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Bimetallic iridium carbene complexes with mesoionic triazolylidene ligands for water oxidation catalysis

Ana Petronilho,[a] James A. Woods,[b] Stefan Bernhard,*[b] and Martin Albrecht*[a]

Dedicated to Professor Ernesto Carmona on the occasion of his 65th birthday and in admiration of his ground-breaking contributions to organometallic chemistry

Keywords: iridium / N-heterocyclic carbene / triazolylidene / water oxidation / bimetallic

Two new di-iridium triazolylidene complexes were prepared as bimetallic analogues of established mononuclear water oxidation catalysts. Both complexes are efficient catalyst precursors in the presence of a cerium ammonium nitrate (CAN) as sacrificial oxidant. Up to 20,000:1 ratios of CAN:complex, the turnover limitation is the availability of CAN and not the catalyst stability. The water oxidation activity of the bimetallic complexes is not better than the monometallic systems at 0.6 mM catalyst concentration. Under dilute conditions (0.03 mM), the complexes double their activity whereas the monometallic complex shows an opposite trend and displays markedly reduced rates, suggesting a benefit of the close proximity of two metal centers in this low concentration regime.

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Introduction

Artificial photosynthesis is considered as a viable and sustainable process for reducing the global dependence on finite fossil fuel resources.[1] A conceivable photosynthetic pathway hence consists of a water reduction cycle (WRC; 2H+ + 2e− → H2) and a concomitant water oxidation cycle (WOC; 2H2O → O2 + 4H+ + 4e−), which results in an overall splitting of water into O2 and H2 as carbon-neutral fuel.[2]

While stunning performance in catalyst development for the WRC have been achieved,[3] WOC is comparably difficult because of the complexity of O2 formation and the uphill thermodynamics. Oxygen evolution activity has been demonstrated with a variety of heterogeneous and heterogenized catalysts.[4] Recent efforts have furthermore concentrated on molecular catalyst precursors, stimulated by the pioneering work of Meyer.[5] Conceptually, molecular catalysts offer intriguing benefits such as a well-defined active site as well as the opportunity to use structure-activity relationship for tailoring catalytic activity. Indeed, the relevance of the ligand framework has been demonstrated in various studies.[5] Appreciable performance was noted with some first row transition metal complexes,[7] though the most active molecular water oxidation catalysts have emerged thus far from ruthenium and iridium complexes.[9] When coordinated to a suitable ligand set, turnover frequencies as high as those of the natural oxygen evolving complex (OEC) have been observed,[9] as well as catalyst longevity that enables turnovers in the 10^4 range.[10] Within this context, triazolylidene ligands,[11] a specific class of mesoionic carbene,[12] have recently been shown to impart attractive and tunable properties for water oxidation catalysis.[10,13]

The key step in water oxidation catalysis is generally accepted to be the rate-limiting O–O bond formation from the crucial oxidized M=O species.[14] Mechanistically, two distinct pathways have been proposed for this step, including either the interaction of two high-valent metal-oxo species (M=O⋯O= M interaction), or the nucleophilic attach of a water molecule to a metal-oxo site (M=O⋯OH2 interaction).[15] These different mechanisms have crucial consequences on the ligand and catalyst design, and also on potential catalyst immobilization strategies. A bimetallic mechanism will obviously benefit from a close proximity of the two metal centers, e.g. through intramolecular linkage, while the nucleophilic attack will require only one metal site and may become deactivated by the close proximity of another metal center.[16] Since direct mechanistic probing of the reaction pathway is extremely challenging due to the multi-electron multi-proton transfer involved in water oxidation,[17] we set out to synthesize a bimetallic system that may improve the kinetics of water oxidation if an interchange of two M=O units is involved in (rate-limiting) O–O bond formation.[18] The known and prolific water oxidation catalyst precursors 1 and 2 provided a valuable starting point for these investigations (Fig. 1).[10,13b]

Figure 1. Triazolylidene iridium complexes 1 and 2 as water oxidation catalyst precursors.

Results and Discussion
Ditopic ligands that comprise the ligand scaffold of 1 and 2, respectively, were readily accessible due to the versatility of copper-catalyzed cycloaddition protocols.\[19] Thus, reaction of diazido-propane with either phenyl or pyridyl acetylene followed by reaction with a methylation agent afforded the desired ligands 3 and 4 in moderate to high yields (Scheme 1). Quaternization of the pyridyl-functionalized di(triazole) intermediate was accomplished both with [Me_2O][BF_4] and with MeOTf, while Mel is not reactive enough to install four methyl groups and methylation occurs only at the pyridine. In contrast, Mel is sufficiently reactive to yield the di(triazolium) salt 3 in high yields (80%).

In both ligands the trimethylene linker is identified by a characteristic triplet for the NCH_2 protons around δ_H 5 ppm and a quintet for the central CH_2 group at δ_H 2.75 ppm (3) or δ_H 2.95 ppm (4). The acidic triazolium proton appears at low field (δ_H 9.23 and 9.25 ppm in 3 and 4, respectively).

![Scheme 1. Synthesis of complexes 5 and 6.](image)

These ligands were metallated according to protocols closely related to those described for the corresponding monometallic complexes 1 and 2.\[10,11] Thus, reaction of di(triazolium) salt 3 with Ag_2O (4 molequiv) for prolonged time at RT followed by transmetallation with stoichiometric quantities of [Ir(Cp^*Cl)_2] afforded the desired complex 5 (Scheme 1). The bimetallic chelating complex 6 was synthesized via a similar transmetallation protocol, though in this case, Ag_2O and the iridium precursor salt were added simultaneously and the metallation was performed at 80 °C. Both complexes are orange, air-stable compounds that dissolve well in MeCN, water, and MeOH. In contrast to the ionic complex 6, the neutral diiridium complex 5 is also well soluble in chlorinated solvents.

Complexes 5 and 6 share common spectroscopic characteristics. Specifically, the Cp^*/ligand ratio indicates the formation of a bimetallic system rather than a chelating di(triazolylidene) complex. Moreover, the NCH_2 protons are shifted to higher field. This shift difference is more pronounced in 5 (Δ_H 1.47 ppm) than in 6 (Δ_H 0.24 ppm). Chelation in 6 is unambiguously deduced from the resonance pattern of the pyridylidene ring, featuring two doublets (Δ_H 8.71 and 8.29 ppm) and a triplet (Δ_H 7.60 ppm), in agreement with the activation of one C = CH bond. In 6, most resonances are broad and the coupling in the linker is poorly resolved, presumably because of the presence of two diastereoisomers due to the chirality at iridium.\[20] The presence of two resonances for the Cp–CH_3 groups in equal ratio (δ_H 1.85 and 1.84 ppm) lends further support to such a model. The iridium-bound carbon resonates at δ_C 149.7 ppm in the ^13C NMR spectrum of 5, and at δ_C 154.5 and 153.9 ppm in 6.

The electrochemical properties of complexes 5 and 6 are unsurprising and do not differ significantly from the monometallic model compounds and from related species.\[21] For example, complex 6 does not show any distinct redox feature below +1 V (aqueous solution, 1 M HNO_3, pH = 0) and reveals solvent discharge, i.e. electrocatalytic water oxidation, above this potential.

Both complexes were evaluated as catalysts for the oxidation of water in the presence of sacrificial [Ce(NO_3)_3][NH_4]_2 (CAN) as terminal oxidant. An initial set of experiments was carried out at approximately 0.6 mM concentration of catalyst in a 0.67 M aqueous solution of CAN. Under these conditions, essentially all CAN was consumed within 90 min and oxygen production was close to the theoretical limit (Fig. 2, Table 1 entries 1–4).

Inspection of the early stages of the reaction indicates only very minor differences in conversion between the monometallic species 1 and the bimetallic complexes 5 and 6 (inset Fig. 2). This similarity is remarkable, as complexes 5 and 6 possess two active metal centers and hence a higher activity would be expected. Monitoring of the rate of oxygen evolution reveals a delicate influence of the ligand scaffold. Thus, the bimetallic complex 5 is significantly slower than the monometallic analogue within the first 1000 s of the reaction (Fig. 3, Table 1).

The maximum turnover frequency (TOF_max) of the catalytically active species derived from 1 is about twice as high as that of the bimetallic precursor (0.29 s\(^{-1}\) vs 0.17 s\(^{-1}\)) corresponding to some 25% activity of the iridium centers in 5 as compared to 1. The trend is opposite when using the chelating pyridylidene-triazolylidene species 2 and 6 as precursors. The TOF_max measured from the bimetallic precatalyst is indeed twice as high as that from the monometallic species (0.14 s\(^{-1}\) vs 0.07 s\(^{-1}\)). Maximum rates for 6 were achieved after about 3 min, i.e. at a stage of the reaction when CAN was still in large excess (<10% CAN conversion, viz. CAN:[Ir] ratio >1000:1). After about 40 min of reaction, the turnover frequencies of 1, 2, 5, and 6 are essentially identical and subsequently decrease gradually further, which may support a mechanistic model that involves a as postulated by Beller and coworkers.\[17] Accordingly, heterogeneous (and kinetically less competent) species become increasingly prevalent as the reaction proceeds, while at initial stages, homogeneously operating catalysts are predominant.
A second set of experiments was subsequently performed under more dilute conditions. Lower concentrations are expected to increase the relevance of mononuclear processes (i.e. water nucleophilic attack) in mononuclear systems, however, in bimetallic complexes O–O bond formation may still occur through a M–O–O–M interaction due to the locally high concentration of metal centers. Water oxidation with the four iridium complexes 1, 2, 5, and 6 were thus carried out at approximately 0.035 mM catalyst concentration with a CAN/complex ratio of ca. 20,000:1 (Table 1, entries 5–8, Fig. 4). Oxygen evolution is complete after around 24 h (Fig. 4). At this stage, the turnover numbers reached values slightly higher than 5000, indicating essentially complete consumption of CAN and efficient conversion of the redox equivalents for O\textsubscript{2} production with all three catalytic systems. The fact that the sacrificial oxidant is turnover limiting rather than catalyst deactivation suggests that turnover numbers may be markedly increased when using a flow reactor instead of the batch system applied here.

In contrast to the experiments performed at higher catalyst loading, inspection of early stage conversions with low iridium concentrations revealed a significantly higher productivity of the bimetallic complex 5 than the monometallic analogue 1 (inset Fig. 4). The different initial reaction rates are illustrated in Fig. 5, which indicates a maximum turnover frequency of complex 5 that is now twice as high as that of 1 (0.47 s\textsuperscript{-1} vs. 0.22 s\textsuperscript{-1}).\textsuperscript{[22]} This behavior is in sharp contrast to the measurements at higher catalyst concentration, where the bimetallic species is less efficient (Table 1). These observations may be directly correlated with a potential change in mechanism for these complexes under dilute conditions. Tentatively, the decrease of rate for the monometallic species may be attributed either to a rapid heterogeneization (formation of catalytically active colloids) or to an increasing relevance of water nucleophilic attack as compared to the interaction of two iridium oxo species.\textsuperscript{[23]} The opposite effect, viz. the rate increase of the bimetallic complexes under dilute conditions may speculatively arise from the suppression of undesired intermolecular processes\textsuperscript{[16]} that may occur at higher catalyst concentrations, and the preponderance of a mechanism involving a bimetallic Ir=O--O=Ir interaction in the key step.

With both mono- and bimetallic complexes containing the bidentate chelating carbene ligand, the maximum turnover rate doubles upon dilution of the catalyst concentration, e.g. from 0.14 s\textsuperscript{-1} to 0.29 s\textsuperscript{-1} for 6. Yet, complex 6 is considerably less active than the precatalyst derived from bimetallic 5 with monodentate bis(carbene) ligand. The lower activity of complex 6 may be attributed to the entropic challenges to reach the appropriate bis(Ir=O) configuration because of the chelating ligand, or indeed to other aspects such as the different partial charge due to the absence or presence of anionic ligands. In any case, the opposite concentration dependence of the rates observed here with monodentate and bimetallic systems is remarkable and seems to disfavor a mere complex degradation and formation of colloidal species as the catalytically active species.\textsuperscript{[17,23]} In agreement with this conclusion, headspace analysis of the reaction at different stages by MS did not reveal any CO\textsubscript{2} above the detection threshold (<1 ppm).

Table 1. Catalytic performance of complexes 1, 5, and 6.\textsuperscript{[a]}

<table>
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<tr>
<th>Entry</th>
<th>Complex (mM)</th>
<th>CAN/complex</th>
<th>TOF</th>
<th>TOF\textsubscript{max} \textsubscript{a} \textsuperscript{b} / s\textsuperscript{-1}</th>
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<tr>
<td>1</td>
<td>1 (0.65)</td>
<td>1100</td>
<td>260</td>
<td>0.29\textsuperscript{±}0.01</td>
</tr>
<tr>
<td>2</td>
<td>2 (0.63)</td>
<td>1100</td>
<td>250</td>
<td>0.07\textsuperscript{±}0.01</td>
</tr>
<tr>
<td>3</td>
<td>5 (0.65)</td>
<td>1100</td>
<td>240</td>
<td>0.17\textsuperscript{±}0.03</td>
</tr>
<tr>
<td>4</td>
<td>6 (0.69)</td>
<td>1100</td>
<td>230</td>
<td>0.14\textsuperscript{±}0.01</td>
</tr>
<tr>
<td>5</td>
<td>1 (0.034)</td>
<td>22,000</td>
<td>5300</td>
<td>0.22\textsuperscript{±}0.05</td>
</tr>
<tr>
<td>6</td>
<td>2 (0.035)</td>
<td>22,000</td>
<td>5400</td>
<td>0.21\textsuperscript{±}0.03</td>
</tr>
<tr>
<td>7</td>
<td>5 (0.033)</td>
<td>22,000</td>
<td>5500</td>
<td>0.47\textsuperscript{±}0.06</td>
</tr>
<tr>
<td>8</td>
<td>6 (0.034)</td>
<td>22,000</td>
<td>5100</td>
<td>0.29\textsuperscript{±}0.02</td>
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[a] Reactions with 0.6 mM complex loading typically performed in 6 mL H\textsubscript{2}O\textsubscript{2} reactions with 0.03 mM complex in 10 mL H\textsubscript{2}O, turnover numbers (TONs) calculated at 10,000 s and at 48 h, respectively.

Figure 2. Oxygen evolution with a CAN/complex ratio of approximately 1000:1 (0.6 mM complex) for complexes 1, 2, 5, and 6; inset: oxygen evolution at initial 15 min of the reaction.

Figure 3. Changes in turnover frequency in water oxidation catalysis with a CAN/complex ratio of approximately 1000:1 (0.6 mM complex) for complexes 1, 2, 5, and 6 over the first 1000 s of O\textsubscript{2} evolution (TOFs measured by manometry using a custom-built transducer set-up, see experimental section). Solid lines represent average of triplicate measurements, faint areas indicates error bands (95% confidence).

Figure 4. Oxygen evolution with a CAN/complex ratio of approximately 20,000:1 (0.03 mM complex) for complexes 1, 2, 5, and 6; inset: oxygen evolution at initial 1.5 h of the reaction.
Conclusions

A straightforward synthetic access to bimetallic triazolylidene iridium complexes has been disclosed. The complexes are active catalyst precursors for CAN-mediated water oxidation. When compared to the monometallic analogues, the activity is improved when water oxidation is performed under dilute catalyst concentrations. This result may point to a change of mechanism that is related to the concentration of iridium complexes. These results thus strongly underline the relevance of reaction conditions, especially when comparing different catalyst systems. Our results tentatively support a bimetallic O–O bond forming mechanism at low iridium concentration, though we cannot confidently rule out an oxidative cleavage of the linker, which curtails any benefits from a dimetallc catalyst precursor especially at high iridium concentrations and may lead to a heterogeneous catalyst. Synthetic efforts directed towards installing linkers with different rigidity between the two triazolylidene iridium active sites are currently in progress.

Experimental Section

General comments. The syntheses of complexes 1[20] and 2[20] are reported elsewhere. The 1,3-diazidopropane was prepared as described previously[20] and was used without isolation as a THF solution (ca. 3 M). All other starting materials and reagents were obtained from commercial sources and were used as received. Microwave reactions were carried out using a Biotage Initiator 2.5, operating at 100 W irradiation power.

Synthesis of 3: Diazidopropane (3 mL, approx 3 M in THF, 9 mmol) and phenylacetylene (1.5 mL, 16 mmol) were dissolved in a mixture of THF/Water (1:1, 15 mL). CuSO₄ (110 mg, 0.70 mmol) and sodium ascorbate (1.4 g, 7 mmol) were added and the mixture was reacted under microwave irradiation at 100 °C for 1 h. The solvents were removed under reduced pressure and the residue was suspended in CH₂Cl₂ and washed consecutively with aqueous NH₄O, water, and brine. After drying over MgSO₄ and solvent evaporation, compound 1 was obtained as a white powder 643 mg (25%). The solid was dissolved in MeCN (15 mL) and Me₆ (1.1 mL, 18 mmol) was added. The mixture was stirred under microwave irradiation at 100 °C for 2 h. Et₃O was added to and the formed white precipitate was filtered off and dried under vacuum, affording 3 (965 mg, 81%). 1H NMR (500 MHz, DMSO–D₆): δ = 9.25 (s, 2H, CH₃), 7.79–7.75 (m, 4H, CH₃), 7.71–7.66 (m, 6H, CH₃), 4.89 (t, JHH = 6.9 Hz, 4H, NCH₂), 4.32 (s, NCH₂), 2.75 (quintet, JHH = 6.9 Hz, 2H, C–CH₂–C).

Synthesis of 4: Diazidopropane (3 mL, approx 3 M in THF, 9 mmol) and 2-ethynylpyridine (1.0 mL, 16 mmol) were dissolved in a THF/water mixture (1:1, 15 mL). CuSO₄ (110 mg, 0.70 mmol) and sodium ascorbate (1.4 g, 7 mmol) were added and the mixture was reacted under microwave irradiation at 100 °C for 1 h. The solvents were removed under reduced pressure and the residue was suspended in CH₂Cl₂ and washed sequentially with aqueous NH₄O, 10% water, and brine. After drying over MgSO₄ and evaporation of all volatiles, the di(triazole) was obtained as a white powder (908 mg, 54%). The triazole (900 mg, 2.7 mmol) was dissolved in a mixture of 1,2-dichloroethane (15 mL) and MeOH (3 mL) and MeOTf (2.5 mL, 23 mmol) was added. After stirring for 48 h at 90 °C, the mixture was cooled to RT. Addition of Et₂O yielded a oily residue, which was separated and washed with copious amounts of Et₂O to give compound 4a (950 mg, 39%) as a white solid.

Another batch of di(triazole) (430 mg, 1.3 mmol) was dissolved in CH₂Cl₂ (10 mL) and [Me₆OBF₆] (1.3g, 10 mmol) was added. The mixture was stirred for 36 h, treated with excess Et₂O, and the precipitate was added. The mixture was stirred for 36 h, treated with excess Et₂O, and the precipitate was isolated and recrystallized from water. The first batch of crystals (79 mg, 12%) yielded analytically pure 4b. Spectroscopic data for 4a and 4b were identical. 1H NMR (500 MHz, DCl): δ = 9.23 (s, 2H, CH₃), 9.18 (d, JHH = 6.1 Hz, 2H, CH₃), 8.78 (t, JHH = 8.0 Hz, 2H, CH₃), 8.35–8.31 (m, 4H, CH₃), 7.70–7.67 (m, 4H, CH₃), 5.02 (t, JHH = 7.3 Hz, 4H, NCH₂), 4.29 (s, NCH₂), 4.27 (s, NCH₂), 2.94 (quintet, JHH = 7.3 Hz, 2H, C–CH₂–C), 13C[1]H NMR (125 MHz, DCl): δ = 149.7 (C₆H₅), 149.7 (C₆H₂-trz), 149.7 (C₆H₂-trz), 133.3 (C₆H₅), 132.8 (C₆H₂-trz), 132.5 (C₆H₅), 131.3 (C₆H₅), 51.3 (NCH₂), 47.5, 39.4 (2 × NCH₂), 27.3 (C–CH₃–C). Anal. Calcd. for C₂₁H₂₁N₅O₂: C, 56.4; H, 4.71; N, 16.3. Found: C, 56.2; H, 4.76; N, 16.3.

Synthesis of 5: Compound 3 (100 mg, 0.16 mmol) and Ag₂O (151 mg, 0.64 mmol) were suspended in dry MeCN (10 mL) and stirred at RT for 3 days in the dark. Subsequently, [IrCp*Cl₂] (129 mg, 0.16 mmol) was added and the mixture was stirred for another 24 h. The mixture was filtered through Celite and the filtrate was evaporated to dryness. The solid residue was dissolved in CH₂Cl₂, filtered through Celite and triturated with Et₂O to give an orange precipitate, which was isolated and dried under vacuum. Yield: 70 mg (41%). 1H NMR (500 MHz, CDCl₃): δ = 7.60 (d, JHH = 6.4 Hz, 4H, HCl₂), 7.43–7.37 (m, 6H, HCl₂), 5.80 (bs, 4H, NCH₂), 3.75 (s, 3H, NCH₃), 3.0–2.9 (m, 2H, C–CH₂–C), 1.36 (s, 3OH, Cp–CH₃). 13C[1]H NMR (125 MHz, CDCl₃): δ = 149.7 (C₆H₅), 130.7 (C₆H₅), 126.8 (C₆H₂-trz), 127.8 (C₆H₂-trz), 129.7 (C₆H₂-trz), 88.1(C₆H₂–Me), 50.6(NCH₂), 37.3(NCH₂), 31.5(broad, C–CH₂–C), 9.0(C₆H₅–C). HR-MS (EI): m/z: 1177.2146 (calcd for [M+Na]⁺: 1177.2200. Anal. Calcd. C₂₁H₁₉ClI₄N₉O₂: C, 42.63; H, 4.54 N, 7.28. Found: C, 42.78; H, 4.26; N, 6.45[2].

Synthesis of 6: Compound 4a (100 mg, 0.15 mmol), [IrCp*Cl₂] (115 mg, 0.15 mmol) and Ag₂O (100 mg, 0.43 mmol) were suspended in dry MeCN (10 mL) and stirred at 80°C for 24 h in the absence of light. After cooling to RT, the reaction mixture was filtered through Celite and Et₂O was added, which induced the formation of an orange precipitate. This precipitate was dissolved in MeOH, filtered, and layered with Et₂O, which induced slow formation of an orange precipitate. Further precipitation was accomplished upon storing the mixture at −23 °C for 2 h. The precipitate was collected.


[22] Turnover frequencies for all complexes were highest within the first 10–30 min of the catalytic experiments, i.e. at a stage when conversions were less than 10% and CAN was present in large excess (ca. 18,000:1 CAN/Ir). At this stage, therefore d[CAN]/dt approximates zero.


[25] Multiple elemental analyses of several different recrystallized batches of complexes 5 and 6 consistently revealed correct C/H values but too low N percentages. Potentially, the bimetallic samples may form hardly combustible iridium nitride fractions that lower the measured fraction of N₂.

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Ditopic triazolylidene iridium complexes were evaluated as water oxidation catalysts; the bimetallic arrangement enhances the maximum turnover frequency considerably in catalytic experiments using low catalyst loadings.

**Keywords:** iridium / N-heterocyclic carbene / triazolylidene / water oxidation / bimetallic