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O_2 Generation

Water Oxidation Catalyzed by Strong Carbene-Type Donor-Ligand Complexes of Iridium**

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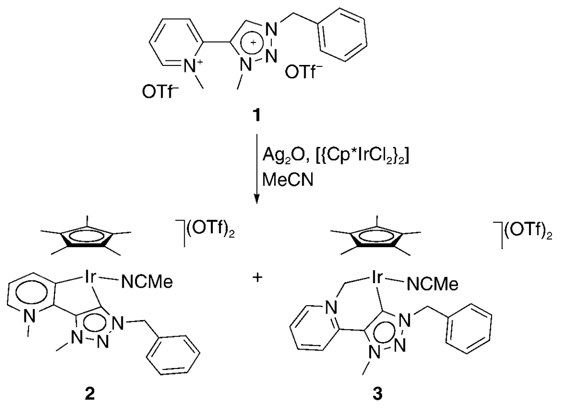
In memory of Fiona O'Reilly

Production of energy from renewable sources has recently become a pressing challenge in energy-related research.[1] The splitting of water into oxygen and hydrogen, inspired by nature's use of water and sunlight as environmentally abundant feedstocks, constitutes a particularly attractive approach towards addressing this issue. In nature, photosynthetic water fixation and splitting is a delicately balanced process, overcoming the energetic barrier of O–H bond cleavage and O–O bond formation by a stunning reaction cascade.[2] The complexity of the photosynthetic machinery requires alternative approaches for artificial photosynthesis,[3] especially for the water-oxidation sequence.[4] High redox-flexibility of the active center constitutes a key element in the design of synthetic complexes for water oxidation, since the formation of O_2 from H_2O requires the transfer of four electrons. Apart from a number of heterogeneous systems,[5] ruthenium complexes, suggested to be oxidizes from Ru^{II} to Ru^{VI} have been successfully developed for the catalytic splitting of water.[6] Ruthenium centers in bi- and tetrametallic complexes were thought to work synergistically and hence require only oxidation to Ru^{IV} and Ru^{III}, respectively, to provide the four electrons for O_2 generation.[7] Complementary to these approaches, bis(cyclometalated) iridium(III) complexes[8] and cobalt-based tetrametallic systems[9] were shown to be active in water oxidation. The photochemical properties of these complexes allowed light to be employed to induce charge separation and subsequent water oxidation, thus mimicking the photosynthetic system very closely. Most recently, cyclometalated iridium(III) cyclopentadienyl complexes were shown to exhibit excellent activity in electrochemically induced water oxidation.[10]

Owing to the multistep redox processes involved in water oxidation, we considered abnormally bound N-heterocyclic carbenes to be advantageous spectator ligands. Abnormal carbenes, that is, formally neutral carbenes that lack a neutral resonance structure, have large contributions from zwitterionic resonance forms,[11] which may assist in stabilizing different metal oxidation states when coordinated to an appropriate transition metal. In addition, the ligands may serve as a transient reservoir of both positive and negative charge, thus providing synergistic effects similar to those observed in bi- and multimetallic complexes.[7] Based on these rationales, combined with the synthetic versatility of triazoles as potential carbene precursors,[12] we concentrated our initial efforts on the metalation of pyridinium-functionalized triazolium salt **1** (Scheme 1). This salt is readily available through copper-catalyzed [2+3] cycloaddition ("click chemistry")[13] starting from commercially available 2-ethynylpyridine and benzylazide generated from NaN_3 and BnBr, and subsequent methylation with MeOTf (OTf = trifluoromethylsulfonate). Metalation with $[\{Cp^*IrCl_2\}_2]$ ($Cp^* = C_5Me_5$) induced double C–H bond activation to give the C,C-bidentate complexes **2** and **3** (Scheme 1).[14] Complex **2** comprises two different abnormally bound N-heterocyclic carbene ligands, that is, a triazolylidene and a 3-pyridylidene, while complex **3** features a rare[15] ylide bonding mode of the pyridinium ligand precursor, along with the abnormal triazolylidene.

Complex **2** could be separated from the reaction mixture by virtue of its insolubility in CH_2Cl_2. The CH_2Cl_2-soluble fraction comprised several species containing a Cp*Ir fragment, as evidenced by the various singlets in the ^1H NMR



Scheme 1. Synthesis of complexes **2** and **3**.

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spectrum around $\delta = 1.9$ ppm. Upon heating this mixture under vacuum, complex **3** formed in moderate yield. Notably, complex **2** did not undergo a thermally induced isomerization to yield complex **3** under identical conditions, but instead decomposed. Hence the pyridylidene bonding mode in **2** is not an intermediate on the route to the ylide complex **3**. More likely, complexes **2** and **3** share a common, monodentate triazolylidene iridium intermediate, which may then undergo C(sp^2)-H or C(sp^3)–H bond activation and cyclometalation.[16]

Support for such an intermediate was obtained by NMR spectroscopy of reactions at room temperature, revealing monodentate complexation of the triazolylidene moiety to the iridium center, but no C–H bond activation of the pyridinium fragment. This model is in agreement with the propensity of triazolium salts to form silver carbene complexes, while similar complexes with pyridylidene compounds have not been reported to date.[12,17] The exocyclic C–H bond activation observed in our case for the N-CH_3 group to afford the ylide complex **3** is unprecedented in pyridinium chemistry, even though it is the classic pathway when pyridinium salts react with a strong base.[18] Related ylide complexes were prepared previously by trapping unstable methylidene complexes M=CH_2 with pyridine.[15] Competitive C(sp^2)-H and C(sp^3)-C-H bond activation was also observed for imidazolium salts alkylated in the 2-position.[19] Our preliminary investigations have shown that the product ratio is strongly affected by steric and electronic effects of the side-chain of the triazolium group. Thus, appropriate substitution of the triazolium-bound benzyl group allows the activation to be directed exclusively towards the C(sp^2)–H bond (formation of analogues of **2**) or to the predominant activation of the N-bound methyl group. Such bond activation processes may also be relevant to recently observed N–C bond cleavage in imidazolylidene chemistry.[20]

Complexes **2** and **3** were fully characterized. In solution, rotation about the N–C_{benzyl} bond is hindered, as indicated by the sharp AB doublet observed for the NCH_2 protons in the ^{1}H NMR spectrum ($^2J_{HH} = 15$ Hz). Similarly, the signals for the methylene protons of the iridium-bound carbon in complex **3** split into an AB doublet ($\delta_H = 5.00$ and 4.99 ppm, $^2J_{HH} = 10.4$ Hz). The signal of the metal-bound carbon of the triazolylidene ligand was observed at $\delta_C = 154.9$ and 147.0 ppm for **2** and **3**, respectively, and the signal for the methylene group coordinating to the iridium center appeared at $\delta_C = 36.6$ ppm.

Further confirmation of the structural assignment in solution was obtained from single-crystal X-ray diffraction analysis.[14] The molecular structures of complexes **2** and **3** show the expected piano-stool geometry (Figure 1), with a five- and a six-membered metallacycle, respectively. The larger ring size in **3** paired with the sp^3-hybridization of the metal-bound carbon and the ensuing longer iridium–carbon bond (2.115(3) Å in **3**, 2.060(3) Å in **2**) results in an increased chelate bite angle of 81.0(1)° in **3** versus 76.4(1)° in **2** (Table 1).[21]

Both complexes are soluble in water. In the presence of $(NH_4)_2[Ce(NO_3)_6]$ (CAN), immediate gas formation was observed, indicating catalytic activity for complexes **2** and **3** toward water oxidation. Further investigations using quantitative analyses revealed appreciable catalytic O_2 production from water (Figure 2, top). Complexes **2** and **3** were both significantly more active catalysts than the benchmark iridium complex $[Ir(ppy)_2(OH_2)_2]OTf$ (Hppy = 2-phenylpyridine).[8] When using a 900:1 Ce^{IV}/catalyst ratio, turnover numbers (TON) were limited by the availability of sacrificial oxidant. Essentially quantitative conversions were reached in less than 2 h. While initial turnover frequencies (TOF) were comparable to those of the benchmark iridium catalyst (1.3 μmole O_2 evolved after 2 min), rates enhanced significantly after this initiation period. The turnover numbers after 1000 s (TON = 42 and 86 for **2** and **3**, respectively) are substantially higher than those of the best ruthenium-based water-oxidation catalysts known to date.[3b,7] The analogous iridium complex containing a C,N-bidentate phenylpyridine rather than a C,C-bidentate carbene ligand showed also similar activity under comparable conditions.[10]

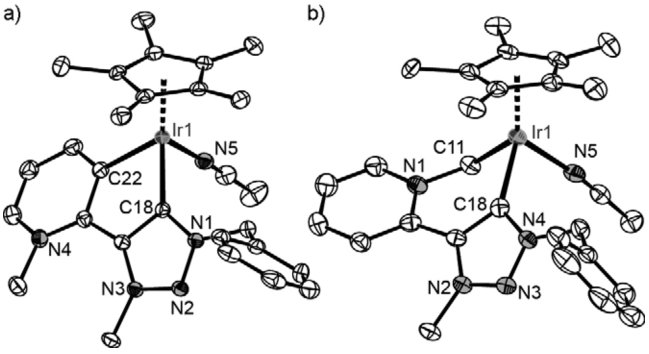

Figure 1. ORTEP representation of complexes **2** (a) and **3** (b); thermal ellipsoids set at 50% probability, non-coordinating OTf^- ions and the hydrogen atoms are omitted for clarity.

Table 1: Selected bond lengths [Å] and angles [°] for **2** and **3**.

Bond	Complex **2**	Complex **3**
Ir1–C18	2.024(2)	2.016(4)
Ir1–C*x*	2.060(3)	2.115(3)
Ir1–N5	2.032(2)	2.050(3)
Ir1–Cp*$_{centroid}$	1.856(1)	1.844(3)
C18-Ir1-Cx	76.38(10)	80.98(13)
C18-Ir1-N5	87.99(9)	87.08(12)
Cx-Ir1-N5	86.49(10)	81.38(13)

[a] *x* = 22 for **2**, *x* = 11 for **3**.

Experiments aimed at probing the longevity of the catalytically active species were carried out at low concentrations of complexes **2** and **3** (Figure 2, bottom).[22] After three days, slightly better performance of complex **2** is apparent and both systems were still active, albeit at lower rate (314 h^{-1} after 10 h and 33 h^{-1} after 70 h for catalyst **2**). Within five days, the TON for complex **2** had nearly reached 10000, which is the largest number reported to date for water oxidation (TON_{max} for complex **3** is 8350). This productivity corresponds to the formation of almost 1.2 L O_2 per mg of iridium. Further optimization of both robustness and activity of the catalysts should be possible through the high flexibility of the ligand synthesis.

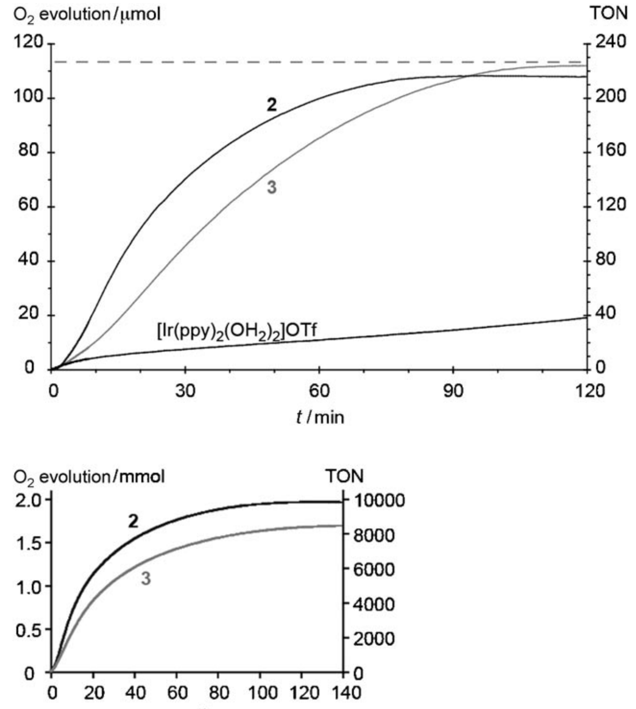

Figure 2. Top: Catalytic water oxidation using 0.5 μmol catalyst and 450 μmol Ce^{IV} as sacrificial oxidizing agent in water (1.0 mL, 25 °C); the dashed line indicates the Ce^{IV}-limited maximum O_2 evolution. Bottom: O_2 evolution (measured by manometry and calibrated by GC) and TONs over 140 h using 0.2 μmol catalyst and 10 mmol Ce^{IV} in water (10 mL, 25 °C).

We suggest that the excellent activity of complexes **2** and **3** in catalytic water oxidation originates from the high electronic flexibility of the mesoionic ligand(s).[23] In their neutral carbene-type resonance form, these ligands stabilize relatively low metal oxidation states. Higher oxidation states, such as the Ir^{V} oxo species, presumed as potent intermediate in water oxidation,[10] may be accessible through an enhanced contribution of zwitterionic resonance forms arising from a more pronounced charge separation within the ligand into a cationic iminium system and a metal-bound anionic, and hence strongly donating, vinyl fragment. Support for the ligand being involved in the catalytic water oxidation was obtained from electrochemical analyses of the complexes. In aqueous solutions (0.1 M KCl as supporting electrolyte), multiple oxidation processes were detected in the +0.7 to +1.0 V potential range. For complex **2** these processes occurred at marginally lower potential (0.76, 0.86, 0.94 V) than for complex **3** (0.77, 0.86, 0.96 V).[14] These oxidations cannot be attributed solely to iridium-centered processes and suggest that the ligand is not innocent at high oxidation potentials. Cooperative behavior between the metal center and the ligand has been noted in other catalytic systems[24] and may also be effective in natural systems where access to high oxidation states is required.

In conclusion, we have disclosed a versatile system for the catalytic oxidation of water by an iridium complex containing carbene-type ligands. The flexibility of the carbene ligand as well as the modularity of the substitution pattern and chelate nature provides ample opportunity for further tailoring of this catalytic system, thus contributing to the development of environmentally benign fuel production. Specifically, it may be possible to adjust the redox properties of the catalyst so that it can be coupled to photosensitized oxidants, thus producing O_2 and H_2 from water and sunlight.

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