Molecular and heterogenized dinuclear Ir-Cp* water oxidation catalysts bearing EDTA or EDTMP as bridging and anchoring ligands

Chiara Domestici ^a, Leonardo Tensi ^a, Francesco Zaccaria ^{a,*}, Nade Kissimina ^{a,b}, Massimiliano Valentini ^c, Roberto D'Amato ^a, Ferdinando Costantino ^{a,*}, Cristiano Zuccaccia ^{a,*}, Alceo Macchioni ^{a,*}

^aDepartment of Chemistry, Biology and Biotechnology, University of Perugia and CIRCC, Perugia 06123, Italy;

^bÉcole Supérieure d'Ingénieurs de Rennes, University of Rennes 1, Rennes 35042, France;

^cDepartment of Chemistry, Sultan Qaboos University, Muscat 123, Oman;

*alceo.macchioni@unipg.it.

Abstract: The development of efficient water oxidation catalysts (WOCs) is of key importance in order to drive sustainable reductive processes aimed at producing renewable fuels. Herein, two novel dinuclear complexes, [(Cp*Ir)₂(μ-κ³-O,N,O-H₄-EDTMP)] (**Ir-H₄-EDTMP**, H₄-EDTMP⁴⁻ = ethylenediamine tetra(methylene phosphonate)) and [(Cp*Ir)₂(μ-κ³-O,N,O-EDTA)] (**Ir-EDTA**, EDTA⁴⁻ = ethylenediaminetetraacetate), were synthesized and completely characterized in solution, by multinuclear and multidimensional NMR

spectroscopy, and in the solid state, by single crystal X-Ray diffraction. They were supported onto rutile TiO_2 nanocrystals obtaining **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂** hybrid materials. Both molecular complexes and hybrid materials were found to be efficient catalysts for WO driven by NaIO_4 , providing almost quantitative yields, and TON values only limited by the amount of NaIO_4 used. As for the molecular catalysts, **Ir-H₄-EDTMP** (TOF up to 184 min^{-1}) exhibited much higher activity than **Ir-EDTA** (TOF up to 19 min^{-1}), likely owing to the higher propensity of the former to generate a coordination vacancy through the dissociation of a Ir–OP bond ($2.123 \text{ \AA}$, significantly longer than Ir–OC, $2.0913 \text{ \AA}$), which is a necessary step to activate these saturated complexes. **Ir-H₄-EDTMP@TiO₂** (up to 33 min^{-1}) and **Ir-EDTA@TiO₂** (up to 41 min^{-1}) hybrid materials showed similar activity that was only marginally reduced in the second and third catalytic runs carried out after having separated the supernatant, which did not show any sign of activity, instead. The observed TOF values for hybrid materials are higher than those reported for analogous systems deriving from heterogenized mononuclear complexes. This suggests that supporting dinuclear molecular precursors could be a successful strategy to obtain efficient heterogenized water oxidation catalysts.

Keywords: renewable fuels, water oxidation, homogeneous catalysis, heterogenized catalysts, organometallic chemistry, dinuclear complexes.

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1. Introduction

The utilization of fuels generated from renewable sources is a target that our society has to achieve in a relatively short period of time, owing to the rapid depletion of fossil fuels reserves and to the dramatic environmental consequences of their massive exploitation. In order to achieve such a target electrons and protons coming from abundant and cheap raw materials are needed. The best candidate (employed also by Nature) has been individuated in H_2O , whose oxidation is a multistep process providing electrons, protons and exclusively O_2 as a benign by-product (Scheme 1) [1,2]. Unfortunately, water oxidation (WO) is highly demanding from the thermodynamic point of view and extremely difficult from the kinetic one. This has caused an explosion of interest for developing

efficient water oxidation catalysts (WOCs) [3–8]. A large variety of homogeneous [9–17], heterogenized [18–24], and heterogeneous [25–32] WOCs has been proposed but, despite the enormous advances, their performance is not technologically satisfactory, yet [33].

Scheme 1 (Color online) Sketch of the step-wise extraction of protons and electrons from water, leading to benign O_2 , “orchestrated” by a suitable transition metal complex ($[\text{M}]$), having several accessible oxidation states (n = oxidation state of the metal). For simplicity, among the well-established water oxidation reaction mechanisms [1,2], only Water Nucleophilic Attack (WNA) is shown.

Molecular catalysts typically guarantee a very high percentage of active centers (in principle, nearly 100%) and broad tunability through proper selection of the metal center and ancillary ligands. As far as the former is concerned, WOCs based on noble metals, like Ir and Ru, are among the most active reported so far, largely outperforming the analogous base metal systems, especially in terms of TON [34–38]. Therefore, many research efforts are currently devoted to the minimization of

precious metals utilization (by means of “noble metal atom economy”) [35,39], in addition to their replacement with earth-abundant elements [40–42].

The libraries of ancillary ligands screened are vast and varied [34–38,43,44]. Nevertheless, the aspiration of establishing clear structure/properties correlations remains largely unaccomplished, as *in situ* structural modifications of the ligands often occur under the strongly oxidative reaction conditions necessary for WO. A particularly interesting case is that of Ir-Cp* complexes (Cp* = pentamethylcyclopentadienyl), which include some of the known most active molecular WOCs [1,45–59]. The Cp* fragment undergoes major oxidative transformations under catalytic conditions; these modifications are likely necessary, in some cases, for precatalyst activation, but complicate the identification of the true active species and, consequently, the rationalization of ancillary ligand effects on activity [20,60–66].

Along with maximizing activity, ancillary ligand design is often oriented to the introduction of suitable functional groups for anchoring the metal complex on a support, resulting in heterogenized WOCs that combine the advantages of molecular (well-defined precursors, high percentage of active sites) and

heterogeneous (robustness, recoverability) systems [22,35]. Typical supports include metal oxide semiconductors like titanium oxide (TiO_2) [19,20,67], hematite (Fe_2O_3) [68], indium tin oxide (ITO) [23,69] or bismuth vanadate (BiVO_4) [24,70,71], as well as porous materials like metal-organic frameworks (MOFs) [72–75]. The anchoring groups are often oxidation resistant carboxylic ($-\text{COOH}$) [67,69,71,73] or phosphonic ($-\text{PO}_3\text{H}_2$) [18,20,24,69,76,77] acids that, upon deprotonation, can bind the solid surface in a mono-, bi- or, only in the latter case, tri-dentate mode (Fig. 1a). In the case of phosphonated ligands, the connection between the catalyst and oxide support typically consists of a combination of $\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{M}$ hydrogen bonding and coordinative $\text{P}=\text{O}\cdots\text{M}$ and $\text{P}-\text{O}-\text{M}$ bonds [78,79]; only the latter two binding modes are possible with carboxylate ligands, instead [22]. Hydroxamic acids [80,81] and silatranes [21,82] (Fig. 1a) have also shown promising properties, along with a variety of other functionalities [83,84].

(a)

Carboxylic acid

Phosphonic acid

Hydroxamic acid

Silatranes

(b)

$[\text{Ir}(\text{H-EDTA})\text{Cl}]\text{Na}$

Figure 1 Structures of (a) typical examples of anchoring groups for molecular WOCs and (b) $[\text{Ir}(\text{H-EDTA})\text{Cl}]\text{Na}$ complex (dangling carboxylic group used as anchor is highlighted in bold, see main text).

Recently, our group became interested in the possibility of exploiting EDTA-type ancillary ligand for developing heterogenized Ir-WOCs (EDTA = ethylenediamine-N,N,N',N'-tetraacetate). For instance, the dangling $-\text{COOH}$ group of the simple $[\text{Ir}(\text{H-EDTA})\text{Cl}]\text{Na}$ complex (H-EDTA = monoprotonated EDTA; Fig. 1b) [85] was identified as a suitable functionality to anchor this molecular species on several supports. First, $[\text{Ir}(\text{H-EDTA})\text{Cl}]\text{Na}$ was heterogenized on rutile TiO_2 , resulting in a roughly two-fold improvement of TOF (up to 17 min^{-1}) with respect to the molecular precursor, in WO driven by cerium ammonium nitrate (CAN) as sacrificial oxidant (SO) [19]. Despite some small leaching of Ir centers only in the first catalytic run, this heterogenized WOC exhibited very good recyclability, remaining active for more than ten catalytic runs [19]. More lately, the same molecular precursor has been successfully immobilized on a Zr-based MOF with UiO-66 structure [74]. In this case, quite satisfying performance has been obtained in the first catalytic run, although this system exhibits a limited durability [74].

Herein, we report the synthesis and extensive characterization of two novel dinuclear iridium complexes (**Ir-H₄-EDTMP** and **Ir-EDTA**) in which EDTA and its phosphonic analogue ethylenediamine-N,N,N',N'-tetra(methylene phosphonate) (EDTMP, Fig. 2) act as bridging κ^3 -O,N,O-ligands for two Cp*Ir moieties. At the same time, we show how it is possible to take advantage of the anchoring potentialities of their carboxylate and phosphonate functionalities for heterogenizing them onto TiO₂. The resulting hybrid materials (**Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂**) represent rare examples of dinuclear heterogenized WOCs [23,86–88], despite the well-known potential beneficial effect of using two instead of one metal center [89]. Molecular and heterogenized catalysts were tested in WO driven by NaIO₄, exhibiting high efficiency and activity. In particular, the hybrid materials exhibit significantly better performances, in term of efficiency, TOF and recyclability, than analogous materials derived from similar mononuclear complexes.

Figure 2 Generic representation of an Ir(III)-Cp* fragment and of the EDTA and EDTMP-type ligand precursors explored in combination therewith in this paper.

2. Experimental

All the reactions were carried out in air, unless otherwise stated. All organic solvents and rutile TiO₂ (nanopowder, <100 nm particle size, spec. surface area 50 m²/g) were purchased from Sigma-Aldrich and used as received. Distilled water was further purified using a Milli-Q Ultrapure water purification system. [Cp*IrCl₂]₂ [90] and [Cp*Ir(H₂O)₃](NO₃)₂ [91] were prepared according to literature procedures. NMR spectra were recorded at 298 K on a Bruker Avance III 400 spectrometer equipped with a smartprobe (400 MHz for ¹H) with a z gradient coil. NMR spectra were referenced to external TMS or DSS (¹H and ¹³C) and 85% H₃PO₄ (³¹P). To describe the multiplicity of the signals, the following abbreviations are used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quadruplet; m, multiplet. HR-MS experiments were performed on an Agilent 6540 time-of-flight (Q-TOF) system, operated in AutoMS/MS mode, with Dual AJS ESI source that operated positive ionization with N₂ as desolvation gas. X-Ray diffraction patterns of the crystals were recorded at 298 K using a Bruker D8 Venture diffractometer equipped with an Incoatec ImuS3.0 microfocus sealed-tube

MoK α ($\lambda = 0.71073$ Å) source and a CCD Photon II detector. The data collected through generic φ and ω were integrated and reduced using the Bruker AXS V8 Saint Software. The structures were solved and all the thermal parameters were anisotropically refined using the SHELXT and SHELXL packages of the Bruker APEX3 software.

2.1. Synthesis of molecular complexes

2.1.1 *Ir-H₄-EDTMP*

[Cp*Ir(H₂O)₃](NO₃)₂ (50 mg, 0.0989 mmol) and H₈-EDTMP (19.62 mg, 0.045 mmol) were dissolved in 3 mL of water at room temperature and stirred for 16 h. Subsequently, the resulting clean yellow solution was stored at room temperature for about four days, allowing to isolate crystals of **Ir-H₄-EDTMP**. The crystals were separated by filtration, washed with a small amount of water followed by methanol and ether, and finally dried. 20.88 mg of **Ir-H₄-EDTMP** were obtained (Yield 30%). ¹H NMR (D₂O, 298 K): 4.05 (s, N-CH₂CH₂-N), 3.09 (m, P-CH₂-N), 1.48 (s, Cp*Ir). ¹³C NMR (D₂O, 298 K): 58.1 (s, N-CH₂CH₂-N), 53.6 (m, P-CH₂-N, $J_{C-P} = 144$ Hz), 8.7 (s, Cp*Ir). ³¹P{¹H} NMR (D₂O, 298 K): 35.1 (s). HR-MS Calc. for C₂₆H₄₆N₂O₁₂Ir₂P₄: 1088.1343, Found: 1088.1354.

2.1.2 *Ir-EDTA*

[Cp*IrCl₂]₂ (63 mg, 0.079 mmol) and Na₂(H₂-EDTA) (24.8 mg, 0.074 mmol) were combined in 5 mL of a MeOH/water 1:1 v/v solvent mixture at room temperature. The orange slurry was stirred at room temperature and, after 24 h, 2 mL of an aqueous solution of NaHCO₃ (25.2 mg, 0.30 mmol) were added. Stirring the mixture for additional 24 h resulted in the formation of a pale yellow solid. The solid was separated by filtration, washed with MeOH and ether, and finally dried. 41.3 mg of **Ir-EDTA** were obtained (Yield 59 %). ¹H NMR (DMSO, 298 K): 3.91 (d, ²J_{HH} = 16.0 Hz, N-CH₂-COO), 3.74 (s, N-CH₂CH₂-N), 3.50 (d, ²J_{HH} = 16.0 Hz, N-CH₂-COO), 1.60 (s, Cp*Ir). ¹³C{¹H} NMR (DMSO, 298 K): 179.0 (s, N-CH₂-COO-Ir), 84.2 (s, Cp_(quaternary)*Ir), 64.0 (s, N-CH₂-COO), 61.5 (s, N-CH₂CH₂-N), 9.2 (s, Cp*Ir). HR-MS Calc. for C₃₀H₄₂N₂O₈Ir₂: 944.2283, Found: 944.2293.

2.2. *Anchoring molecular WOCs onto TiO₂*

The immobilization of complexes **Ir-H₄-EDTMP** (4.6 mg), **Ir-EDTA** (2.1 mg) onto TiO₂ was achieved by simply contacting rutile TiO₂ nanoparticles (1 g) with a water solution of each complex (5 mL). The suspension was stirred for 24 h. The solid was then recovered by centrifugation, washed several times with water, followed by acetonitrile and dichloromethane, and finally dried under vacuum.

The iridium content was determined by ICP-OES analysis. A weighed amount of catalyst (ca. 200 mg) was dissolved in 4 mL of HF (40%). After the complete dissolution of the solid, the solution was diluted with fuming HNO_3 to a final volume of 25 mL and then analyzed.

2.3. Catalytic tests

Manometric measurements were performed using two homemade jacketed glass reactors coupled to a Testo 521-1 manometer, following previously optimized procedures [54]. In a typical run with molecular catalysts, the NaIO_4 solution in 5 mL of buffered water (pH 7 by 0.2 mol/L phosphate buffer) were loaded into the first reaction vessel (working cell), while an equal amount of neat water was loaded into the second one (reference cell). Both reactors were sealed with a rubber septum, connected to the manometer, kept at a constant temperature of 25 °C and placed under stirring for 20 min. Acquisition was started. When a steady baseline was achieved, a volume of a solution of catalyst in buffered water was injected into the working cell. The concentration of the stock solution of catalyst was adjusted, depending on the final concentration desired, in order to have a maximum injection volume of 250 μL . The total gas evolved was estimated by

measuring the differential pressure between the working and reference cell. The resulting p vs. t profiles were processed as reported in Ref. [54].

In a typical heterogeneous-phase water oxidation experiment, the immobilized catalysts were suspended in 4.5 mL of buffered water, and the catalysis was started by injecting 0.5 mL of a stock solution of sacrificial oxidant. After each run, the mixture was centrifuged. The solid was separated from the supernatant solutions, and re-used for the subsequent experiment under the same conditions used for the previous run. The mass of the solid catalysts remains nearly constant before and after the catalytic runs, although minor loss of material cannot be excluded, due to the absorption of some phosphate groups on the TiO_2 support during the catalysis (*vide infra*) slightly altering the composition of the samples. The supernatant solution was filtered and then tested for catalytic activity.

3. Results and Discussion

3.1. Synthesis and characterization

3.1.1. Molecular catalysts

The reactivity of the Ir-Cp* precursors with EDTA and EDTMP, which can potentially bind at iridium in κ^1 to κ^6 modalities, was initially investigated *in situ*

by means of NMR spectroscopy. As a case study, the results obtained for H₈-EDTMP (i.e., fully protonated EDTMP), possessing P atoms as convenient spectroscopic probes, are discussed more in detail. Addition of a sub-stoichiometric amount of [Cp*Ir(H₂O)₃](NO₃)₂ (**Ir-H₂O**) to a solution of H₈-EDTMP in D₂O resulted in the partial consumption of the starting phosphonic acid, as evidenced by the decrease of the signal at 8.4 ppm in the ³¹P NMR spectrum, and the appearance of two new peaks with comparable integrals at 6.8 and 35.8 ppm, which are typical values for free and coordinated phosphonate moieties, respectively. Analogously, analysis of the ¹H NMR spectrum revealed the drop of the singlet at 3.86 ppm and the doublet at 3.50 ppm, relative to the N-CH₂CH₂-N and the N-CH₂-P protons of H₈-EDTMP, respectively, and the formation of two new sets of corresponding multiplets at 4.15–3.96 and 3.49–3.09 ppm. Furthermore, the typical singlet of Ir-Cp* protons appeared at 1.48 ppm. These observations are consistent with the κ^3 -coordination of a partially deprotonated H₆-EDTMP ligand to a Ir-Cp* moiety by means of two oxygen and one nitrogen donor atoms (**Ir-H₆-EDTMP** in Scheme 2).

Scheme 2 Reaction pathway for the synthesis of **Ir-H₄-EDTMP**.

A further addition of **Ir-H₂O** to the mixture, besides increasing the amount of **Ir-H₆-EDTMP**, led to the formation of a new species exhibiting a single ^{31}P NMR resonance at $\delta_{\text{P}} = 35.1$ ppm. The formation of the latter compound was nearly complete when about two equivalents of **Ir-H₂O** had been added (Fig. 3). Such species appears to have a symmetric EDTMP backbone; integration of ^1H NMR signals (Fig. 3) shows a 2:1 molar ratio between **Cp*** and EDTMP moieties. These results indicate the formation of a dinuclear complex in which **H₄-EDTMP** binds two **Ir-Cp*** fragments, using its two PNP halves as dianionic tridentate ligands (**Ir-H₄-EDTMP** in Scheme 2). It should be noted here that aged solutions of **Ir-H₄-EDTMP** in unbuffered water always contains a small fraction of **Ir-H₆-EDTMP**, indicating that this complex undergoes relatively facile hydrolysis (Fig. 3; see below for further discussion).

Ir-H₄-EDTMP was successfully synthesized on a larger scale using a slight excess of **Ir-H₂O** with respect to H₈-EDTMP (see Experimental Section), while attempts to isolate the mononuclear **Ir-H₆-EDTMP** were unsuccessful (see the Supplementary materials). **Ir-H₄-EDTMP** single crystals of good quality for X-Ray diffractometric studies were obtained from its saturated aqueous solutions. Crystallographic analysis provided the structure reported in Fig. 4a, confirming the conclusions reached by NMR investigation. To the best of our knowledge, this is the first dinuclear EDTMP complex thoroughly characterized by NMR and single crystal X-ray diffraction; rare examples of analogous compounds were reported for some first row transition metals like Fe, Ni and Cu several decades ago [92–94].

Figure 3 (Color online) Representative ^1H (left) and ^{31}P (right) NMR spectra (298 K, D_2O) of **Ir-H₄-EDTMP** and **Ir-H₆-EDTMP** mixtures, obtained by dissolving crystals of **Ir-H₄-EDTMP** in D_2O and aging the resulting solution. Blue and red labels refer to **Ir-H₄-EDTMP** and **Ir-H₆-EDTMP**, respectively (see Scheme 2).

Ir-H₄-EDTMP exhibits a highly symmetric structure with an inversion point lying in the middle of the ethylene bridge (Fig. 4a). The Ir–N (2.26 Å) and Ir–O (2.11–2.12 Å) distances are comparable to those found in other Ir(III)-Cp* amine [95] and phosphonate [96] complexes. The Ir–Cp* centroid distance (1.758 Å) is slightly lower than that found in similar compounds (1.77–1.82 Å) [46,52,55,95,96], indicating a relatively high electrophilicity of the metal center. Phosphonate groups establish H-bonds with water, as well as with other **Ir-H₄-EDTMP** molecules in their proximity (see the Supplementary materials).

Figure 4 (Color online) ORTEP representations of complexes **Ir-H₄-EDTMP** (a) and **Ir-EDTA** (b); structure at 50% probability level, hydrogen atoms and solvent molecules omitted for clarity. Selected bond distances (Å) and angles (°) for **Ir-H₄-EDTMP**: Ir–O1 = 2.123(1), Ir–O4 = 2.113(1), Ir–N = 2.257(1), Ir–Cp* = 1.758, O1–Ir–N1 = 83.49(5), O4–Ir–N1 = 76.32(5) O1–Ir–Cp* = 125.25, O4–Ir–Cp* = 129.48, N1–Ir–Cp* = 138.70. Selected bond distances (Å) and angles (°) for **Ir-EDTA**: Ir–O1 = 2.0913(19), Ir–O3 = 2.0784(19), Ir–N = 2.206(2), Ir–Cp* =

1.766, O1–Ir–N1 = 77.77(7), O3–Ir–N1 = 78.99(7), O1–Ir–Cp* = 129.11, O3–Ir–Cp* = 128.57, N1–Ir–Cp* = 139.13.

The reaction of **Ir-H₂O** with H₄-EDTA proceeded analogously to that with H₈-EDTMP. Nevertheless, the addition of a base, like NaHCO₃, was necessary to deprotonate the carboxylate groups of the ligand; higher yields were obtained using [Cp*IrCl₂]₂ (**Ir-Cl**) rather than **Ir-H₂O** precursor (Scheme 3 and Experimental Section). The ¹H NMR spectrum of **Ir-EDTA** in DMSO-*d*₆ (Fig. 5) is consistent with a dinuclear structure analogous to that proposed for **Ir-H₄-EDTMP**. Also in this case, X-ray studies of single crystals, obtained by slowly cooling down a hot saturated aqueous solution, confirmed the dimeric structure deduced by NMR spectroscopy (Fig. 4b). The crystal structure of **Ir-EDTA** exhibits many similarities with that of **Ir-H₄-EDTMP**. Despite this, Ir–O (2.07–2.09 Å) and Ir–N (2.21 Å) bonds are shorter than in **Ir-H₄-EDTMP**, whereas Ir–Cp* centroid bond (1.77 Å) is longer. This points to a somewhat stronger binding of EDTA at the metal center. The two O–Ir–N angles are very similar to each other (77.8° and 79.0°), while a small but appreciable difference is observed in **Ir-H₄-EDTMP** (76.3° and 83.5°). Dinuclear complexes with bridging EDTA ligands have been already reported for a variety of main group [97–100] and transition

[101-110] metals, as well as for some lanthanides [111] and actinides [112]. Concerning Group 9 elements, the dinuclear Co-Cp* [113] and Rh-Cp* [114] EDTA complexes are known, although no crystal structure is available, whereas the one described here is the first example of the Ir-based analogue, to the best of our knowledge.

Scheme 3 Reaction pathway for the synthesis of **Ir-EDTA**

Figure 5 ^1H NMR spectrum ($\text{DMSO-}d_6$, 298 K) of **Ir-EDTA**.

3.1.2. Immobilization of molecular catalysts onto TiO_2

Ir-H₄-EDTMP and **Ir-EDTA** were supported by dispersing TiO_2 in the aqueous solutions of these complexes, and then carefully recovering and washing the solid particles (see Experimental Section). The iridium content in heterogenized catalysts, **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂**, was determined by ICP-OES analysis to be 0.823 and 0.463 $\mu\text{mol/g}$, respectively. The higher iridium loading in **Ir-H₄-EDTMP@TiO₂** might be due to the slightly higher amount of molecular catalysts used in the synthesis of this system, as well as to the known higher effectiveness of the phosphonate group to serve as anchor on TiO_2 [22]. SEM images of the two catalysts are reported in Fig. S1 (online), showing homogeneously shaped nanometric particles in both cases. A homogenous distribution of iridium and, in the case of **Ir-H₄-EDTMP@TiO₂**, phosphorous centers is observed (Fig. 6), meaning that the complex is very likely well distributed over the TiO_2 particles surface, without formation of aggregates. However, the small amounts present hamper accurate quantification by EDX analysis.

Figure 6 (Color online) EDX maps of (a) **Ir-H₄-EDTMP@TiO₂** and (b) **Ir-EDTA@TiO₂** before catalytic runs.

3.2 Catalytic tests in homogeneous phase with **Ir-H₄-EDTMP** and **Ir-EDTA**

Ir-H₄-EDTMP and **Ir-EDTA** were tested as homogenous WOCs using sodium periodate (NaIO₄) as SO at pH 7 by phosphate buffer (0.2 mol/L); the course of reaction was monitored measuring the evolved O₂ by differential manometry. Iridium and SO concentrations were varied in the 2.5–20 µmol/L and 2.5–20 mmol/L range, respectively. As the two metal centers in the dinuclear complexes can potentially act as independent active sites, iridium rather than catalyst nominal concentrations are considered. The results are summarized in Table 1, while additional selected experiments, using the Clark electrode to probe oxygen evolution, are reported in the Supplementary materials.

Table 1 Summary of catalytic experiments with **Ir-H₄-EDTMP** and **Ir-EDTA** in homogeneous phase ^{a)}.

Entry	Cat	[Ir] (µmol/L)	[NaIO ₄] (mmol/L)	TON	Yield (%)	TOF _{max} (min ⁻¹)
1	Ir-H₄-EDTMP	2.5	20	3786 ± 38	95	184 ± 18

2	Ir-H₄-EDTMP	5	2.5	180 ± 18	72	25 ± 2
3	Ir-H₄-EDTMP	5	5	454 ± 45	91	70 ± 7
4	Ir-H₄-EDTMP	5	10	980 ± 98	98	111 ± 11
5	Ir-H₄-EDTMP	5	20	1967 ± 197	98	122 ± 12
6	Ir-H₄-EDTMP	10	20	998 ± 100	>99	102 ± 10
7	Ir-H₄-EDTMP	20	20	433 ± 43	87	85 ± 8
8	Ir-EDTA	2.5	20	2712 ± 27	68	19 ± 2
9	Ir-EDTA	5	2.5	257 ± 26	>99	5.8 ± 0.6
10	Ir-EDTA	5	5	482 ± 48	96	8.6 ± 0.9
11	Ir-EDTA	5	10	929 ± 93	93	13 ± 1
12	Ir-EDTA	5	20	1489 ± 15	74	14 ± 1
13	Ir-EDTA	10	20	767 ± 77	77	12 ± 1
14	Ir-EDTA	20	20	449 ± 45	90	10 ± 1

^{a)} Experimental conditions: 25 °C, 5 mL H₂O, pH 7 by phosphate buffer. 10 % error assumed on TON and TOF values [54].

Figure 7 (Color online) Kinetic trends for **Ir-H₄-EDTMP** (25 °C, 5 mL H₂O, pH 7 by phosphate buffer) at different catalyst (a) and NaIO_4 (b) concentrations.

Both species appear to be suitable precatalysts for WO, with yields of O_2 (based on utilized NaIO_4 concentration) above 90% in most cases; minor fluctuations in yield have been observed also in previous studies, and are attributed mainly to

experimental uncertainty [54]. The performance of **Ir-H₄-EDTMP** is comparable to that of the fastest Ir-Cp* based WOCs [34–38], with TOFs up to $\sim 184 \text{ min}^{-1}$ (Table 1; entries 1–7). Two sets of experiments, carried out by selectively varying [Ir] (entries 1, 5–7 and Fig. 7a) or [NaIO₄] (entries 2–5 and Fig. 7b), allowed to derive the reaction orders in active metal centers and SO, respectively (Fig. S2 online). The former order is found to be lower than one and of about 0.6, possibly indicating the *in situ* formation of aggregated multinuclear active species. The order in [NaIO₄] is ~ 0.7 , which is a typical value for molecular Ir-WOCs under analogous reaction conditions [54]. Importantly, catalytic tests reported here were performed using freshly prepared catalysts solutions in water, to prevent significant hydrolysis of **Ir-H₄-EDTMP** prior to injection in the reactor (*vide supra*). Indeed, boosts of activity are observed in duplicate experiments when catalysts solutions aged over several hours were used, likely due to the formation of sizable amounts of the highly active **Ir-H₂O** [47,54].

The catalytic performance of **Ir-EDTA** (Table 1, entries 8–14) is appreciably lower than that of **Ir-H₄-EDTMP**. For instance, under the representative conditions [Ir] = 5 $\mu\text{mol/L}$ and [NaIO₄] = 20 mmol/L , the TOF of **Ir-EDTA** (14 min^{-1} ; Table 1, entry 12) is approximately one order of magnitude lower than that

of the phosphonate analogue (122 min^{-1} ; Table 1, entry 5). Also in the case of **Ir-EDTA**, reaction orders in iridium and SO were determined, and found to be about 0.7 and 0.4, respectively (Figs. S1 and S3 online).

It is important to outline that both **Ir-H₄-EDTMP** and **Ir-EDTA** are 18 electrons, coordinately saturated, organometallic complexes, which have to open up one coordination site in order to act as WOCs. This can occur *via* the detachment of a phosphonate/carboxylate group by protonolysis of the Ir–O bond (Scheme 4a), likely followed by the aforementioned degradation of the Cp* ligand that ultimately leads to the active species. Alternatively, but less likely, a η^5 - η^3 oxidative slippage of Cp* might initially occur; this should result in several η^3 (or even η^2) oxidized ligands [61,66], therefore liberating a coordination site at the iridium center, while still preserving a fully O,N,O-coordinated EDTMP/EDTA ligand (Scheme 4b). However, previous studies demonstrated that the latter route is difficultly viable when saturated Ir complexes, like the aforementioned Kläui-type compounds [20,24], are reacted with a SO; this is likely due to the fact that Cp* degradation is initiated by an Ir-(di)oxo species, which can be formed only if the SO can approach the metal center [61]. It appears therefore plausible that activation of the dinuclear Ir-WOCs studied here occurs via the route depicted in

Scheme 4a. The higher tendency of the phosphonate rather than carboxylate group to detach from iridium, highlighted in the above discussed NMR studies, might result in an easier activation of **Ir-H₄-EDTMP**, likely explaining its higher catalytic activity with respect to **Ir-EDTA**.

Scheme 4 (Color online) Two possible activation pathways of **Ir-H₄-EDTMP** and **Ir-EDTA**: (a) detachment of a phosphonate/carboxylate group or (b) η^5 - η^3 oxidative slippage of Cp*. E = C or P –OH; red arrows highlight the coordination vacancy.

Finally, it is worth mentioning that opposite activity trends have been observed, for instance, for molecular WOCs based on Ru complexes with bipyridyl diphosphonate vs. dicarboxylate ligands [115,116]. In that case, however, the effects on activity appear to be directly linked to the specificities of those

complexes, as the replacement of the parental --COO^- with --PO(OH)O^- groups resulted in a change in the mechanism of O–O bond formation from bimolecular coupling of two Ru-oxyl species to monomolecular water nucleophilic attack to a Ru-oxo intermediate. These profound changes were evidenced also by a significant variation of the bite angle of the substituted bipyridyl ligands, with a less strained configuration obtained with the phosphonate groups that, consequently, bind the Ru center more strongly than the carboxylate analogues [115,116]. The above described close similarity of the **Ir-H₄-EDTMP** and **Ir-EDTA** structures, and the pieces of evidence for a more labile phosphonate ligand coordination to Ir, indicate that no straightforward comparison can therefore be made with those ruthenium WOCs.

3.3 Catalytic tests in heterogeneous phase with supported catalysts

Having proved that **Ir-H₄-EDTMP** and **Ir-EDTA** competently catalyze WO, the performance of their heterogenized analogues **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂** was explored, as well. Reactions were carried out under analogous experimental conditions to those described in the previous section. Results are summarized in Table 2.

Table 2 Summary of catalytic experiments with **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂** in heterogeneous phase ^{a)}.

Entry	Cat	Run	TON	Yield (%)	TOF _{max} (min ⁻¹)
1	Ir-H₄-EDTMP@TiO₂	I	927 ± 93	93	33 ± 3
2	Ir-H₄-EDTMP@TiO₂	II	850 ± 85	85	31 ± 3
3	Ir-H₄-EDTMP@TiO₂	III	886 ± 86	89	22 ± 2
4	Ir-EDTA@TiO₂	I	863 ± 86	86	41 ± 4
5	Ir-EDTA@TiO₂	II	922 ± 92	92	39 ± 4
6	Ir-EDTA@TiO₂	III	896 ± 90	90	32 ± 3

^{a)} Experimental conditions: [NaIO₄] = 20 mmol/L, 25 °C, 5 mL H₂O, pH 7 by phosphate buffer, [Ir] = 10 µmol/L.

Figure 8 (Color online) Kinetic trends for the first, second and third catalytic runs recorded using (a) **Ir-H₄-EDTMP@TiO₂** or (b) **Ir-EDTA@TiO₂**. ([NaIO₄]=20 mmol/L, 25 °C, 5 mL H₂O, pH 7 by phosphate buffer, [Ir] = 10 μmol/L; see also Table 2). TON vs. *t* plots for the first supernatant solutions are shown for comparison (see main text).

Experiments were performed at [Ir] = 10 μmol/L and [NaIO₄] = 20 mmol/L. Three successive runs were carried out for each system, to preliminary evaluate their recyclability. After each run, the hybrid material was recovered and separated

from the supernatant, and both fractions were further tested at $[\text{NaIO}_4] = 20$ mmol/L (Table 2). Interestingly, all supernatants did not show any activity (Fig. 8), whereas high yield was observed for both **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂** in all runs ($> 85\%$), with high TOF values that exhibited just a little decrease from one run to the other (Table 2; see below for further discussion on this point). A blank test, performed with commercial TiO₂, resulted in no catalytic activity, in line with previous reports [19].

TOF values observed for **Ir-H₄-EDTMP@TiO₂** (up to 33 min^{-1}) are similar to those of **Ir-EDTA@TiO₂** (up to 41 min^{-1}), and among the highest ever reported for heterogenized catalysts. For example, the aforementioned $[\text{Cp}^*\text{Ir}\{\text{P}(\text{O})(\text{OH})_2\}_3]\text{@TiO}_2$ showed a maximum TOF value of 23.7 min^{-1} , under similar experimental conditions, which rapidly drop to 11.1 and 7.5 min^{-1} in the second and third catalytic run, respectively [20]. This indicates that **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂** are promising catalytic systems for WO not only because of their remarkable activity but also for their increased stability and recyclability.

It is somewhat surprising that, once anchored to TiO_2 , **Ir-EDTA** catalytic precursor leads to comparable and even slightly higher performances than **Ir-H₄-EDTMP**, while markedly higher TOFs are observed for the latter catalyst in homogeneous phase. Nevertheless, it has to be recalled that **Ir-H₄-EDTMP** easily undergoes decoordination of the phosphonate arm(s) in solution, whereas decoordination of a carboxylic group is more difficult in **Ir-EDTA**, likely making the activation of the latter molecular catalyst rather slow (*vide supra*). However, it can be speculated that the anchoring of **Ir-EDTA** on the TiO_2 surface occurs through a dangling carboxylic arm that, in difference to $[\text{Ir}(\text{H-EDTA})\text{Cl}]\text{Na}$ (Fig. 1b) [19], has to be formed by detachment from the iridium center. The same could occur for **Ir-H₄-EDTMP**, although this complex might also exploit the additional –OH functionality as anchoring group. That necessary opening up of **Ir-EDTA** therefore facilitates the generation of the active species, likely explaining the leveling off of **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂** activities and also the unusual boost of activity on passing from molecular **Ir-EDTA** (up to 19 min^{-1}) to heterogenized **Ir-EDTA@TiO₂** (TOF up to 41 min^{-1}).

Post-catalysis SEM characterization shows that no evident changes in the morphology of the particles occurred with both heterogenized catalysts (Fig. S5

online). Some non-crystalline phosphate groups are observed, which likely derive from adsorption of the phosphate used as buffer on titanium oxide; no accurate quantification is possible due to the small amounts present. It should be noted here that the mass of solid catalysts recovered after WO experiments is nearly identical to the initial one. However, due to the small variation of catalyst composition, it cannot be excluded that a minor loss of material occurred during the filtration procedure, and that the absorbed phosphate on TiO_2 apparently compensated this loss. In line with the latter hypothesis, a small decrease of the nominal iridium content was detected by ICP-OES for the two materials after catalytic tests (from 0.823 to 0.712 $\mu\text{mol/g}$ for **Ir-H₄-EDTMP@TiO₂** and from 0.463 to 0.396 $\mu\text{mol/g}$ for **Ir-EDTA@TiO₂**). This might contribute to explain the small decrease of nominal TOF observed in the second and third catalytic runs (Table 2).

4. Conclusions

The dinuclear complexes **Ir-H₄-EDTMP** and **Ir-EDTA** are found to be versatile complexes exhibiting rather similar structural features, but markedly different stability and catalytic performance in water oxidation driven by NaIO_4 . Particularly, the weakness of the Ir-phosphonate bond, compared to the Ir-carbonate one, facilitates the generation of coordination vacancy and,

consequently, of the active species, thus leading to increased WO activity (TOF up to 184 min^{-1}). Nevertheless, once supported on TiO_2 , hybrid materials **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂** are obtained, which behave similarly as heterogenized WOCs; this might be explained considering that anchoring the complexes on TiO_2 necessarily requires the detachment of a binding group from the iridium center, therefore annihilating the difference between phosphonate and carboxylate ligands for what concerns the generation of the coordination vacancy. Remarkable performance was observed for **Ir-H₄-EDTMP@TiO₂** and **Ir-EDTA@TiO₂**, both in terms of TOF (up to 41 min^{-1}) and recyclability, which are significantly higher than those of similar materials derived from mononuclear complexes. This suggests that anchoring dinuclear complexes might be a successful strategy for developing highly active WOCs, which deserves to be further investigated.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Alceo Macchioni and Ferdinando Costantino designed the research and interpreted the data; Chiara Domestici, Leonardo Tensi, Nade Kissimina, Roberto D’Amato and Massimiliano Valentini performed the synthesis, characterization and testing of the catalysts; Francesco Zaccaria analyzed the data and wrote the manuscript together with Alceo Macchioni; Cristiano Zuccaccia designed and performed reactivity studies by NMR spectroscopy; all the authors discussed the results and commented on the manuscript.

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Chiara Domestici is a Ph.D. student at University of Perugia under the supervision of Prof. Alceo Macchioni. During her undergraduate studies, she worked on organometallic catalysts for a hydrogen-based economy, joining the Prof. Muller's group at the Freie Universität Berlin (Germany) as visiting master trainee. Her current scientific interests concern the development and characterization of iridium based complexes for catalysis and energy applications.

Francesco Zaccaria gained his Ph.D. degree in Chemical Sciences from the Federico II University of Naples with Prof. Busico (2018), and he was a visiting student in the UK at the Imperial College London with Prof. Britovsek (2017) and at the University of East Anglia with Prof. Bochmann (2014). Now, he is a post-doctoral fellow at the University of Perugia, working with Prof. Macchioni on olefin polymerization and water oxidation catalysis.

Ferdinando Costantino received his Ph.D. degree in Chemistry from University of Perugia in 2005 and in 2006 worked in Rennes as Post-Doc fellow. He is associate professor of inorganic chemistry at the University of Perugia. His scientific interests are on hybrid materials based on phosphonates and MOFs for gas adsorption, catalysis and proton conductivity.

Cristiano Zuccaccia obtained his Ph.D. degree from the University of Perugia, where he holds the position of associate professor since 2015. His research interests include development and application of NMR methodologies for (i) the investigation of ion pairing and other non-covalent interactions in solution, (ii) mechanistic studies to rationalize structure-reactivity relationships of early and late transition metal organometallics relevant to catalytic transformations such as olefin polymerization and production of renewable fuels.

Alceo Macchioni is Full Professor of General and Inorganic Chemistry at the University of Perugia. His research interests include the development of catalysts relevant to the production of renewable fuels and the investigation of the structure/activity relationships in organometallic catalysts for olefin polymerization, by means of multinuclear and multidimensional NMR spectroscopy.