Carbene Iridium Complexes for Efficient Water Oxidation: Scope and Mechanistic Insights

James A. Woods, Ralte Lalrempuia, Ana Petronilho, Neal D. McDaniel, Helge Müller-Bunz, Martin Albrecht, Stefan Bernhard

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Iridium complexes of Cp* and mesoionic carbene ligands were synthesized and evaluated as potential water oxidation catalysts using cerium ammonium nitrate as a chemical oxidant. Performance was evaluated by turnover frequency at 50% conversion and by absolute turnover number, and the most promising precatalysts were subjected to further study. Molecular turnover frequencies varied from 190 to 451 per hour with a maximum turnover number of 38,000. While the rate of oxygen evolution depends linearly on iridium concentration, concurrent spectroscopic and manometric monitoring of stoichiometric additions of oxidant suggests oxygen evolution occurs as two sequential first order reactions. Under the conditions herein, the oxygen evolving species appears to be well defined and molecular based on the kinetic effects of careful ligand design, reproducibility, and the absence of persistent dynamic light scattering signals. Outside of these conditions, the complex mechanism is highly dependent on reaction conditions. While confident characterization of the catalytically active species is difficult, especially under high-turnover conditions, this work indicates IrOx is not essential for the formation of catalytically active water oxidation species.

Introduction

Global demand for energy is projected to increase significantly over the next three decades. Fortunately, estimates for annual total solar insolation exceed the current and projected global demand for energy by almost four orders of magnitude. Harnessing this under-utilized resource is then a natural consideration for energy researchers. Because sunlight is transient, a critical issue is the effective and efficient transformation of sunlight into a storable source of energy. Despite significant improvements from multi-junction photovoltaic systems, silicon photovoltaic systems require expensive and slow-charging batteries for energy storage. Thermochemical heat engines and biological mimicry are also exceptionally promising technologies but rely on mechanisms resistant to controlled tuning.

A photocatalytic cycle could conceivably be tailored to function with any number of well-studied reductive pathways including carbon dioxide to methanol, metal salt to metal, and water to hydrogen. Despite the various potential reductive pathways, complementary oxidative half-reactions producing molecular oxygen are necessary. This simplifies reactant delivery in an energy system by employing the atmosphere as an oxidant reservoir and conveyance. Water, due to its abundance and benignity, represents an ideal feedstock for this process. Unfortunately, water redox is plagued by the mechanistic complexity and high thermodynamic potential necessary to advance the oxidation reaction. Well-defined molecular catalysts are one avenue of study yielding direct characterization, structural tunability, and greater atom economy through homogenous reaction conditions.

Citing just a small portion of the broad interest in molecular water oxidation: ruthenium dimers, cobalt tetramers, manganese dimers along with recent work detailing single-site catalysts all illustrate the diversity of successful catalysts. More recently, a variety of Cp*Ir complexes (Cp* = C5Me5) have been shown to act as efficient water oxidation precatalysts. These complexes are remarkable for their high activity compared to original iridium catalysts with 2-phenylpyridine ligand spheres. Mechanistic work under different reaction conditions led to controversial conclusions: while a heterogeneous mode of action has been put forward in some studies, support for homogeneous catalysis has been obtained e.g. from experiments using a quartz microbalance as a probe and from catalyst immobilization. Direct comparison of results across the broad range of mechanistic investigations reported in literature is difficult due to varying reaction conditions including the use or absence of organic co-solvents and buffered or unbuffered aqueous conditions. Following our initial discovery of triazolylidene iridium complexes as potent water oxidation catalysts, we engaged in careful ligand modification in an attempt to improve catalyst performance and to expand our understanding of oxidation mechanisms with application to a broad variety of...
fuel producing photosystems. Here we report on the synthesis and catalytic activity in water oxidation of an expanded family of cationic Cp*Ir complexes containing either C,C-bidentate or a C,N-bidentate coordinating carbene iridium complexes.

**Results and Discussion**

**Synthesis and characterization of the complexes**

A series of cationic Cp*Ir complexes 1–10 containing either C,C-bidentate or a C,N-bidentate coordinating chelate was prepared using C–H bond activation chemistry mediated by silver cations (Scheme 1). The type of chelating sites varies considerably from the original C,C bidentate set explored previously. Thus, one set of complexes features chelating C,N-bidentate ligands that contain a neutral N-bound triazole unit paired with a formally neutral abnormal pyridylidene fragment (Cppy, Naryl-bidentate; complexes 1 and 3) or with an anionic phenyl chelate (Caryl,Ntrz-bidentate; complex 2). A second set of ligands comprises a triazolylidene core with different substitution patterns and an N-bound pyridine as chelating group (Npyr,Ctrz-bidentate; complexes 4–6). C,C-Bidentate chelates constitute a further class of ligands, featuring a triazolylidene ligand and an anionic phenyl ligand (Caryl,Ctrz-bidentate; complex 7), or a triazolylidene and a formally neutral pyridylidene ligand (Cpyr,Ctrz-bidentate; complexes 8 and 9), or an sp³-hybridized ylidic ligand (Cpyr,Ctrz-bidentate; complex 10).

The formation of complexes 1–10 provided some interesting insights into the donor properties of the ligand and the reactivity of the iridium center. In the absence of a chelating nitrogen donor, cyclometalation via Caryl–H bond cleavage took place (cf complexes 2, 7). Cyclometalation involved exclusively the aryl ring bound to a nitrogen of the heterocyclic core. This reactivity pattern was observed previously also in triazolylidene palladium chemistry and suggests an electrophilic bond activation. Obviously, Caryl–H activation is competitive to Cpyridinium–H bond activation, and the course of the reaction is dependent on whether N2 or N3 of the triazole ring is coordinated to the iridium center (cf. formation of a mixture of 1 and 2 from the same ligand precursor). Exchange of the aryl substituent at N1 of the ligand precursor by a methyl group prevents the formation of a chelate via N2 bonding. Consequently, exclusive coordination via N3 and ensuing Cpyridinium–H bond activation was observed, which afforded the chelating pyridylidene-triazole complex 3.

All complexes featuring a nitrogen donor ligand were prepared in CH2Cl2 and were obtained as monocationic species comprising an iridium-bound chloride ligand. This chloride was readily abstracted by classical methods using AgOTf to yield the dicationic complexes. In contrast, complexes with a C,C-bidentate ligand were synthesized in MeCN and were isolated as the dicationic complexes directly from the iridation reaction. This behavior is in line with considerably stronger donor properties of these C,C-bidentate ligands compared to their C,N-homologues, thus inducing a higher electron density at iridium and a destabilization of the putative Ir=Cl bond. The stronger donor properties of such abnormal formally neutral carbene ligands as compared to imines may be rationalized by their pronounced mesoionic character. This notion enhances the relevance of a formally anionic carbon bound to the iridium center and a (remote) intermolecular stabilization of the negative charge by an iminium fragment.

Formation of complexes 4–6 with pyridine-functionalized triazolylidenes was straightforward when using equimolar ratios of iridium precursor and triazolium salt. In the presence of (slight) excess of triazolium salts, a second product appeared that was identified as the bis(carbene) complex 11 on the base of the two sets of ligand signals in the ¹H NMR spectrum in 1:1 ratio. The different shielding of the two sets of pyridyl protons indicates a bincarbene complex 11 comprised of one monodentate, and one C,N-bidentate triazolylidene ligand (Scheme 2). Unambiguous confirmation of the formation of complex 11 was obtained from an X-ray diffraction analysis from crystals that grew from a reaction mixture.

The site of metatation in the new complexes 1–8 was readily deduced from NMR spectroscopic analysis of the complexes in CD3CN solution. N-bound triazole ligands featured a diagnostic low-field signal in the 8.6–9.3 ppm range in the ¹H NMR spectrum of complexes 1–8.

**Scheme 1**
the presence of the triazole proton at C(5) (complexes 1–3). Pyridyl-type bonding due to C(pyridinium)–H bond activation was identified by three characteristic resonances at low field (doublets at δH 8.7 and 8.3, and doublet of doublets at δH 7.6) assigned to the H(4), H(6), H(5) protons respectively of the pyridine heterocycle (complexes 1, 3, and 8). In contrast, four pyridine resonances were clearly distinguishable in complexes featuring N-coordinated pyridine or non-bound pyridinium substituents (complexes 4–7). In the 13C NMR spectrum, the iridium-bound carbon of the triazolylidene ligand experiences the largest shift-difference upon metalation (δC) around 155 in complexes 4–8, ca. Δδ ca. 30 ppm compared to the ligand precursor. The pyridylidene carbon attached to iridium was observed at slightly lower field (around 160, complexes 1, 3, 8), while the iridium-bound carbon of the phenyl group in complexes 2 and 7 appeared at 148.8 and 144.1 ppm, respectively.

In aqueous solutions, the complexes exist as equilibria between two species. The behavior of complex 4a is representative. Two sets of pyridyl signals were observed in D2O, the major one featuring a low field doublet for the pyridyl H(6) proton at 8.98 ppm. All signals of the minor species are downfield shifted by 0.1–0.2 ppm (e.g. pyridyl H(6) proton at δH 9.16). The ratio of the two species is concentration and pH dependent and shifts towards the major species at high concentrations (e.g. 9:1 at 20 mM solution vs. 7:3 at 1.7 mM), indicating an equilibrium between complex 4a and a dicationic aquo complex. In agreement with such a notion, addition of KCl completely suppresses the presence of the minor species. Likewise, in less coordinating solvents such as CD3OD or acetone-d6, only one species was detected. Unambiguous evidence for the formation of such a dicationic species was obtained from irreversible abstraction of the chloride in 4a with AgOTf in aqueous CH2Cl2 (Scheme 3). The NMR spectrum of the formed bis(aquo) complex 4c matches those of the minor species. Of note in particular with regards to catalytic applications is the inertness of the complexes under strongly acidic conditions. For example, spectroscopic monitoring of the stability of complex 4a in 1 M HCl (D2O, pH = 0) did not indicate any changes over time (> 48 h) and no diagnostic signals due to presence of triazolium or pyridinium salts were observed. Accordingly, acidolysis of the Ir–Ctrz bond and ensuing ligand dissociation does not occur in detectable quantities under highly acidic conditions. A similar robustness was observed for the Ir–Cpyr bond in complex 8, indicating that both normal carbene–iridium bonds are fully acid-resistant.

All complexes except 2 and 4b were analyzed by single crystal X-ray diffraction. The molecular structures (Figure 1) confirmed the expected connectivity patterns. The Ir–Cpyr bond lengths are in the expected range,52 and are consistently shorter than the corresponding Ir–Ntrz bond lengths. Similarly, the Ir–Cpyr bonds are substantially shorter than the dative Ir–Npyr contacts. They are even slightly shorter than the Ir–Caryl bond in complex 7. The ligand bite angle shows little variation, as may be expected when considering that all metallocycles in complexes 1–8 are comprised of four sp2-hybridized carbon/nitrogen atoms and that the C–N vs C–C bond length difference is only minute.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(Eir-Epyr)</th>
<th>Ir–Epyr</th>
<th>E–Ir–Epyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Ntrz/Cpyr)</td>
<td>2.042(2)</td>
<td>2.053(3)</td>
<td>76.82(11)</td>
</tr>
<tr>
<td>3 (Ntrz/Cpyr)</td>
<td>2.068(2)</td>
<td>2.040(3)</td>
<td>77.23(9)</td>
</tr>
<tr>
<td>4a (Cpyr/Npyr)</td>
<td>2.017(2)</td>
<td>2.129(2)</td>
<td>76.08(8)</td>
</tr>
<tr>
<td>5 (Cpyr/Npyr)</td>
<td>2.027(6)</td>
<td>2.124(5)</td>
<td>75.7(2)</td>
</tr>
<tr>
<td>6a (Cpyr/Npyr)</td>
<td>2.013(2)</td>
<td>2.134(2)</td>
<td>76.10(9)</td>
</tr>
<tr>
<td>6b (Cpyr/Npyr)</td>
<td>2.032(2)</td>
<td>2.131(2)</td>
<td>76.58(9)</td>
</tr>
<tr>
<td>7 (Cpyr/Cpyr)</td>
<td>2.039(3)</td>
<td>2.070(3)</td>
<td>78.44(12)</td>
</tr>
<tr>
<td>8 (Cpyr/Cpyr)</td>
<td>2.0175(14)</td>
<td>2.0488(14)</td>
<td>76.02(6)</td>
</tr>
</tbody>
</table>

Catalytic activity

The reaction of complexes 3–10 with cerium(IV) ammonium nitrate was monitored with differential digital manometry as previously described. Reaction end-points were verified with mass spectrometry. Stoichiometric oxygen yields (100±4%) were observed for all new complexes (Figure 2) and in contrast to previously explored catalysts,20 no carbon dioxide was observed during later-stages of the reaction. Close inspection of the performance of 3–10 reveals distinct differences in the catalytic activity. These differences, in conjunction with persistent NMR spectra at similar values and ionic strength albeit in the absence of cerium, suggest retention of the carbene-containing ligands. Further evidence of ligand retention is afforded by predictable ionic effects on catalyst activity however the presence of a induction period necessitates comparison of turnover frequencies at 50% conversion (Table 2).
Figure 2: Catalytic activity of complexes 3–10 and [Ir(ppy)2(OH2)2]OTf at 0.5±0.05 mM catalyst and 0.45 M cerium(IV). Dotted line corresponds to complete stoichiometric consumption of cerium(IV).

Analogous to similar ruthenium-catalyzed water oxidation reactions,24 steric bulk on the triazole N1 position leads to a decrease in catalytic activity (cf. activity of 4a vs 6a and 8 vs 9). Changing the ylide-carbene motif in complex 10 to a dicarbene system improved catalytic activity from 191 h\(^{-1}\) to 451 h\(^{-1}\), suggesting the role of electronic tunability of catalytic performance. The C-C chelate appears to effect greater activity than a N-C chelate from a comparison of complexes 4a and 8. And, as illustrated by the poor performance of complex 3, increasing the ligand donor properties from triazole N-coordination to triazoylidene C-bonding (c.f. 8) is beneficial and leads to greater activity.

Table 2. Turnover frequencies at 50% conversion, TOF\(_{50}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>3</th>
<th>4a</th>
<th>5</th>
<th>6a</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF(_{50}) (h(^{-1}))</td>
<td>190</td>
<td>365</td>
<td>197</td>
<td>301</td>
<td>327</td>
<td>451</td>
<td>279</td>
<td>191</td>
</tr>
</tbody>
</table>

In contrast to reports suggesting the formation of a heterogeneous species implicated as an active intermediate in the water oxidation reaction,

exploratory reactions yielded no particles visible to the naked eye and prompted further study. While later experiments employing dynamic light scattering were able to observe the nucleation of dioxygen, no scattering attributable to iridium nanoparticles was observed from any reaction of complexes 4a/4c or 8 at least to the limits of detection (ca. 0.3 nm).

Mechanistic details

Definitively interpreting the reaction progress into discrete mechanistic steps is complicated by numerous factors: the initial pre-equilibrium due to solvolysis, disproportionation between catalytic intermediates and various cerium(III)/cerium(IV) species,8–60 the effects of ionic strength, and the potential interactions of any supporting ions with reaction intermediates. There is also a high likelihood that reactions driven by the ostensibly single-electron oxidant cerium would have significantly different electron transfer mechanisms than periodate driven reactions which would be different still from electrode driven reactions61–63 and render direct mechanistic comparisons inconclusive. Moreover, any investigation involving ex situ analysis, for example electron microscopy following solvent evaporation, may lead to potentially misleading conclusions as the sample preparation will inherently affect the constitution of the observed species. We therefore set out to analyze reactions with non-invasive “in operando” techniques.64

Despite the complex reaction kinetics, important information can be garnered from in-depth investigations conducted on the most active complexes, 4a and 8. Turnover number and frequencies from a 5 μM solution of 8 and a 4 μM solution of 4a, both in the presence of a saturated aqueous solution of cerium ammonium nitrate (0.835 M), are presented in Figure 3. Following an induction period, total turnovers in excess of 30,000 were common in extended oxidation experiments with 10-day turnover counts of 33,100 and 38,000 for complexes 8 and 4a respectively.

Varying the concentration of 4a from 1 μM to 10 μM with a strong excess of cerium(IV) further illustrates the complicated kinetics. The rate determining step appears to vary based on the concentration of 4a, rendering a trivially interpreted rate law for the overall process difficult (Figure 4). At low catalyst

Figure 3: Turnover number and frequencies after addition of a sufficient quantity of compounds 4a and 8 to produce the indicated concentration in 20 mL solutions of cerium ammonium nitrate (0.835M).

Figure 4: Top: O\(_2\) formation for complex 4a at concentrations ranging up to 10 μM following addition to 20 mL aqueous cerium ammonium nitrate solutions (0.835 M). The dotted trace describes a least squares fit employing the integrated rate law described in the Supporting Information. Bottom: Plot of maximum rate of O\(_2\) formation from above illustrating concentration-dependent mechanism.

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concentrations (≤ 2 μM), oxygen evolution was found to be linear with respect to time while at higher concentrations of 4a (> 2 μM) the reaction appears to be limited by sequential (pseudo)first order reactions. Combined first and second-order linearized plots of the oxygen evolution traces clearly describe the two different behaviors where initial activity emulates an overall second-order reaction that gives way to slower, first-order behavior as the reaction progresses (See Figure a representative example as applied to the data from Figure 4). This behavior indicates the oxygen-evolving step is predicated by two sequential first order reactions (Scheme 4). As seen by the dotted traces in Figure 4, there is excellent agreement between the integrated rate law from Scheme 4 and the experimentally observed oxygen evolution data from all three regions of catalytic activity (overall second order, sigmoidal, overall first order).

Scheme 4

Additionally, the maximum rate of oxygen evolution for 4a was found to be linearly correlated to catalyst concentration over the range of 2 μM to 10 μM with deviation from linearity at concentrations below 2 μM (Figure 4, bottom) while a log-log plot of rate vs. catalyst concentration indicates the presence of a mixed order reaction (Slope of 1.5, Supporting Information).

The effect of varying the cerium concentration from 3 mM to 0.865 M while holding the concentration of 4a at 8.6 μM is shown in Figure 5. Cerium solutions were buffered in 1N HNO₃ for four primary reasons: to prevent the thermodynamic decay of cerium(IV) at higher values; to avoid reaction complexity by limiting the speciation of ions present; and to take advantage of faster reaction kinetics and to preclude the precipitation of cerium(III) species. These conditions may also increase the solubility or decrease the propensity for aggregation of iridium species.

Under these conditions the maximum rate of oxygen evolution occurs at 50 mM cerium(IV) with 0.18 mmol O₂ h⁻¹ (TOF 20.9 h⁻¹). Prior to this maximum, between 0-20mM cerium(IV) or roughly 300-2400 cerium(IV) equivalents, the rate of maximum oxygen evolution appears to increase linearly. A gradual decrease in the maximum rate of oxygen evolution is observed from 100 mM cerium(IV) upward. As cerium(IV) in 2M perchloric acid is believed to exist predominantly as a dimeric species, this concentration-dependent inhibition could arise due to similar speciation in nitric acid or through complex equilibria as is the case with cerium(III). Regardless of the actual oxidant speciation, quantitative consumption occurs in all cases over time frames greater than 10 days.

We attempted to further investigate the short-term activity under conditions where cerium is not in gross excess but quantitative consumption also occurs; this effectively probes the initial rate determining steps. As observed previously with related Ir(Cp*) complexes, addition of CAN induced a color change of the initial yellow solution to blue within seconds. While the formation of a blue mixture or a blue layer has periodically been attributed to IrO₂ formation due to the oxide’s general tendency to absorb broadly around 580 nm similar color changes have previously been noted in high-valent iridium aqua complexes.

An experiment was performed using the previously described digital pressure transducers to manometrically follow the evolution of oxygen from several equal additions of oxidant with concurrent UV/Vis measurements.

When a single addition of 20 equivalents of CAN was added to a 0.5 mM solution of 4a no measurable oxygen production was observed (Figure 6) though there is a rapid color change from yellow to blue and back over the course of 15 minutes (Figure 7, Top). After 8 hours, a second aliquot of 20 equivalents of CAN was added and 8 hours later another addition of 20 equivalents. This process was repeated for a total of 8 steps or 160 total equivalents of CAN over 64 hours. A sub-stoichiometric quantity of oxygen was produced during the second through fourth additions with the deviation from stoichiometric predictions decreasing on each subsequent addition. Approximately 30 equivalents of cerium in total are unaccounted for by manometry.

No carbon dioxide was observed via headspace mass
spectrometry even when the experiment was repeated with double the concentration of catalyst. The gas analyser employed is ostensibly sensitive into the ppm range; but, more conservatively if even one mole of CO₂ was produced per mole of catalyst it would occupy 1-2% mol of the overall headspace i.e. well within the limits of detection. One feasible contribution to the cerium discrepancy investigated was oxidation of the initial chloride ligand to perchlorate either by cerium or oxidized catalyst via 

\[
\text{ClO}_3^- + 4 \text{H}_2\text{O} + 8e^- \rightarrow \text{Cl}^- + 8\text{OH}^- \quad \text{at} \quad 0.56 \, \text{V.}
\]

As a control, the experiment was repeated with an aqua complex, 4c, yielding no significant differences from the chloride analogue 4a (Figure 6, red overlay). The initial oxidant discrepancy is currently unresolved but may involve reversible cerium or peroxide speciation. Further experiments employing concurrent Raman spectroscopy are underway to determine the speciation resulting in the initial oxidant discrepancy.

Progressively examining each oxygen evolution through the method of first and second-order linearizations yields the same sequential first order behavior observed from Figure 4 however concurrent UV-vis monitoring was unable to identify clearly correlated changes in absorbance. As such, the intermediate speciation of the rate determining steps is unknown at this time. Least squares fitting of the integrated rate equation (Scheme 4) to the final four oxygen evolution steps yields first order rate constants, \(k_{\text{A}}\) and \(k_{\text{C}}\), of ca. 40 hr\(^{-1}\) and 13 hr\(^{-1}\) respectively (See Supporting Information for plots and residuals). The first four steps were also evaluated but were poorly fit by the sequential first order model. The presence of an additional, faster gas-producing reaction is suggested by the initial phase of the linearization of steps 2-4.

Long-term catalyst deactivation was assessed by plotting the rate of oxygen evolution vs. the quantity of oxygen evolved\(^{69}\) for the final four steps. These plots yielded overlapping traces demonstrating the absence of catalyst deactivation following the initial induction period; the active catalyst species in the experiments with a gross excess of cerium are therefore likely the same species present after the fourth addition of cerium in the stepwise experiments.

Figure 7 Left: Chronological spectra from the first (top) and fourth (bottom) addition of 20 equivalents cerium(IV). Spectra are indexed in hours relative to the preceding cerium(IV) addition. Right: Absorbance traces with experimental and calculated oxygen evolution traces in purple and light blue for the first (top) and fourth (bottom) addition of 20 equivalents of cerium(IV).

Figure 8: Comparison of observed (red, spectrum obtained 0.5 hr after the 8th addition with initial subtracted) with TD-DFT-derived spectra of proposed intermediate structure S1 (blue).

Chronological UV/Vis spectra of the first and fourth additions are shown on the left side of Figure 7 while the right side of Figure 7 shows the concurrent pressure and UV/Vis traces at relevant wavelengths. Absorbance at 370 nm captures the shoulder of cerium(IV) absorption and illustrates how quickly cerium(IV) is consumed in the reaction. After the initial addition, the solution absorbs most strongly at 450 nm and 612 nm but quickly decays to the initial spectra.

TD-DFT calculated spectra\(^{70,79}\) of complex 4c in an \(\text{H}^\text{IV}-\text{OH}\) state predict the pattern of broad and sharp absorption at 670 and 460 nm observed following 8 additions of 20 cerium(IV) equivalents (Figure 8). Calculated spectra of additional conceivable intermediates and in Supporting Information). Notably absent are spectral features consistent with the loss of the Cp* moiety (Figure S5).

Comparing the chronological UV/Vis spectra of the first addition with the fourth suggests the transition from 612 nm to 584 represents a catalytic step prior to the oxygen evolving step, but after the catalyst resting state. Logically, this would represent a transition state similar to the calculated structure S4 (\(\text{H}^\text{IV}-\text{OH}\)). Indeed, there are strong similarities between the calculated spectra of S4 and the initial spectra obtained from the 4th through the 8th injections (cf. Figure S7, S4 doublet; Figure 7, Bottom left, traces 0.01-0.34 h). However, the majority of oxygen production occurs during the first hour of reaction, well before many other potential significant spectral changes and consequently no spectral features were found to directly correlate with the measured rate determining steps of oxygen evolution detailed in Scheme 4.\(^{71}\)

In contrast to Grotjahn et al.\(^{33}\) no precipitate was observed at any point. Dynamic light scattering measurements of a 5 mM solution of 4a in 1N HNO₃, following addition of 20 equivalents of CAN produced variable scattering intensities over time. Scattering indicating sizes as large as 1000 nm were observed by the fourth addition of 20 equivalents; however application of a slight vacuum to the solution causes a decrease in the observed size. Additionally, after 40 hours at atmospheric pressure, particle sizes returned to the baseline measurements of typical cerium(IV)/cerium(III) solutions\(^{71}\) (cf. ibid.; Fig SI-31 and this work; Fig. SI2). These two observations strongly suggest that any scattering intensity observed via DLS is derived from the nucleation of dioxygen and not from nanoparticulates or nanoclusters.

In an attempt to further elucidate the reaction mechanism, NMR measurements under identical conditions indicated that 4a undergoes rapid solvolysis when dissolved in water to produce a
mixture of 4a and 4c with a chloride counter ion in a 4:1 ratio. Following addition of 10 equiv. cerium(IV) to the 1 mM NMR sample, integrals of both 4a and 4c decrease and the ratio of 4a:4c decreases from 4:1 to 2:1. Repeating the experiment with the addition of 2 equiv cerium(IV) establishes a 3:1 ratio of 4a:4c. The integrals and ratios remained constant over several days, yet all signals disappeared upon addition of a second 10 equiv cerium(IV), indicating the formation of a paramagnetic species. Addition of 20 equiv CAN to a fresh solution of 4a buffered in 1 N HNO₃ yielded identical results. NMR signals at 8.25 ppm lends support to the formation of formaldehyde which is in agreement with proposed oxidation mechanisms of carbone wingtip methyl groups.²² Although the Cp* methyl signal is noticeably absent from the spectra of 4a following addition of CAN, broadened signals of the chelating carbone are clearly present.

One explanation that encompasses the DLS, NMR, UV/Vis, and manometric data is fast iridium(III) oxidation to iridium(IV)/V) followed by slower, rate limiting oxygen evolution³³ with a potentially concurrent reaction leading to oxidation of the Cp* methyls. However, calculated UV/Vis spectra suggests retention of the Cp* moiety at least up to 160 equivalents of cerium(IV) with 0.5 mM 4a.

In spite of the sigmoidal reaction kinetics, which are frequently associated with the formation of a heterogeneous active species, negative results from dynamic light scattering experiments, a lack of carbon dioxide from headspace gases, and significantly faster rate of reaction compared to IrO₂ all reinforce the molecular nature of active species derived from 4a following a reaction that is dependent on the ligands around the Cp*Ir fragment. While it is difficult, with complete certainty, to eliminate the presence of a heterogeneous species active towards water oxidation, this work shows the most competent catalytically active species under these conditions is likely a molecular, species catalysing sequential first-order molecular reactions leading to oxygen evolution. Mesoionic triazolylidenes may be particularly suitable as ligands for the ensuing redox processes, as their strongly mesoionic character is capable of stabilizing various redox states and should assist in proton-coupled electron transfer (PCET) steps. Proton transfer from a putative iridium hydroxide intermediate to the triazolylidine ligand and may thus support the oxidation of the iridium center (Scheme 5). Previous results with related abnormal carbene ligands demonstrated that the mesoionic carbene ligand is involved in hydrogen exchange reactions and in metal-catalyzed E–H bond breaking processes (Scheme 4).⁷⁴,⁷⁵

\[
\text{[Ir]} = \text{Ir(Cp*)}
\]

Scheme 5

Conclusions

A variety of iridium complexes comprising mesoionic carbene ligands were synthesized and found to serve as competent precatalysts for the oxidation of water. Turnovers above 30,000 were recorded for the most active catalytic system. This turnover number is limited by the availability of sacrificial oxidant and not by the robustness of the catalyst, which suggests these types of catalysts for continuous water oxidation processes. Mechanistic investigations, especially under stoichiometric or near stoichiometric conditions, strongly support a tunable molecular species. Additionally, dynamic light scattering measurements support the absence of light scattering particles not incipiently present in cerium solutions. While it is not possible to definitively exclude multiple active catalytic species of differing composition, strict adherence to a universal interpretation of the data presented in this work strongly suggests the presence of a homogeneous, tunable, and long-lived iridium water oxidation catalyst with further support from mechanistic studies of similar dinuclear iridium complexes.²⁶ Future work is directed towards developing an intimate understanding of the catalytic mechanism and exploiting that understanding to increase catalytic activity as well as to incorporate the complexes into a photochemically powered system that does not require the presence of a sacrificial oxidant.

Experimental Section

General

All syntheses of the iridium complexes were carried out under an inert atmosphere of N₂ using Schlenk technique and dry solvents. Purifications, including column chromatography, were performed in air using commercial solvents. All ¹H and ¹³C [¹H] NMR spectra were recorded at room temperature on Bruker or Varian spectrometers and chemical shifts were referenced to SiMe₄ for organic solvents and to the temperature-correction residual DHO peak in aqueous experiments (δ in ppm, J in Hz). The ligand precursors L₁, L₁, and L₁,₂₄ the precursor compounds 2-(1-methyl-1H-1,2,3-triazol-4-yl)pyridine,²₄ 2-(1-phenyl-1H-1,2,3-triazol-4-yl)pyridine,²₄ 5-methyl-1-phenyl-1H-1,2,3-triazole,⁷⁷ [Cp*IrCl₂]⁻; and the complexes 9 and 10 were prepared according to literature procedures. All other reagents were purchased from commercial sources and were used as received.

L₁: A suspension of 2-(1-phenyl-1H-1,2,3-triazol-4-yl)pyridine (460 mg, 2.07 mmol) and MeOTf (0.41 mg, 2.48 mmol) in CH₂Cl₂ (5 mL) was stirred at 0°C for 30 minutes. Excess Et₃O was added and the supernatant was removed by decantation. The tan oil was repeatedly washed with Et₂O. NMR spectroscopy of the crude sample indicated non-selective methylation and the presence of two compounds L₁ and L₁ in approximate 2:1 ratio. They were separated by preparative TLC using SiO₂ plates and MeCN/CH₂Cl₂ (1:3 v/v) as eluent. L₁ eluted first,²₄ the second band contained L₁ and was extracted from SiO₂ by stirring in MeOH and subsequent filtration. The volatiles were removed under reduced pressure and the residue was dissolved in CH₂Cl₂ and filtered again. The solvent was evaporated and pentane was added. The precipitate was collected and dried in vacuo, thus giving L₁ as a white solid (150 mg, 20%). ¹H NMR (CD₂CN, 400 MHz): 9.09 (s, 1H, H₁), 8.79 (d, ²JHH = 6.2 Hz, 1H, H₁), 8.58 (t, ²JHH = 8.0 Hz, 1H, H₁), 8.51 (d, ²JHH = 8.0 Hz, 1H, H₁), 8.0 (dd, ²JHH = 8.0 Hz, ²JHH = 8.2 Hz, 1H, H₁), 7.97 (d, ²JHH = 7.4 Hz, 2H, H₁), 7.68 (d, ²JHH = 7.4 Hz, 2H, H₁), 7.59 (t, ²JHH = 7.4 Hz, 1H, H₁), 4.53 (s, 3H, N₃-C₃H₃). ¹³C [¹H] NMR (CDCl₃, 100 MHz): 147.4, 146.3, 145.8, 139.5, 136.5, 130.3, 130.1, 129.2,
127.1, 126.7 (N<sub>ar</sub>-CH<sub>3</sub>). Anal. calc. for C<sub>14</sub>H<sub>19</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub> (488.38): C, 29.51; H, 2.89; N, 11.47 %. Found: C, 30.22; H, 3.01; N, 11.29 %.

**Complexes 1 and 2:** A mixture of L<sub>1</sub> (92 mg, 0.25 mmol), AgOAc (63 mg, 0.37 mmol) and [Cp*IrCl<sub>2</sub>] (100 mg, 0.13 mmol) in MeOH (10 mL) was refluxed for 24 h and then filtered through Celite. The filtrate was concentrated to ca. 2 mL, which induced crystallization of the orange complex 1 (50 mg, 20%). The mother liquor was evaporated and the residue washed with copious amounts of CHCl<sub>3</sub> until the washing was essentially colorless, thus leaving complex 2 as a yellow solid (30 mg, 12%).

Analytical data for 1: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz): δ 9.06 (s, 1H, H<sub>ar</sub>), 8.71 (d, J<sub>HH</sub> = 7.2 Hz, 1H, H<sub>ar</sub>), 8.31 (d, J<sub>HH</sub> = 6.1 Hz, 1H, H<sub>ar</sub>), 8.03 (d, J<sub>HH</sub> = 7.7 Hz, 2H, H<sub>ar</sub>), 7.75–7.66 (m, 3H, H<sub>ar</sub>), 7.59 (dd, J<sub>HH</sub> = 7.2 Hz, J<sub>HH</sub> = 6.1 Hz, 1H, H<sub>ar</sub>), 4.46 (s, 3H, N<sub>ar</sub>-CH<sub>3</sub>), 1.80 (s, 15H, Cp<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C[<sup>19</sup>F] NMR (CD<sub>3</sub>CN, 100 MHz): δ 165.4 (C<sub>ar</sub>-Fr), 152.0, 150.4, 147.4, 139.2, 136.4 130.8, 128.5, 127.4, 124.8 (C<sub>ar</sub>-H), 121.3, 90.9 (C<sub>py</sub>), 47.9 (N<sub>ar</sub>–CH<sub>3</sub>), 8.5 (C<sub>ar</sub>–CH<sub>3</sub>). Anal. calc. for C<sub>24</sub>H<sub>17</sub>F<sub>3</sub>IrN<sub>3</sub>O<sub>3</sub>S (478.24): C, 40.13; H, 3.64; N, 7.49 %. Found: C, 39.59; H, 3.52; N, 7.32 %. Single crystals of 1 that were suitable for X-ray diffraction were obtained from the tetraphenyldiatrace salt. This salt was obtained by adding NaBPh<sub>4</sub> (20.5 mg, 0.06 mmol) to a solution of 1 (10 mg, 0.01 mmol) in MeOH (2 mL). After stirring for 30 minutes, the yellow precipitate was collected, washed twice with MeOH and finally with Et<sub>2</sub>O and then dried in vacuo. The <sup>1</sup>H NMR spectrum does not show any significant change except for the new resonances at δ 7.30, 7.01 and 6.86 due to the BPh<sub>4</sub> anion. The <sup>19</sup>F NMR spectrum is empty and does not show any signal in the range expected for the triflate anion.

Analytical data for 2: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz): δ 9.17 (s, 1H, H<sub>ar</sub>), 8.79 (d, J<sub>HH</sub> = 6.1 Hz, 1H, H<sub>ar</sub>), 8.62 (t, J<sub>HH</sub> = 8.0 Hz, 1H, H<sub>ar</sub>), 8.50 (dd, J<sub>HH</sub> = 8.0 Hz, J<sub>HH</sub> = 1.4 Hz, 1H, H<sub>ar</sub>), 8.05 (ddd, J<sub>HH</sub> = 8.0 Hz, J<sub>HH</sub> = 6.2 Hz, J<sub>HH</sub> = 1.4 Hz, 1H, H<sub>ar</sub>), 7.90, 7.79 (2 × d, J<sub>HH</sub> = 7.4 Hz, J<sub>HH</sub> = 1.3 Hz, 1H, H<sub>ar</sub>), 7.32 7.25 (2 × t, J<sub>HH</sub> = 7.4 Hz, J<sub>HH</sub> = 1.3 Hz, 1H, H<sub>ar</sub>), 4.56 (s, 3H, N<sub>ar</sub>–CH<sub>3</sub>), 1.82 (s, 15H, Cp<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C[<sup>19</sup>F] NMR (CD<sub>3</sub>CN, 125 MHz): δ 148.8 (C<sub>ar</sub>-Fr), 147.6, 145.9, 140.0, 139.5, 137.2, 133.9, 129.5, 129.3, 127.4, 124.1 (C<sub>ar</sub>-H), 123.5, 113.7, 90.4 (C<sub>py</sub>), 48.8 (N<sub>ar</sub>–CH<sub>3</sub>), 8.4 (C<sub>ar</sub>–CH<sub>3</sub>). Anal. calc. for C<sub>24</sub>H<sub>17</sub>F<sub>3</sub>IrN<sub>3</sub>O<sub>3</sub>S (478.24): C, 40.13; H, 3.64; N, 7.49 %.

**Complex 3:** Compound L<sub>3</sub> (120 mg, 0.37 mmol), AgOAc (124 mg, 0.74 mmol) and [Cp*IrCl<sub>2</sub>] (147 mg, 0.18 mmol) was refluxed in dry MeOH (12 mL) for 18 h. The reaction mixture was filtered through Celite and concentrated to ca. 4 mL. Crystallization was induced upon standing at room temperature and afforded pure 3 as an orange solid (60 mg, 35%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 MHz): δ 8.65 (dd, J<sub>HH</sub> = 7.7 Hz, J<sub>HH</sub> = 0.7 Hz, 1H, H<sub>ar</sub>), 8.52 (s, 3H, H<sub>ar</sub>-CH<sub>3</sub>), 8.24 (dd, J<sub>HH</sub> = 5.9 Hz, J<sub>HH</sub> = 0.7 Hz, 1H, H<sub>ar</sub>), 7.53 (dd, J<sub>HH</sub> = 7.7 Hz, J<sub>HH</sub> = 5.9 Hz, 1H, H<sub>ar</sub>), 4.33 (s, 3H, N<sub>ar</sub>–CH<sub>3</sub>), 4.29 (s, 3H, N<sub>ar</sub>–CH<sub>3</sub>), 1.74 (s, 15H, Cp<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C[<sup>19</sup>F] NMR (CD<sub>3</sub>CN, 125 MHz): δ 161.5 (C<sub>ar</sub>-Fr), 151.6, 150.6, 146.2, 138.5, 127.6 (C<sub>ar</sub>-H), 125.1, 90.3 (C<sub>py</sub>), 47.4 (N<sub>ar</sub>–CH<sub>3</sub>), 38.6 (N<sub>ar</sub>–CH<sub>3</sub>), 8.11 (C<sub>ar</sub>–CH<sub>3</sub>–CH<sub>2</sub>). Anal. calc. for C<sub>24</sub>H<sub>17</sub>F<sub>3</sub>IrN<sub>3</sub>O<sub>3</sub>S (686.17): C, 35.01; H, 3.67; N, 8.17 %.

Found: C, 34.88; H, 3.49; N, 7.99 %.

**Complex 4a:** A suspension of L<sub>4</sub> (70 mg, 0.216 mmol), AgOAc (50 mg, 0.216 mmol) and [Cp*IrCl<sub>2</sub>] (86 mg, 0.108 mmol) in
CH₂Cl₂ (15 mL) was stirred for 18 h. After filtration through Celite, the volume was reduced to ca. 1 mL and excess Et₂O was added. The resulting precipitate was filtered off and purified by column chromatography (SiO₂: CH₂Cl₂/MeCN). The yellow fraction was collected, evaporated, and dried in vacuo to give complex 4a as a yellow solid (80 mg, 54%). ¹H NMR (CD₂CN, 300 MHz): δ 8.74 (d, 3J₃HH = 5.7 Hz, 1H, H₃Py), 8.10–8.02 (m, 2H, H₄Py), 7.49–7.41 (m, 1H, H₂Py), 4.51, 4.30 (2 × s, 3H, N₃Py=CH₃). 1³C¹H (¹H) NMR (CD₂CN, 125 MHz): δ 157.5 (C₄−Ir), 153.9, 149.8, 147.9, 139.9, 126.4, 121.4, 91.1 (C₃Py), 39.9, 38.9 (2 × N₃Py=CH₃), 8.8 (C₅Py=CH₃). Anal. calc. for C₃H₃₂Cl₃IrN₃O₃S (866.17): C, 35.01; H, 3.67; N, 8.17 %. Found: C, 34.98; H, 3.68; N, 8.06 %.

Complex 4b: A mixture of 4a (100 mg, 0.15 mmol) and AgOTf (56 mg, 0.218 mmol) was refluxed in MeCN (10 mL) for 24 h. It was filtered through Celite and the filtrate was evaporated to dryness, washed with CHCl₃ (4 × 1 mL) and dried, in vacuo, thus affording complex 4b as a yellowish solid (78 mg, 78%). ¹H NMR (CD₂CN, 300 MHz): δ 9.20 (d, 3J₃HH = 5.6 Hz, 1H, H₃Py), 8.27–8.14 (m, 2H, H₄Py), 7.69 (dd, 3J₃HH = 7.4 Hz, 3J₄HH = 5.6 Hz, 1H, H₅Py), 4.59, 4.53 (2 × s, 3H, N₃Py=CH₃), 1.70 (s, 15H, C(CH₃)₃). ¹³C¹H (¹H) NMR (CD₂CN, 125 MHz): δ 154.6 (C₄−Ir), 151.1, 149.4, 149.3, 141.5, 127.3, 122.3, 93.7 (C₃Py), 40.5, 39.1 (2 × N₃Py=CH₃), 8.7 (C₅Py=CH₃). Anal. calc. for C₃H₃₂Cl₃IrN₃O₃S (840.84): C, 32.85; H, 3.36; N, 8.33 %. Found: C, 32.88; H, 3.15; N, 8.33 %.

Complex 4c: Complex 4a (60 mg, 0.087 mmol), AgOTf (45 mg, 0.17 mmol) and a drop of water (20 µL, 1.2 mmol) in CH₂Cl₂ (10 mL) was sonicated during 10 min. at 40 °C and subsequently stirred for 16 h at room temperature. The crude mixture was filtered through Celite. Slow evaporation of the filtrate afforded pale yellow crystals that were washed with Et₂O (62 mg, 87%). ¹H NMR (500 MHz, D₂O) δ 6.94 (d, 1H, 3J₃HH = 5.5 Hz, H₃Py), 8.31 (t, 1H, 3J₃HH = 8.0 Hz, H₄Py), 8.22 (d, 1H, 3J₃HH = 8.0 Hz, H₅Py), 7.76 (t, 1H, 3J₃HH = 6.6 Hz, H₆Py), 4.59 (s, 3H, N₃Py=CH₃), 4.52 (s, 3H, N₃Py=CH₃), 1.80 (s, C(CH₃)₃), 15H. ¹³C¹H (¹H) NMR (125 MHz, CDCl₃): δ 155.2 (C₄−Ir), 153.6 (CH₅), 150.0 (C₃Py), 149.0 (C₅Py), 141.4 (C₆Py), 127.2 (CH₇), 121.7 (CH₈), 90.6 (C₃Py), 40.3 (N₃Py=CH₃), 38.5 (N₃Py=CH₃), 8.5 (Me). Anal. calc. for C₃H₃₂Cl₃IrN₃O₃S: C, 30.88; H, 3.04; N, 6.55. Found: C, 30.84; H, 3.33; N, 6.85 %.

Complex 5: A mixture of L5 (100 mg, 0.26 mmol), Ag₂O (61 mg, 0.26 mmol), and [Cp²IrCl₂] (104 mg, 0.03 mmol) in CH₂Cl₂ (12 mL) was stirred at room temperature for 24 h. After filtration through Celite, the volume of the filtrate was reduced to ca. 1 mL and excess Et₂O was added. The formed precipitate was isolated and dried, giving 5 as an orange solid (82 mg, 31%). ¹H NMR (CDCl₃, 500 MHz): δ 8.85 (dt, 3J₃HH = 5.7 Hz, 3J₄HH = 1.0 Hz, 1H, H₃Py), 8.31–8.29 (m, 2H, H₄Py), 7.82–7.73 (m, 6H, H₅Py=H₆Py), 2.67 (s, 3H, C₃Py=CH₃), 1.83 (s, C₃Py=CH₃), 15H. ¹³C¹H (¹H) NMR (CDCl₃, 125 MHz): δ 152.7 (C₄−Ir), 151.9, 150.5, 142.9, 142.6, 134.7, 132.2, 130.4, 127.9, 129.8, 114.7, 91.8 (C₃Py), 30.0 (C₅Py=CH₃), 8.9 (C₇Py=CH₃). Anal. calc. for C₃H₃₂Cl₃IrN₃O₃P (744.13): C, 38.74; H, 3.66; N, 7.53 %. Found: C, 38.59; H, 3.52; N, 7.48 %.

Complex 6a: Compound L6 (88 mg, 0.24 mmol), Ag₂O (55 mg, 0.24 mmol), and [Cp²IrCl₂] (95 mg, 0.12 mmol) were suspended in CH₂Cl₂ (15 mL) and stirred for 18 h. The mixture was filtered through Celite and concentrated to ca. 1 mL. Addition of excess Et₂O resulted in the precipitation of yellow solid, which was isolated and purified by flash chromatography using SiO₂ and CH₂Cl₂/MeCN (1:4 v/v), yielding 6a as a yellow solid (110 mg, 61 %). ¹H NMR (CDCl₃, 300 MHz): δ 8.76 (d, 3J₃HH = 5.8 Hz, 1H, H₃Py), 8.20 (d, 3J₃HH = 7.8 Hz, 1H, H₄Py), 8.08 (td, 3J₃HH = 7.8 Hz, 4J₃HH = 1.4 Hz, 1H, H₅Py), 8.06–8.0 (m, 2H, H₆Py), 7.66–7.58 (m, 3H, H₇Py), 7.44 (dd, 3J₃HH = 7.8 Hz, 3J₄HH = 5.8 Hz, 4J₄HH = 1.4 Hz, 1H, H₈Py), 4.71 (s, 3H, N₃Py=CH₃), 1.47 (s, 15H, C(CH₃)₃). ¹³C¹H (¹H) NMR (CDCl₃, 125 MHz): δ 155.9 (C₄−Ir), 153.1, 149.3, 148.7, 141.0, 138.1, 130.9, 129.8, 125.8, 125.6, 121.9, 91.1 (C₃Py), 39.5 (N₃Py=CH₃), 8.9 (C₅Py=CH₃). Anal. calc. for C₃H₃₂Cl₃IrN₃O₃S (748.24): C, 40.13; H, 3.64; N, 7.49 %. Found: C, 39.98; H, 3.60; N, 7.25 %.
(CD$_3$CN, 100 MHz): $\delta$ 154.6 (C$_{uz}$-Ir), 154.0 (C$_{py}$-Ir), 152.9, 152.6, 148.7, 139.9, 125.2, 110.2 (NCC$_3$H$_7$), 94.6 (C$_p$), 49.6 (N$_{ux}$-CH$_3$), 43.8 (N$_{py}$-CH$_3$), 39.9 (N$_{ux}$-CH$_3$), 8.8 (C$_p$-CH$_3$), 4.6 (NCC$_3$H$_7$). Anal. calcld. for C$_{89}$H$_{110}$BrIrN$_{20}$O$_{12}$S$_5$: C, 33.72; H, 3.54; N, 8.19 %. Found: C, 33.59; H, 3.52; N, 7.92 %.

**Dynamic Oxygen Evolution Measurement:** Complexes were investigated for water oxidation by mixing them with ceric ammonium nitrate (CAN) in water buffered with 1N nitric acid with pressure monitoring and GC analysis as previously described. Extended reactivity experiments were conducted in 20/40/60 mL EPA vials as well as sealed cuvettes enabling concurrent UV/vis spectroscopy.

**Time-dependent DFT (TD-DFT).** Time dependent calculations were performed at the optimized ground-state geometry via Gaussian 03 software. The unrestricted B3LYP functional was used and the LANL2DZ basis set was applied to all atoms since that basis set has previously resulted in superior agreement of TD-DFT spectra with experimental data.

The energy, oscillator strength, and rotational constants were computed for each of the 70 lowest singlet excitations. Electronic transitions were expanded as Gaussian curves with a FWHM (full width at half-maximum) for each peak set to 2.41 eV (3000 cm$^{-1}$).

**Crystal structure determinations.** Crystal data were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector. Crystals were measured with a Bruker APEX diffractometer using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector. Crystals were measured with a Bruker APEX diffractometer.

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**Notes and references**
