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Tunable single-site ruthenium catalysts for efficient water oxidation†

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The catalytic water oxidation activity of mononuclear ruthenium complexes comprising a pyridine-functionalized abnormal triazolylidene ligand can be adjusted by modification of the triazolylidene substituents, which is readily achieved through click-type cycloaddition chemistry, affording some of the most active ruthenium catalyst known thus far for water oxidation (TONs > 400, TOFs close to 7000 h⁻¹).

Efficient water splitting is one of the grand challenges in current chemical research, aiming at disclosing new fuel technologies for covering the increasingly growing global energy needs.1 While catalysts for water reduction have been available for long time, efficient water oxidizing methodologies are much rarer.2 This lack is in part due to the high potential and molecular complexity that need to be overcome in order to accomplish the 4-electron transfer required to generate O₂ from H₂O.

The natural evolution of O₂ at the Mn₄ core of photosystem II1 has provided much stimulus for synthetic advances.3 Multimetallic systems,4 including clusters,5 have been implemented in an attempt to distribute the multielectron transfer over several active sites, thus lowering the number of accessible oxidation states needed for a given metal center. Monometallic complexes, which may offer advantages such as facile ligand tunability and the deduction of structure-activity relationships, have only recently been reported to be active in water oxidation.7 While in some cases, the accessibility of less usual oxidation states has been proposed,8 other systems introduced ligand cooperativity in order to accommodate the extra charges (and holes) during the catalytic cycle.9 Abnormal carbenes such as 1,2,3-triazol-5-yldienes10 may be particularly suitable for such cooperative behavior, as these ligands feature a pronounced mesionic resonance contribution that entails simultaneously electron accepting and donating properties. The recent application of this ligand in the ruthenium-catalyzed base-free oxidation of alcohols may underpin this concept.11 Moreover, mononuclear iridium triazolylidene complexes have shown to be highly active in water oxidation, reaching turnover numbers (TONs) around 10,000.12 Here we report on the expansion of this approach to monometallic ruthenium complexes containing an easily tunable chelating triazolylidene ligand functionalized with a pyridyl donor. Tailoring of the catalytic activity, still rare in water oxidation catalysis, is readily achieved by appropriate modification of the substituent at the triazolylidene nitrogens.

The triazolium salts used as carbene precursors were readily accessible via Cu-mediated [3+2] cycloaddition of azides and alkynes,13 and subsequent methylation at the triazole N3 position (Scheme 1).‡ The ruthenium complexes 2 were prepared from the corresponding pyridine-substituted triazolium salts 1 with AgOTf and subsequent transmetalation using [Ru(cymene)Cl₂]₂. Halide abstraction from 2 with AgOTf and thermal cymene dissociation in refluxing MeCN afforded the dicationic solvent complexes 3 in appreciable yields.14 The formation of the triazolylidene complexes 2 was indicated by NMR spectroscopy, which revealed the disappearance of the resonance around δH 8.5 assigned to the triazolium proton in 1 (CD₂CN solution). In the ¹H NMR spectrum, the ruthenium-bound carbon appears around 172 ppm, corresponding to an approximate 20 ppm downfield shift as compared to the ligand precursor. The exact chemical shift is dependent on the substituent at nitrogen (δC 174.1, 172.9, 172.4, and 174.0 for 2a–2d, respectively), pointing to a moderate tunability of the electron density at this carbon via wingtip substitution.15 Chelation of the pyridine unit in solution is supported by the highfield resonance of the proton in the pyridine ortho position, which shifted from δH 8.4 in 1 to 9.4. The corresponding dicationic acetoniirile complexes 3 displayed similar spectroscopic characteristics for the bidentate triazolylidene ligand. Most diagnostic is the absence of the resonances due to the cymene ligand, and the upfield shift of the ortho-pyridine H to δH 9.1. In the ¹³C NMR spectrum, the ruthenium-bound carbon experiences a slight yet noticeable shift. In particular, the different sequence (δC – 176.3, 174.5, 172.3, and 168.4 for 3a–3d, respectively) suggests some flexibility of the ligand in responding to the altered electronic environment at the ruthenium center in cationic 2 and dicaticionic 3.

Evidence for the connectivity pattern in complexes 2 and 3 was obtained by X-ray crystallographic analyses.16 The molecular structures of complexes 2a and 3a are representative and confirm the C,N-bidentate chelation of the ligand as deduced from solution

‡ Electronic Supplementary Information (ESI) available: Experimental procedures for ligands 1, and complexes 2 and 3, details on catalytic experiments, and crystallographic details for complexes 2a, 2b, 2c, 3a, 3b, 3c, 3d, 4, and 5. See http://www.rsc.org/suppdata/xx/b0/b000000x/
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Studies (Fig. 1). While the Ru–C bond lengths fall within the expected 2.0–2.1 Å range,14 subtle differences have been noted. In the dicaticionic complexes 3, the Ru–C bond distance is 1.999(6) Å and hence significantly shorter than in the monocaticionic complexes 2 (Ru–Ctriarylidyldene 2.028(7) Å). Likewise, the Ru–pyridine distance shrinks from 2.129(7) Å in 2 to 2.092(3) Å in 3. As a consequence of these bond length variations, the ligand bite angle is slightly larger (78.6(12) in 3 vs 76.59(6) in 2), though it remains rather acute. In complexes 3, the Ru–NMCN bond lengths trans to the triazolylidene ligand average to 2.114(7) Å and are thus about 0.08 Å longer than the analogous bonds trans to the pyridine ligand (Ru–N 2.032(2) Å), reflecting the markedly stronger trans influence of the triazolylidene ligand as compared to pyridine.

Electrochemical analyses of the complexes revealed a quasi-reversible oxidation at 1.42 V (vs. SCE) for complexes 2 and at slightly lower potential for complexes 3 (Table 1). Analysis of the oxidation potentials demonstrates a close correlation between electron donor ability of the wingtip group and the ruthenium oxidation potential. Thus, complex 2d comprising a withdrawing Ph substituent displays the highest oxidation potential (E1/2 = 1.445 V) and this potential decreases with increasing donor ability of the substituent R (E1/2 = 1.433 V for R = Me, 1.427 for R = Et, and 1.425 for R = i-Pr). A different trend was observed in the dicaticionic complexes 3 with the oxidation potential increasing from Me < i-Pr < Et << Ph.8 Possibly, stereoelectronic effects may become more dominant in these formally octahedral complexes. Accordingly, bulky substituents at the triazole nitrogen may interfere with the cis coordinating MeCN ligand, resulting in significant distortion from ideal octahedral geometry and thus reducing the ligands’ donor ability into relevant d orbitals. Such a model is further supported by solid-state analyses, which reveal that the angle between the pyridyl nitrogen and the trans coordinated MeCN (i.e. cis to the triazolylidene) deviates more distinctively in 3b and 3c than in 3a.

Complexes 2 and 3 were all active in the oxidation of water using CeIV as sacrificial oxidant (Table 1). The cyrene-containing complexes 2 generated substantial amounts of CO2 along with O2 according to mass spectrometric analysis of the products. The relative CO2 portion gradually increased over time, and was considerably higher with bulkier N-substituent, increasing in the order Me < Et < i-Pr < Ph. In contrast the corresponding dicaticionic complexes 3 produced O2 exclusively. We therefore assume that cyrene rather than the carbene ligand is sensitive towards oxidation. Bulky wingtip groups induce steric congestion and thus tend to facilitate cyrene dissociation.

The dicaticionic complexes 3 are oxidatively stable, producing essentially no detectable CO2, and showing appreciable activity towards O2 formation. Complex 3d is an exception and revealed small but noticeable quantities of CO2, which may be related to the propensity of N-bound phenyl groups to undergo cyclometalation.15

Complex 3a as the most active catalyst precursor of the series was further evaluated under different reaction conditions. At a 1:100 catalyst/oxidant ratio (1 mM catalyst), a marked reduction of catalyst performance was observed after about 10 turnovers, perhaps due to the formation of catalytically inactive dimeric species at high ruthenium concentrations. At a 1:10,000 catalysts/oxidant ratio (0.025 mM catalyst), the turnover numbers (TONs) increased substantially, reaching 105 mol O2 per mol ruthenium after 45 min (i.e. 420 turnovers), and oxidation activity was still ongoing. Hence, catalyst deactivation is efficiently suppressed under dilute reaction conditions.

Catalytic runs at different concentrations indicate a linear relationship between the concentration and the initial turnover frequency, thus supporting homogeneous O2 production at molecular catalytic sites rather than at aggregates. At an 8 mM complex concentration (1:100 catalyst/oxidant), initial turnover frequencies as high as 6660 h-1 were observed. These initial rates are amongst the highest for mono- and dimallic ruthenium complexes reported to date.57 In particular the methyl-substituted complexes 3a is about 100 times more active than previously tested pyridine- and phthalazine-based mononuclear ruthenium complexes.57 The overall TONs seem to correlate with the stereoelectronic effects deduced from electrochemical analyses and thus point to the relevance of electron donating groups for providing easy access to higher oxidation states.

Comparison of complex 3a with the homologous and sterically similar complex 4 comprising a normal imidazol-2-ylidine NHC ligand (Fig. 2) showed the latter complex to be a poor catalyst, providing significant quantities of CO2 as well as low TONs and TOFs. These activity differences thus underline the advantageous role of the arnolinal triazolylidene scaffold. Possibly, triazolylidene ligands may cooperatively assist bond cleavage and oxidation processes through reversible tautomerization of the mesoionic triazolylidene ruthenium aqua complex A to a carbene-

| Complex | E1/2 (V) | rel O2 (%) | rel CO2 (%) | TOF1000s (h-1) | TON |
|---------|---------|------------|------------|----------------|-----|
| 2a      | +1.433  | 99         | 1          | 198            | 18  |
| 2b      | +1.427  | 98         | 2          | 144            | 11  |
| 2c      | +1.425  | 83         | 17         | 21              | 1   |
| 2d      | +1.445  | 66         | 34         | 25              | 2   |
| 3a      | +1.358  | 99.5       | <0.5       | 1080            | 19  |
| 3b      | +1.368  | 99.5       | <0.5       | 612             | 14  |
| 3c      | +1.363  | 99.5       | <0.5       | 576             | 13  |
| 3d      | +1.42‡  | 99         | 1          | 216             | 10  |
| 3e      | +1.500  | 97         | 3          | 7               | 2.4 |
| 5       | n.a.    | 97         | 3          | 7               | 13  |

* Potentials from differential pulse voltammetry using Bu4NF as supporting electrolyte and referenced to SCE using Fe3+/Fe2+ as internal standard; complexes 2 measured in CH2Cl2 (Fc/Fc' +0.46 vs SCE), complexes 3–4 in MeNO2 (Fc/Fc' +0.35 vs SCE).8 Catalytic runs performed with catalyst (1 mM), oxidant (100 mM) in triflic acid solution (0.1 M, pH = 1; 2.0 mL). ‡ relative O2 and CO2 concentrations measured by MS after 100 s. † TOF1000s is the turnover frequency after 1000 s. a broad oxidation and reduction peaks.

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Fig. 1 ORTEP representation of complex 2a (a) and complex 3a (b); 50% probability ellipsoids, non-coordinating anions and hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°) for 2a; Ru–Cl 2.032(1), Ru–N4 2.126(1), Ru–Cl 2.4036(3), Cl–Ru–N4 76.53(4); for 3a; Ru–C7 1.9922(13), Ru–N5 2.0954(11), Ru–N5 2.1166(12), Ru–N6 2.0315(11), C7–Ru–N1 78.34(5).

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type hydroxide complex B (Scheme 2), thus transforming the neutral water ligand into an anionic hydroxide without formally changing the metal oxidation state. Further support for a different (and less efficient) pathway for water oxidation with normal carbene ruthenium complexes may be deduced from the higher TOVs accomplished with the dimetallocatic species 4, though also the bimetallic system produces considerably more CO₂ and is kinetically less competent than the triazolylidine complexes 3.

In summary, a new and simple family of ruthenium-based water oxidation catalysts has been developed. The complexes are readily accessible, and the core triazolylidine ligand is broadly tunable via flexible click-type [3+2] cycloaddition synthesis. The catalytic activity is remarkable, in particular when considering the low complexity of the ligand system, which may become useful for designing synthetic devices for efficient water splitting.

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† The reaction of the pyridine-functionalized triazole with MeOTf was not chemoselective and gave mixtures of the triazolium and the pyridinium salt, indicated by the 'H NMR shift of the pertinent heterocyclic protons; they were separated by preparative TLC.
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Tunable single-site ruthenium catalysts for efficient water oxidation

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Ruthenium complexes comprising a broadly tunable triazolylidene ligand are efficient and robust water oxidation catalysts, producing O₂ exclusively and essentially no CO₂.
