cm⁻¹ in the IR spectrum supports the presence of the carbonyl group. ESI-MS at $m/z = 522.098$ is attributed to $[\text{M}-\text{H}_2\text{O}-\text{OTf}]^+$ (SI, Figure S9a).

With the intent to isolate a possible intermediate, the reaction was quenched after 6 h, and an irida^{III}-oxetane dimer, **2**, was obtained. Another oxetane analogue, **3**, was also isolated using L². Complex **2** has a crystallographically imposed inversion center, and only half of the molecule appears in the asymmetric unit, whereas for complex **3**, bearing chiral ligand L², the full dimer appears in the asymmetric unit. Molecular structures (Figures 2 and 3) confirm four-membered metalla-oxetane ring formation with Ir–O distances of 2.085(4) Å for **2** and 2.087(6) and 2.098(5) Å for **3**. One chelate-bound ligand, the olefinic bond of COD, and the metalla-oxetane ring around Ir constitute each

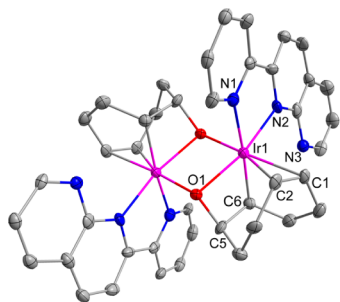


Figure 2. Molecular structure of the dicationic unit $[\text{Ir}(\text{C}_8\text{H}_{12}\text{O})(\text{L}^1)_2]$ in **2**.

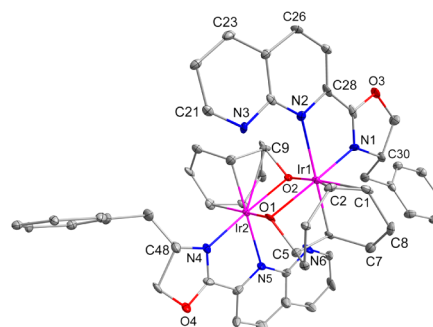


Figure 3. Molecular structure of the dicationic unit $[\text{Ir}_2(\text{C}_8\text{H}_{12}\text{O})_2(\text{L}^2)_2]$ in **3**.

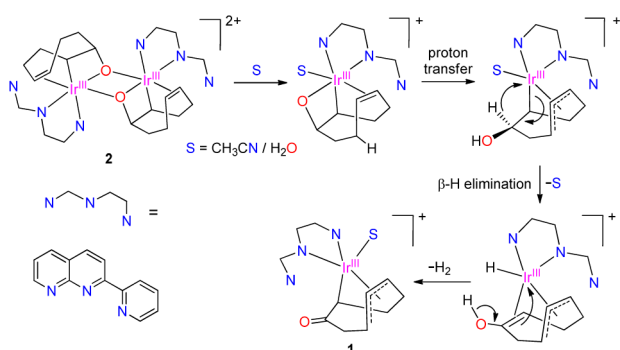
monomer. Oxygen coordination from the metalla-oxetane ring of one monomer to the other completes the sixth coordination site of Ir and forms the dimeric structures (Ir–O = 2.137(5) Å for **2**; 2.105(7) and 2.095(8) Å for **3**).

Both complexes were also characterized by ¹H NMR spectroscopy (SI, Figures S6 and S7). For complex **2**, four olefinic CH signals and two Ir–O–CH signals of COD appear in the range between $\delta = 5.07$ and 5.96 ppm, while complex **3** shows additional oxazoline ring protons and benzylic protons in this region, appearing together in the range between $\delta = 2.90$ and 5.85 ppm. The ESI-MS of **2** resembles that of **1**, suggesting a rapid conversion under mass spectroscopy conditions, whereas **3** shows a mass peak at m/z 1361.293 ($z = 1$) corresponding to $[\text{M}-\text{OTf}]^+$ (SI, Figure S9c).

The intermediacy of metalla-oxetanes has been proposed in catalytic homogeneous and heterogeneous olefin oxygenation processes.¹³ A handful of metalla-oxetane and hydroxy-metalla-allyl compounds have been structurally characterized which are accessed via the reaction of metal-bound COD with H₂O₂ or molecular oxygen (for selected examples, see SI, Scheme S1).¹⁴ Klemperer et al. reported oxidation of $[\text{Ir}(\text{P}_3\text{O}_6)(\text{COD})]^{2-}$ by molecular oxygen to give a four-membered 2-irida-oxetane intermediate, which upon thermal treatment rearranged to a more stable 5-hydroxy-6-irida(1,2,3)-allyl complex.¹⁵ Following a similar reaction between $[\text{Rh}(\text{PhN}_3\text{Ph})(\text{COD})]$ and molecular oxygen, Tejel et al. were able to isolate 2-rhoda-oxetane as a dimer, which after rearrangement gave a polymeric hydroxy-allyl complex in solution.¹⁶ The formation and reactivity of 3-rhoda-1,2-dioxolane and 2-rhoda-oxetane were extensively studied by Gal et al.¹⁷ The simplest 2-rhoda-oxetane was obtained by the reaction of Rh(I)-ethylene complex with H₂O₂.^{17a}

COD oxygenation with water, assisted by naphthyridine ligands, appears to be a reliable reaction. The use of L³ following a protocol identical to the synthesis of **1** afforded an oxo-irida-allyl complex, **4**, which was characterized by X-ray crystallography (see SI, Figure S17) as well as other spectroscopic techniques. The nature of products clearly depends on the type of ligands used. Both irida-oxetane **2** and oxo-irida-allyl **1** were isolated for L¹. Irida-oxetane **3** and oxo-irida-allyl compound **4** were obtained exclusively from L² and L³, respectively. Compound **2**, which was isolated by careful manipulation of the reaction conditions, further converted to **1** over time, with the evolution of dihydrogen gas. The evolution of H₂ was confirmed by GC.¹⁸ It is therefore prudent to assume that the formation of the oxo-irida-allyl compound proceeds through the metalla-oxetane intermediate. A tentative mechanism is proposed in Scheme 3. In coordinating solvent, the metalla-oxetane dimer dissociates into two monomers.¹⁹ Allyl proton transfer to the oxetane

Scheme 3. Conversion of Metalla-oxetane to Oxo-metalla-allyl Complex



oxygen gives the hydroxy-metalla-allyl complex,^{16,20} which undergoes β -hydride elimination followed by dehydrogenation to afford the oxo-metalla-allyl compound. The proposed mechanism explains why metalla-oxetane product is obtained when allylic proton is absent.^{17a} Furthermore, the use of a tris-chelate capping ligand blocks the *cis* position necessary for β -hydride elimination, causing the reaction to cease at the hydroxy-metalla-allyl stage.¹⁵ In the present study, the L² ligand, possessing a bulky benzyl substituent, impedes structural reorganization of the COD unit, preventing allyl proton transfer and subsequent β -hydride elimination. The final product is thus the metalla-oxetane product **3**, despite the presence of the COD allyl proton. Neither prolonged reaction time nor heating in acetonitrile converts **3** to the corresponding oxo analogue. For L¹ and L³, where no such steric hindrance arises, the corresponding oxo-metalla-allyl complexes **1** and **4**, respectively, are obtained.

A strict anaerobic condition was maintained to exclude the possibility of dioxygen in the reaction mixture. Nonetheless, to confirm the source of oxygen, synthesis of **1** was carried out with H₂O¹⁸. The product was subjected to high-resolution mass spectrometry and IR analysis. On the basis of the masses and isotopic distribution patterns, the signals at $m/z = 524.123$, 565.149, and 585.172 are assigned to [Ir(L¹)(C₈H₁₀O¹⁸)]⁺, [Ir(L¹)(C₈H₁₀O¹⁸)(CH₃CN)]⁺, and [Ir(L¹)(C₈H₁₀O¹⁸)(CH₃CN)(H₂O¹⁸)]⁺, respectively (Figure 4), which reveal a

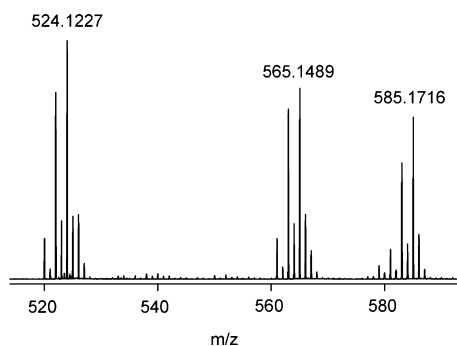
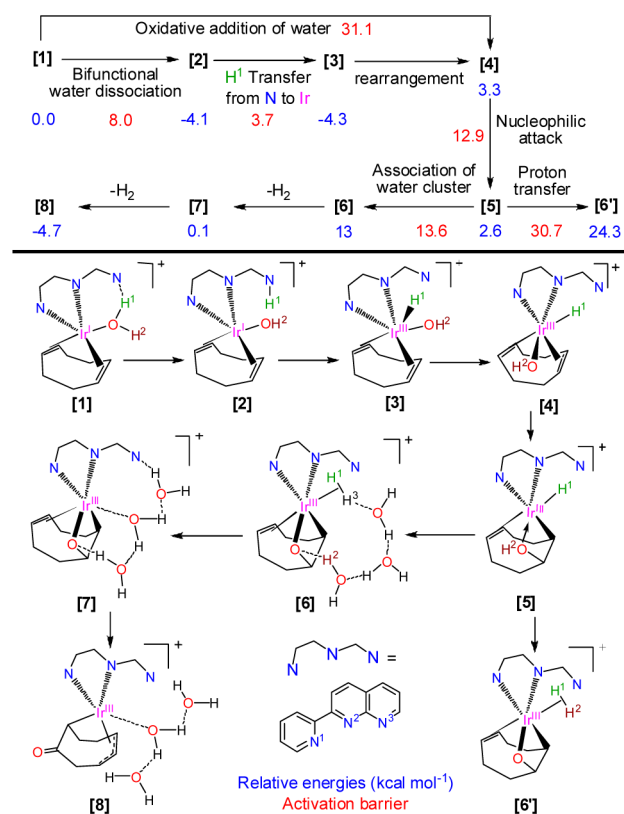


Figure 4. ESI-MS spectrum of O¹⁸ analogue of **1**.

two-unit increase of mass for the first two cases and a four-unit increase of mass for the last case, compared to the O¹⁶ analogue of **1**. The CO stretching band at 1666 cm⁻¹ for complex **1** shifted to the lower energy region at 1645 cm⁻¹, a shift of 21 cm⁻¹, which is attributed to isotopic replacement (SI, Figure S12). These studies clearly show O¹⁸ incorporation in the final product, the source of which is H₂O¹⁸.

The free nitrogen present in the ligand architecture plays a crucial role for heterolytic water dissociation and the subsequent oxygenation process.^{2a} Under identical reaction condition, the bipyridine (bpy) analogue [Ir(bpy)(COD)](OTf) (SI, Figure S18), which lacks a free nitrogen, does not react with water to give the COD-oxygenated product. A reaction pathway for metalla-oxetane formation supported by DFT calculations is given in Scheme 4. Optimized structures of the intermediates and

Scheme 4. Proposed Reaction Pathway for 2-Irida-oxetane Formation by H₂O

the transition states are collected in SI, Figure S19, and a computed energy profile in acetonitrile is given in SI, Figure S20. A water adduct, [Ir(pyNP)(COD)(H₂O)]⁺ [**1**], is calculated on the potential energy surface where water is coordinated to the metal (Ir–O = 2.109 Å) and simultaneously hydrogen-bonded to the free nitrogen, N³, of the naphthyridine unit (N³...H¹ = 1.982 Å). Migration of the water proton (H¹) to the naphthyridine nitrogen affords a metal hydroxy species, [**2**] (Ir–O = 2.051 Å, N³–H¹ = 1.038 Å). This process is exothermic by –4.1 kcal/mol and has a small activation energy barrier (ΔE_a) of 8.0 kcal/mol. Subsequent proton shift from the naphthyridine to the metal center leads to an Ir^{III}–hydride intermediate, [**3**], with Ir–H/OH distances 1.546/2.049 Å, respectively. Formation of [**3**] is a slightly downhill process by 0.2 kcal/mol, and the ΔE_a is 3.7 kcal/mol. An alternative proton shift at a later stage after the hydroxy attack to COD is, however, an energetically uphill process (SI, Scheme S2 and Figure S21). The next logical step is nucleophilic attack of the hydroxide to one of the COD double bonds. The hydroxide in [**3**] is not suitably disposed for such an attack, but isomer [**4**], conversely, is. The rearrangement of [**3**]→[**4**] can be envisioned as a multi-step process involving rearrangement of hydroxide and hydride around the metal center, an uphill process by 7.6 kcal/mol. Direct oxidative addition of H₂O at the metal to

yield the species [4] is an energetically difficult process with very high ΔE_a (31.1 kcal/mol). Ligand-assisted water dissociation is thus computed to be a favorable process compared to direct oxidative addition.

Nucleophilic attack of hydroxy to the metal-bound olefinic double bond leads to the intermediate [5], featuring a four-membered metallacycle. A normal-mode analysis of TS [4-5] confirms this transformation. The ΔE_a and relative reaction energies are 12.9 and -0.7 kcal/mol, respectively. A similar reaction with D_2O did not afford deuterium-incorporated product, as evidenced from the ^{13}C NMR spectrum (SI, Figure S5) and ESI-MS, discounting the possibility of a competitive hydride migration to the olefinic double bond.

For the oxetane ring formation, a proton shift from O–H to the metal is expected, which would essentially lead to an Ir-dihydrogen complex, [6']. The transformation [5]→[6'] is found to be a highly endothermic process and demands a very high $\Delta E_a = 30.7$ kcal/mol. Since the reaction includes water, a model was designed to calculate the same proton shift step via water cluster. Proton shuttling via the water cluster is anticipated to release the strain of the four-membered transition structure [5-6'] and hence lower the activation barrier for [5]→[6] to 13.6 kcal/mol. The pertinent TS structure [5-6] includes three water molecules. The resultant product [6] is a dihydrogen complex ($Ir-H^1/H^3 = 1.782/1.754$ Å, $H^1-H^3 = 0.841$ Å). Removal of H_2 from [6] is an exothermic process and leads to the oxetane monomer [7]. Overall, the transformation of [1]→[7] is merely an isothermal process in acetonitrile. Further removal of H_2 from [7] is an exothermic process and yields the stable oxo complex [8]. The transformation [7]→[8] is a complex process, as proposed in Scheme 3, and not explicitly studied here by DFT.

In conclusion, we present here the first report of COD oxygenation by water on an iridium center aided by an unbound nitrogen atom on the naphthyridine ligand. Metalla-oxetane and oxo-metalla-allyl compounds, which are potential intermediates in the catalytic oxygenation process, are isolated, with dihydrogen as the side product. The steric bulk and rigidity of the ligands dictate the nature of the products. A ligand-assisted water activation pathway is proposed, supported by DFT studies. The challenge remains to make this reaction catalytically viable.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, supporting schemes and figures, and crystallographic table. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03055.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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- (18) Calculated amounts of [IrCl(COD)]₂, TlOTf, and L¹ were taken in 5 mL of acetonitrile in a sealed reaction vessel. A 10-fold excess of degassed, deionized water was added, and the reaction mixture was allowed to stir at room temperature. The evolved gas was injected into the GC instrument. H₂ was identified by comparison with the retention time of the authentic sample.
- (19) ESI-MS of 3 in acetonitrile reveals a major signal (100%) for [Ir(C₈H₈O)(L²)⁺ along with a minor signal (<2%) for the dimer, suggesting dissociation in solution (see SI, Figure S11).
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