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Synthesis of Pyridine-Alkoxide Ligands for Formation of Polynuclear Complexes

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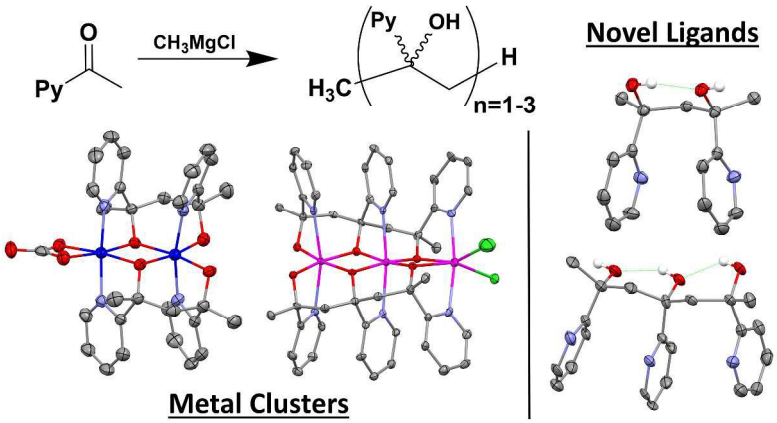
ABSTRACT:

We have prepared and characterized a series of novel polydentate N,O-donor ligands derived from our well-studied ligand 2-(2-pyridyl)-isopropanol (**pyalkH**), having the general formula $Me\{C(OH)(2\text{-}py)CH_2\}_nH$, where n = 2 or 3. Like **pyalkH**, these analogues bind via N and O with deprotonation at the latter, thus extending the strongly donor pyridine-alkoxide chelation power of **pyalkH** to polydentate forms. The greater denticity allows for more effective binding and polynuclear cluster formation with first-row transition metals. Several stable alkoxo-bridged polynuclear clusters of these ligands with Mn, Cu, Co and Ni have been prepared; all reported ligands and complexes have been characterized, including by X-ray crystallography. We report a one-step synthesis of these ligands, alongside **pyalkH**, on a multi-gram scale from inexpensive starting materials. We have also developed a new scalable procedure for the isolation of **pyalkH** that avoids the need for chromatography, making large-scale production of this ligand commercially viable.

TOC TEXT

A series of novel polydentate N,O-donor ligands strongly favour formation of polynuclear complexes.

TOC



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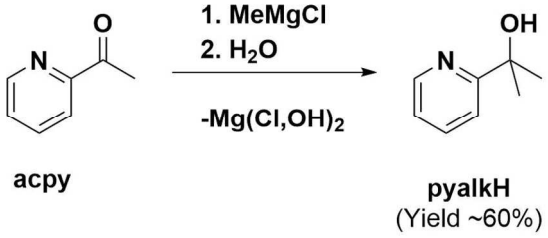
INTRODUCTION

Polynuclear complexes of redox active metals are of current interest[1] because they can be effective catalysts for multielectron reactions,[2] such as water oxidation. Indeed, the oxygen-evolving complex in photosynthesis, as well as several synthetic water-oxidation catalysts (WOCs) contain multiple metal centers.[3] Polynuclear complexes of the first row require appropriate ligand frameworks[2b,4] to avoid ligand lability. Multiply chelating polydentate ligands may help stabilize the cluster and prevent ligand loss on redox cycling.[5] At the same time, however, synthesis of large, intricate ligands can be a very time-consuming and costly process, offsetting the benefit of using cheap, first-row metals. An ideal ligand would bear the desirable functionality while at the same time be easily synthesized from inexpensive precursors.

The oxidation-resistant, bidentate **pyalkH** ligand, 2-(2-pyridyl)-isopropanol (Scheme 1), has proved useful in stabilizing unusually high oxidation states,[6] such as Rh(IV),[7] in which cases it deprotonates to give the alkoxide **(pyalk)** on coordination. Catalysis is also seen in the case of our iridium **pyalk** complexes that act as robust homogeneous and heterogenized WOCs.[2c,7a] This ligand has several desirable properties,[7a] including strong donor power, high resistance to oxidative degradation, amphiphilic solubility, and stable binding.[8] However, its bidentate character limits the ability to promote stable polynuclear clusters.

The previously reported synthetic procedure for **pyalkH** (Scheme 1) was suboptimal in needing costly column chromatography, which negated the benefit of employing cheap precursors.[9] We now report an improved procedure for **pyalkH** that eliminates any chromatography and allows straightforward mole-scale production of the ligand using standard laboratory equipment. This advancement is particularly significant as **pyalkH** has found commercial applications.[ref]

Scheme 1. Synthesis of pyalkH via Grignard methylation.



In an important advantage of the improved process, we can now isolate a series of new polydentate ligands related to **pyalkH** (Scheme 2), which are formed during its synthesis. These aliphatic-backbone tetradentate dimers and hexadentate trimers have the same functionality as **pyalkH** but with higher denticity, allowing for binding of multiple metals. Due to the structural constraints, it is practically impossible for any of these ligands to bind to a single metal center with more than 3 out of 4 or 4 out of 6 coordinating groups, which encourages coordination to additional metal centers. Furthermore, the deprotonated alkoxo groups are very electron-rich, and as a result are commonly observed to coordinate to two metal centers. The combination of these

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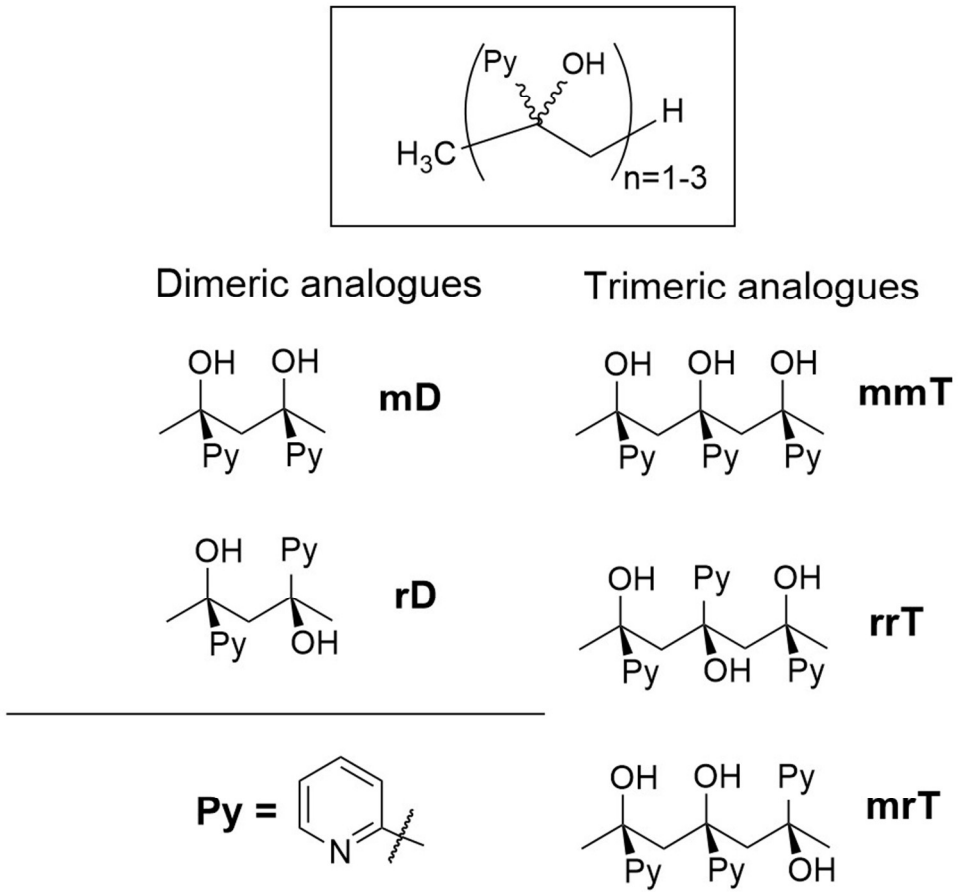
two features makes these ligands especially suitable for the preparation of transition metal clusters.

Several stable oligonuclear complexes of these ligands with first-row metals (Mn, Co, Ni, and Cu) have now been characterized, demonstrating robust cluster formation. We report a procedure for preparing these ligands on a multi-gram scale in a single step, along with a significantly improved isolation procedure for the original **pyalkH** ligand.

Scheme 2. Isolated oligomeric pyalkH derivatives. Top: Generalized polymer structure showing the relationship between the ligands: pyalkH (n = 1), mD and rD (n = 2), mmT, rrT, and mrT (n = 3). Chiral species isolated as racemic mixtures.



RESULTS AND DISCUSSION

Ligand synthesis

We were initially alerted to the existence of the oligomeric pyridinols of Scheme 2 by the unexpected formation of crystals of **1** (Figure 1) in a reaction between $CoCl_2$ and an excess of crude **pyalkH** ligand that had not been purified by column chromatography. Prior reported ligand separation conditions (ethyl acetate/hexane) result in very broad TLC bands that seem

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consistent with the sole presence of 2-acetylpyridine starting material and **pyalkH**. Adding 1% triethylamine to the eluent improved the separation, resulting in the resolution of two new elution bands following the **pyalkH** band. A large scale synthesis showed these to be the *rac* and *meso* diastereomers of the methylene-bridged dimer structure ($Me\{C(OH)pyCH_2\}_nH$, n = 2), **rD** (first band) and **mD** (second band) respectively (Scheme 2). At larger scales, three additional lesser bands are revealed, and proved to be the three trimer diastereomers **mmT**, **rrT**, and **mrT** (Scheme 2).

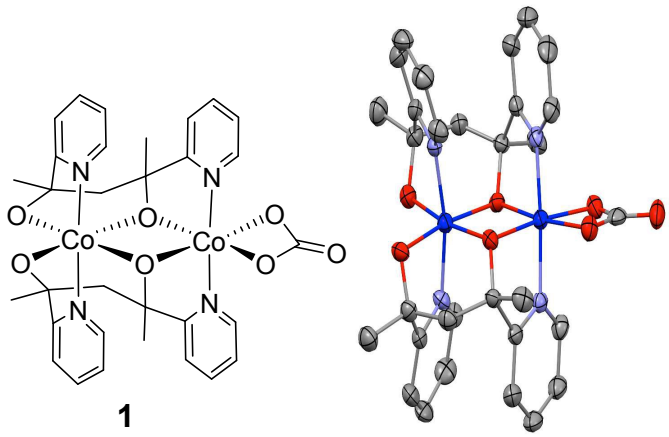

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Figure 1. Schematic and crystallographic structure of complex **1**. Thermal ellipsoids drawn at 50% probability level; hydrogen atoms are omitted for clarity.

Formation of these oligomers can be rationalized in terms of common Grignard side reactions. Scheme 3 shows how deprotonation of 2-acetylpyridine by the Grignard to form the enolate anion, followed by an aldol coupling with 2-acetylpyridine could give a monodeprotonated ketol (**aD**) that could then be methylated by the Grignard to **mD** or **rD**. A second aldol reaction between **aD** and another enolate could form a keto-diol (not isolated) followed by methylation to give **rrT**, **mrT** or **mmT** (Scheme 4). This aldol-chain reaction also presumably forms heavier oligomers, but these could not be isolated due to diminishing abundance and increased polarity and isomer multiplicity. In addition to the saturated pyridinols, product mixtures also contained 2-acetylpyridine and **aD**, even when a considerable excess of Grignard reagent was added, implying that their deprotonated states cannot undergo methylation.

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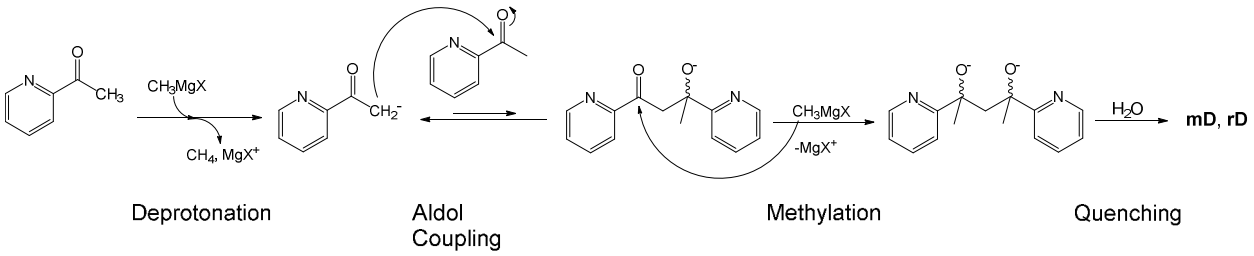
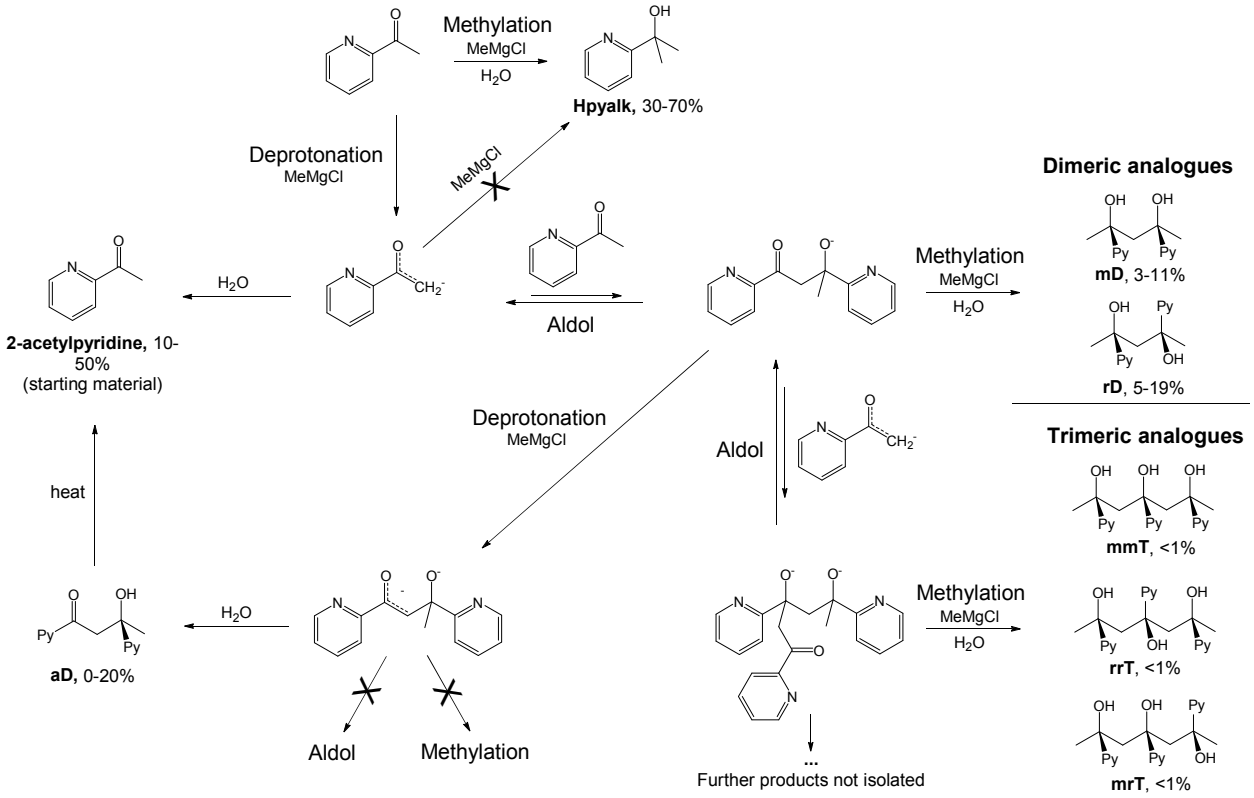
Scheme 3. Proposed reaction mechanism leading to the formation of the dimeric ligands mD and rD.



Scheme 4. Proposed ligand synthesis reaction roadmap leading to the various observed products, with ranges of yields based on various reaction conditions attempted.



While we obtain the oligomers from a simple one-step reaction, their yields are fairly low and variable. However, despite various attempts to selectively prepare them in greater yields, we were ultimately unable to improve on the original conditions, yielding 20-30% combined oligomers (a more detailed discussion is presented in SI). Given the low cost of the starting materials, we favored performing the one-step Grignard reaction on a large scale despite the limited oligomer yield, since the primary byproduct, **pyalkH**, is also a useful ligand. However,

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this strategy would not be feasible if the entire product mixture had to be separated by chromatography, as previously reported.[10] We found that large-scale workup is facilitated by first removing the monomeric species, **pyalkH** and 2-acetylpyridine (which account for the majority of the crude material), by distillation under reduced pressure, followed by oligomer separation in a smaller-scale chromatography step. **PyalkH** and acetylpyridine can then be efficiently separated on a large scale by exploiting their pK_a difference. Titration with acid allows selective protonation of **pyalkH**, after which the two can be separated via an aqueous/organic partition (e.g., H_2O/EtOAc). Neutralized **pyalkH** can be recrystallized (see Experimental), giving highly pure product, while the 2-acetylpyridine extract can be recycled. This simple and scalable isolation protocol allows for facile preparation of large quantities of this useful ligand at a multi mole scale.

The remaining distillation residue could be separated by silica gel chromatography using an incrementally varied mixture of hexane, ethyl acetate, acetone, and triethylamine, (See Experimental) giving two dimer and three trimer species, all diastereomers arising from the chirality of the quaternary carbons. The two dimers are the isotactic *meso* compound **mD** and the syntactic *racemo* compound **rD**, while the three trimers are the isotactic *meso, meso* **mmT**, the syntactic *racemo, racemo* **rrT**, and the atactic *meso, racemo* **mrT** (Scheme 2). Proton and carbon NMR spectroscopy shows the expected peak patterns, with the methylene protons being the most diagnostic (see SI). For **mD**, these give a geminally coupled diastereotopic pattern, while for **rD** they appear as a singlet due to the twofold rotational symmetry. Both isomers show a single pyridine and methyl signature due to their symmetry. Trimer **rrT** has one set of split diastereotopic methylene protons, though with smaller splitting than for **mmT**, while **mrT** has one weakly split and one strongly split set. As expected by symmetry, compounds **mmT** and **rrT** show two pyridine and one methyl signals, while **mrT** gives three pyridyl and two methyl signals.

Although these compounds are initially isolated as highly viscous yellow or brown oils, letting the concentrated material stand undisturbed eventually resulted in spontaneous crystallization, ranging in time from less than one day for **mD** and **mmT** to approximately one year for **mrT**. Only once this spontaneous crystallization had occurred for a specific compound could it be readily recrystallized in subsequent batches to give highly pure material (though uncrystallized material is sufficiently pure for use), no doubt as a result of seeds of the material being present in the laboratory. X-ray crystallography confirmed the expected structures (Figure 2).

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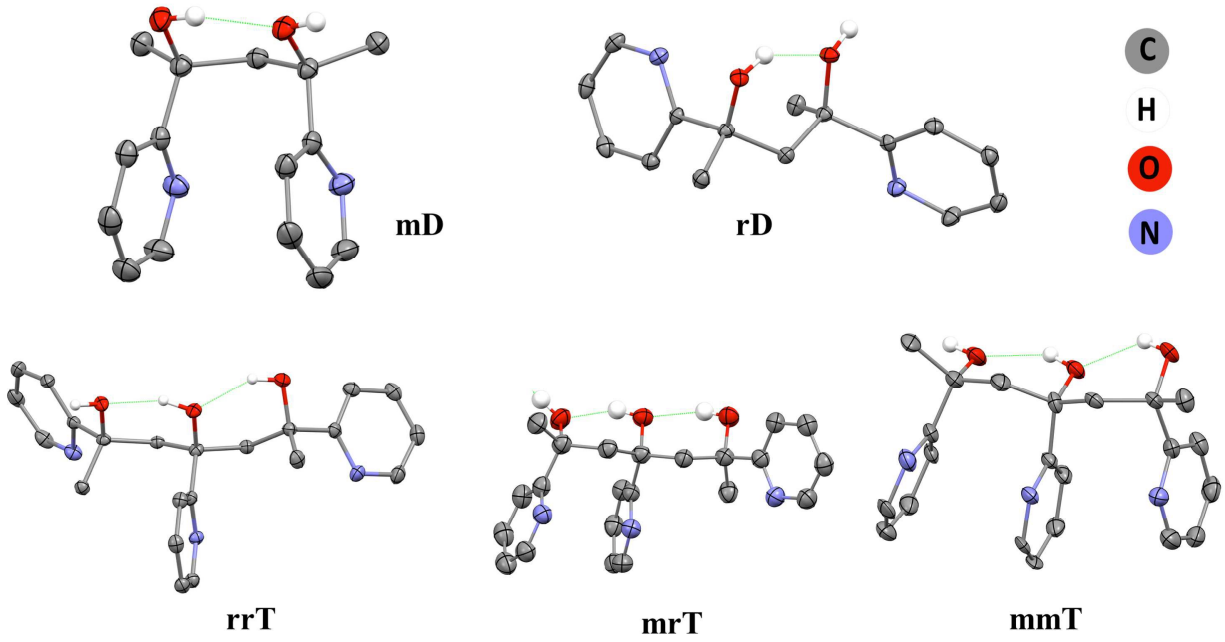

Figure 2. Crystal structures of the oligomeric ligands (50% probability). Hydrogen atoms other than OH protons have been omitted for clarity.

Synthesis of metal complexes

The ligand series reacted with divalent Cu, Ni, Co and Mn salts to give oligonuclear complexes of different nuclearities depending on the conditions. As expected[10] in all complexes besides **12** the OH groups are deprotonated and bind as a mixture of terminal and bridging alkoxides. All compounds are stable to handling at ambient conditions, and the stability of complexes **1-4**, **6**, **8**, and **12** (shown below) in solution was checked using UV-visible spectroscopy. Absorption spectra of these complexes remain unchanged even after solutions have been allowed to stand for one week, highlighting their stability. Another advantage of these ligands is the favorability of crystallization of their coordination complexes using standard techniques (See experimental for details), which allows for easy purification.

Copper

Three different Cu(II) complexes (Scheme 5) were accessible by varying the conditions (see Experimental). For Cu **mD** complexes, the nuclearity of the product was dependent on the solvent: acetonitrile gave monomer **2** while methanol gave dinuclear cluster **3**, even if the starting material stoichiometries are swapped. Square planar **2** features an internal O-H···O (H···O; 1.79 Å) hydrogen bond between the pendant **mD** alcohol groups and the basic coordinated alkoxide. Dinuclear complex **3** is inversion-symmetric and contains a diamond core formed by two five-coordinate copper centers with bridging alkoxides, bound asymmetrically to each Cu atom. A strong Jahn-Teller distortion is present as would be expected, with one Cu-bridging O bond at 1.925(2) Å and the other at 2.300(2) Å. Coordination with **rD** instead of **mD**

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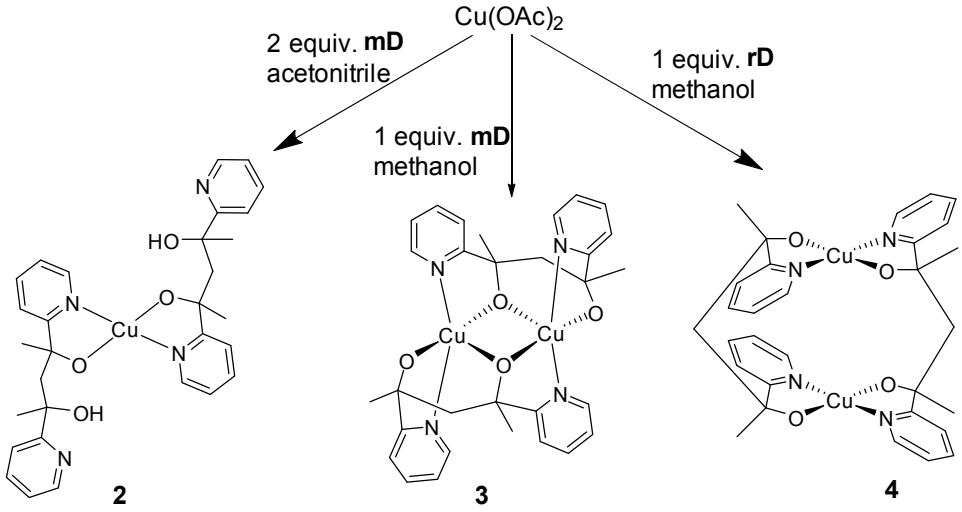
gives **4**, in which the two Cu centers are square planar and unbridged rather than five-coordinate (Cu-Cu distance >3 Å). Complexes **2**-**4** are pale blue in color, with λ_{max} between 592 and 605 nm (Table S2). The complexes all display redox features at oxidizing potentials in cyclic voltammetry experiments (Figure 4, Table S1). While **4**, with spatially separated Cu centers, shows one oxidation wave, **3** shows two separate features, consistent with coupling of the Cu centers (Figure 4). The monomeric complex **2** also shows only one quasi-reversible oxidation wave (See SI). Based on their potentials, we propose these features are $Cu^{II/III}$ couples; however, work on isolating oxidized species is ongoing,

Scheme 5. Synthesis of copper complexes with mD and rD.



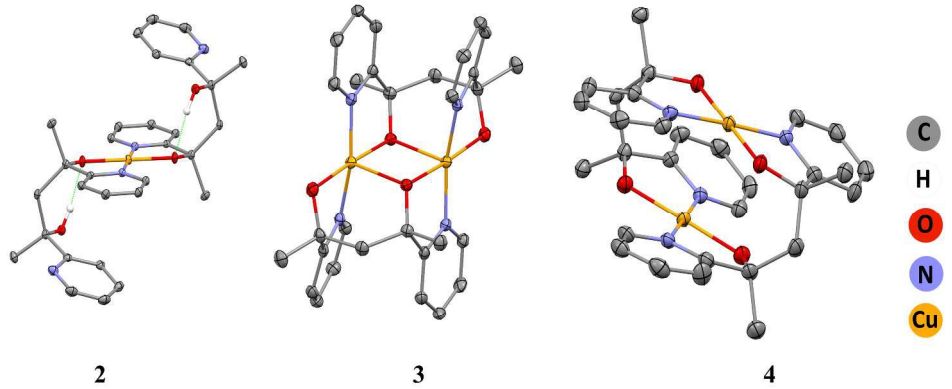


Figure 3. Crystal structures of the copper complexes **2**-**4** (50% probability). Hydrogen atoms other than OH protons have been omitted for clarity.

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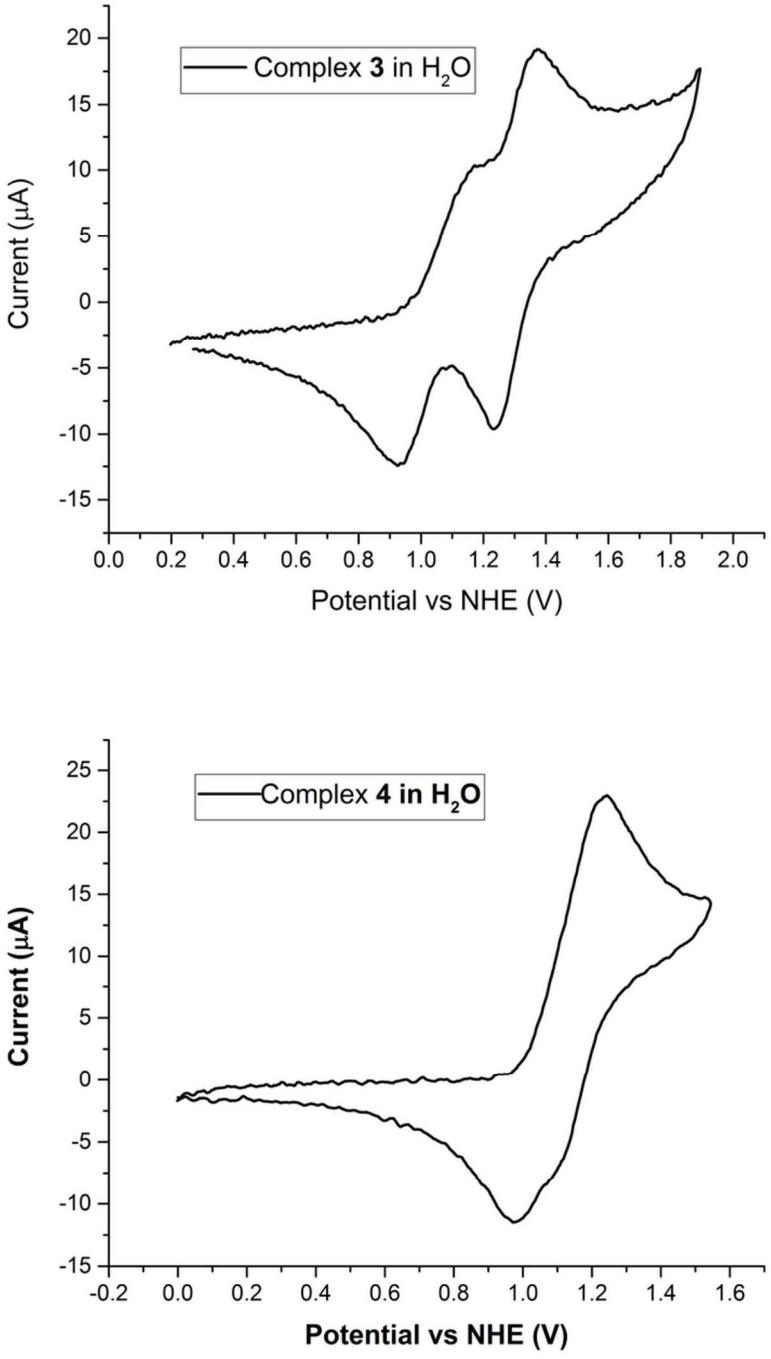

Figure 4. Cyclic voltammograms of complexes **3** and **4.** Experiments run in aqueous KNO_3 (0.1M) with boron doped diamond working electrode and Ag/AgCl reference electrode.

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Manganese

Manganese complexes of polydentate N,O ligands are effective in catalytic oxygen evolution,[3a,11] therefore we sought to investigate these new ligands. Using **mD** or **mmT** and acetonitrile and methanol as solvents, we prepared five polynuclear Mn complexes from simple Mn(II) salts (Scheme 6), utilizing H_2O_2 to afford less labile high oxidation states of Mn. Treating $MnCl_2$ with **mD** gives two clusters, **5** and **6**, which are separable by extraction and precipitation. The Mn(III,III,III)-trimer **5** has a Mn_3(**mD**)$_3$O core reminiscent of the Mn(III)-acetate trimer. It is a partial cubane and distantly resembles the Mn_4O_4Ca oxygen-evolving complex in photosystem II. The carbonate-bridged dimer-of-dimers **6** was assigned as a Mn(II, II, III, III) species, based on charge balance and bond lengths. The Mn(II) and Mn(III) centers are bound to two and four alkoxides, respectively, and the Mn(III) centers have Jahn-Teller axes along the Mn-N direction. Complex **6** is the thermodynamic product, and can be formed in higher yields by heating the reaction mixture for several hours. Because we were able to selectively prepare **6**, we explored its redox properties (Figure S1); its cyclic voltammagram shows two quasi-reversible redox features at 0.714 and 1.270 V vs. NHE, respectively (Table S1). Additionally, we found that applying a fixed potential of 1 V vs. NHE to **6** in an aqueous KNO_3 solution gives quantitative formation of Mn(II,IV)-dimer **7** (Scheme 6), in which the carbonate bridge has been hydrolysed. The bond length data and the absence of Jahn-Teller distortion is consistent with a Mn(II,IV) rather than a Mn(III,III) assignment. We could also prepare a similar Mn(II,IV) complex, **8**, with bridging acetate groups, by starting with $Mn(OAc)_2$ (see Experimental). Using the trimeric ligand **mmT** with $MnCl_2$ gives two products, the linear trinuclear Mn(II,III,III)-complex **9** and the related dinuclear Mn(III,III)-complex **10.** Complexes **6** and **8** were further characterized by UV-visible spectroscopy, and showed λ_{max} of 411 and and 475 nm, respectively (Table S2).

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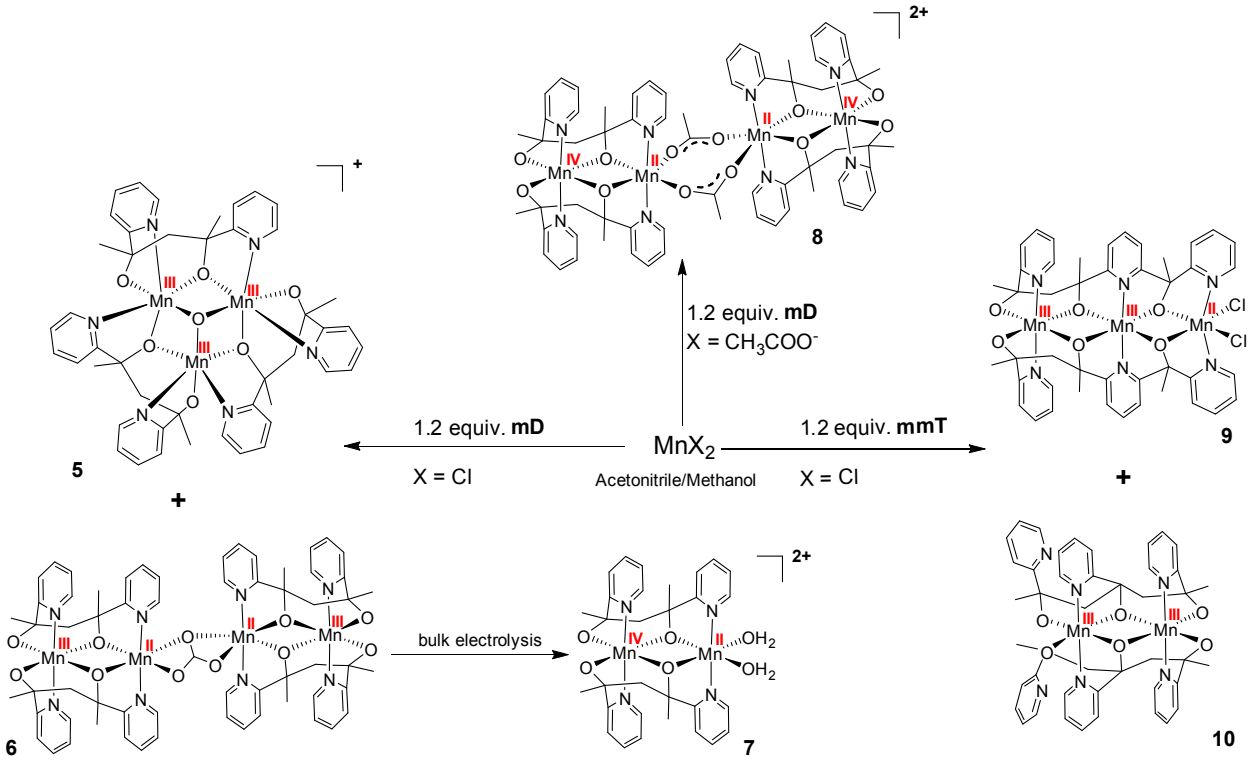
Scheme 6. Formation of manganese complexes with mD and rrT.



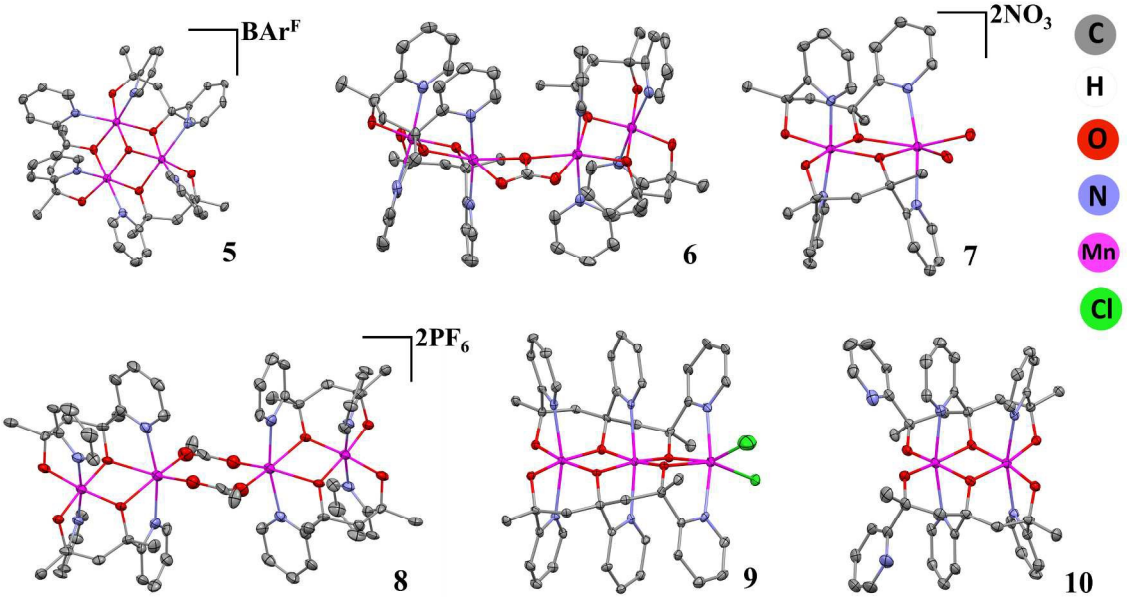


Figure 5. Crystal structures of the manganese complexes **5-10** drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity, except when present on alcohol groups.

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Nickel and Cobalt

We also prepared complexes of **mD** using Ni and Co. Ni monomer and dimer species were prepared as for Cu, with the same solvent dependence: acetonitrile gives monomer **11**, while methanol gives dinuclear **12** (Scheme 7). The latter is the only compound in which we find protonated alcohol ligands. The cyclic voltammogram of dimeric complex **12** contains a reversible redox feature at 0.870 V vs. NHE and an irreversible feature at 1.164 V vs. NHE (Table S1).

Treating $CoCl_2$ with **mD** followed by addition of Na_2CO_3 and H_2O_2 gives the Co(III,III) dimer (**1**, described above) in good yield. This carbonate-capped complex is remarkably stable, resisting loss of mD or carbonate in strong acid (p-toluenesulfonic acid) at elevated temperature (ca. 100°C). Treating $Co(OAc)_2$ with **mmT** also affords a dinuclear Co(III,III) cluster, **13** (See SI and Experimental for details)**.** Complexes **1** and **12** were characterized by UV-visible spectroscopy and give λ_{max} values of 535 and 602 nm, respectively (Table S2).

Scheme 7. Formation of nickel complexes with mD.

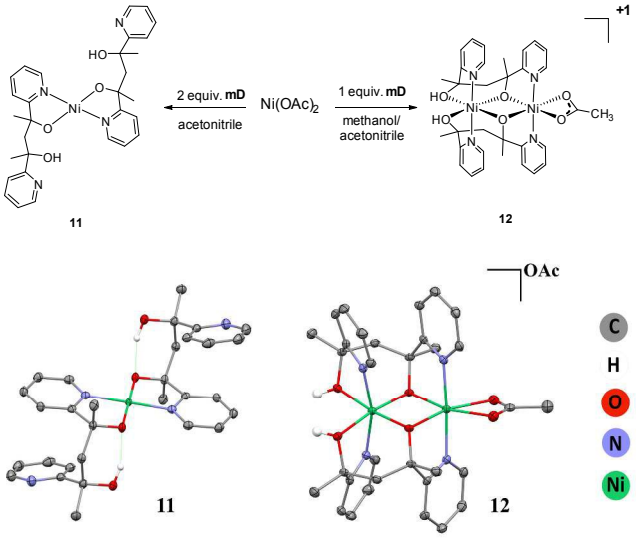

Figure 6. Crystal structures of the nickel complexes **11-12** (50% probability). Hydrogen atoms other than in OH groups have been omitted for clarity.

Conclusions

We report a family of polynucleating pyridine-alkoxide ligands, dimeric and trimeric relatives of the oxidation resistant **pyalkH** ligand, which has previously been shown to be very effective for oxidation catalysis and for stabilization of unusually high oxidation states. We also report a new purification technique for **pyalkH** itself, allowing large quantities of pure ligand to be synthesized from cheap starting materials. Finally, we have successfully synthesized and characterized several first-row metal complexes of the new ligands. The ligands are versatile as

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they have been shown to form stable clusters with various metals (Co, Mn, Ni and Cu) under different conditions.

Our ligand synthesis involves only one step and uses very cheap starting materials (2-acetylpyridine and methylmagnesium halide), features noteworthy for the preparation of larger, polydentate ligands. The primary byproducts of this process are **pyalkH**, a highly useful ligand in its own right, and 2-acetylpyridine, recyclable starting material. Thanks to our separation protocol, these two species can now be isolated on a large scale without chromatography, simplifying the separation of the oligomeric ligands.

These new ligands have a natural tendency to form polynuclear clusters with first-row transition metals. Such polynuclear structures hold promise for the development of first-row transition metal catalysts. Redox properties of the clusters presented, higher oxidation states, catalytic studies will be the subject of future reports.

EXPERIMENTAL METHODS

Physical Methods

NMR Spectroscopy. NMR spectra (^{1}H and ^{13}C $\{^{1}$H$\}$) were recorded on an Agilent DD2 600 MHz spectrometer equipped with a chilled probe. Chemical shifts are reported after calibration with solvent residual peaks.

UV−Visible Spectroscopy. Absorption spectra were collected using a Cary 50 spectrophotometer for 0.1 mM solutions in dichloromethane, water and methanol.

FTIR spectroscopy. All IR spectra were recorded on a Thermo Scientific Nicolet 6700 spectrometer outfitted with a Smart Orbit diamond ATR cell. Powder samples of pure analyte were pressed onto the cell window.

High-Resolution Mass Spectroscopy (HRMS). Mass spectrometry analyses were performed by the Mass Spectrometry and Proteomics Resource of the W.M. Keck Foundation Biotechnology Resource Laboratory at Yale University, using a 9.4 T Bruker Qe FT-ICR MS instrument in positive ion mode.

Electrochemistry. Cycliv voltammograms were performed using standard three-electrode measurements carried out on a Princeton Applied Research VersaSTAT-4 or a Pine AFCBP1 bipotentiostat. Aqueous experiments were performed with a boron-doped diamond working electrode, a platinum wire counter electrode and a saturated aqueous Ag/AgCl reference electrode (+0.197 V vs. NHE, purchased from Bioanalytical Systems, Inc.). For experiments in organic solvent, a glassy carbon working electrode and platinum wire counter electrode were used. A silver wire was used as a pseudoreference electrode and the potential was referenced using a ferrocene internal standard.

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General

Unless otherwise specified, solvents and reagents were purchased from commercial sources and used as received. Full crystallographic information for all novel ligands and complexes is reported in the SI.

Synthesis of pyalkH, aD, mD, rD, mmT, mrT, rrT

To a 3-neck 4-liter round bottom flask were added 112 mL (1 mol) 2-acetylpyridine and 110 mL dry degassed THF. The solution was cooled in an ice bath and 350 mL of a 3 M THF solution of MeMgCl was added dropwise over 3 hours under a flow of nitrogen. During addition, the mixture was stirred rapidly (~1000 RPM) with a motor stirrer, while the temperature was monitored to not exceed 10 ˚C. 200 mL of additional THF was added during the course of MeMgCl addition to minimize formation of solids and facilitate mixing. Subsequently, solids were manually scraped off the walls of the flask and readded to the mixture, which was then stirred for 1 hour at room temperature. Approximately 1 L water was added and the resulting slurry mixed well, after which the products were extracted with approx. 1 L ethyl acetate. The organic extract was dried with $MgSO_4$ and the solvent was removed under reduced pressure. *Note: **pyalkH** is volatile; leaving the mixture under prolonged reduced pressure after the solvent is removed may result in some product loss.*

Isolation of 2-(2-pyridinyl)-2-propanol (pyalkH)

The compounds **pyalkH** and 2-acetylpyridine were distilled simultaneously from the resulting mixture under reduced pressure at ca. 95 ^{o}C (pressure-dependent, ca. 180 ^{o}C at 150 mbar). The distillate was diluted with ca. 200 mL water and layered with ca. 200 mL ethyl acetate. The mixture was titrated with H_2SO_4 until no **pyalkH** remained in the organic layer; the aqueous layer was separated and washed twice with ca. 200 mL ethyl acetate. The aqueous layer was again layered with ethyl acetate and partially neutralized with $NaHCO_3$ until the aqueous layer was mostly free of 2-acetylpyridine (this step to be performed only if necessary). Monitoring the composition of the two phases was done by TLC in 30% ethyl acetate and 1% triethylamine in hexane (2-acetylpyridine elutes first); aqueous aliquots were first neutralized with excess $NaHCO_3$ and extracted into ethyl acetate.

The aqueous phase was neutralized with excess $NaHCO_3$, extracted into ethyl acetate, and evaporated under reduced pressure. The viscous oil was diluted with ca. 500 mL of pentane and crystallized by cooling to approx. 10 ^{o}C and introducing a seed crystal, followed by further cooling to –25 ^{o}C overnight. Without warming, the supernatant was removed and the crystals washed three times with cold pentane, warmed to room temperature, and dried under ambient conditions. Larger crystals of high purity can be obtained by recrystallization in pentane via slow evaporation at room temperature for several days in the presence of a seed crystal. *Note: **pyalkH** obtained by distillation may persist in supercooled/supersaturated liquid form in the absence of seed crystals. Seed crystals can most often be formed in agitated evaporating pentane solutions.* Yield: 43.84 g, 32%.

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Separation of mD, rD, mmT, rrT, mrT

The viscous dark residue remaining after distillation was extracted with several portions of hexane until only dark insoluble solids remained. This solid was dissolved in minimal DCM, precipitated with hexane and filtered. This process was repeated 2-3 times. The solutions were combined and concentrated in vacuo to give a light brown oil (*note: initial reduction of these colored impurities is nontrivial as they will co-elute with the products and interfere with their final purity and ability to crystallize*). The oil (ca. 23 g) was diluted with a minimum of dichloromethane and loaded into a large (10 x 40 cm) silica gel column presoaked with hexane and run with a solution of 30% ethyl acetate and 1 % triethylamine in hexane until leftover 2-acetylpyridine, followed by **pyalkH,** eluted. The amount of ethyl acetate in the eluent was gradually increased to 66% as **rD** and then **mD** eluted. For elution of the trimeric species, the eluent was gradually spiked with acetone up to 50%, while keeping a 2:1 ratio of ethyl acetate:hexane. Compound **rrT** elutes first at ca. 10% acetone, followed by **mrT** and finally **mmT**. All of the compound fractions were evaporated under reduced pressure and initially isolated as yellow or brown oils. The **pyalkH** was combined with the distilled fraction and purified by repeated crystallizations from concentrated pentane solution at low temperature. The compounds were crystallized from a saturated DCM/octane solution. The crystallization occurred readily only after spontaneous crystallization from the neat oil had occurred. The timescale of this spontaneous crystallization varied from several hours for **mD** and **mmT** to several weeks or months for the other ligands.

*meso-2,4-di(2-pyridynyl)-2,4-pentanediol•H_2O (**mD**)*: Yield 5.03 g, 4.0%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (m, 2H, Ar-H), 7.31 (m, 2H, Ar-H), 7.17 (m, 2H, Ar-H), 6.79 (m, 2H, Ar-H), 6.25 (s, 2H, O-H), 3.03 (d, *J* = 14.8 Hz, 1H, HC-H), 2.55 (d, *J* = 14.8 Hz, 1H, HC-H), 1.46 (s, 6H, CH_3). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.43, 146.91, 136.04, 120.89, 120.07, 75.75, 50.55, 32.91. HRMS (FT-ICR): Calculated $[C_{15}H_{18}N_2O_2]Na^+$: 281.1266. Found: 281.1270.

*racemo-2,4-di(2-pyridynyl)-2,4-pentanediol•H_2O (**rD**)*: Yield 8.24 g, 6.5%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.50 (m, Ar-H, 2H), 7.69 (m, Ar-H, 2H), 7.60 (m, Ar-H, 2H), 7.16 (m, Ar-H, 2H), 6.22 (s, O-H, 2H), 2.54 (s, CH_2, 2H), 1.16 (s, CH_3 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.48, 147.56, 137.22, 121.88, 119.61, 75.75, 51.18, 30.74. HRMS (FT-ICR): Calculated $[C_{15}H_{18}N_2O_2]H^+$: 259.1447. Found: 259.1445.

*meso,meso-2,4,6-tri(2-pyridynyl)-2,4,6-heptanetriol (**mmT**)*: Yield 440 mg, 0.4%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, Ar-H, 2H), 7.76 – 7.73 (m, Ar-H, 1H), 7.25 – 7.22 (m, Ar-H, 2H), 7.10 (t, *J* = 1.0 Hz, Ar-H, 1H), 7.08 (t, *J* = 1.1 Hz, Ar-H, 1H), 6.79 – 6.76 (m, Ar-H, 1H), 6.69 – 6.66 (m, Ar-H, 2H), 6.63 – 6.61 (m, Ar-H, 1H), 6.39 – 6.36 (m, Ar-H, 1H), 3.11 (d, *J* = 14.6 Hz, HC-H, 2H), 2.48 (d, *J* = 14.6 Hz, HC-H, 2H), 1.39 (s, CH_3, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.27, 162.33, 146.92, 146.72, 135.53, 134.58, 120.60, 120.37, 119.82, 119.60, 79.82, 75.78, 52.09, 32.90. HRMS (FT-ICR): Calculated $[C_{22}H_{25}N_3O_3]Na^+$: 402.1794. Found: 402.1779.

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*racemo,racemo-2,4,6-tri(2-pyridynyl)-2,4,6-heptanetriol (**rrT**):* Yield 730 mg, 0.6%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.53 – 8.49 (m, Ar-H, 1H), 8.43 – 8.38 (m, Ar-H, 2H), 7.78 – 7.75 (m, Ar-H,1H), 7.69 – 7.64 (m, Ar-H,1H), 7.57 (td, *J* = 7.7, 1.8 Hz, Ar-H, 2H), 7.39 (dt, *J* = 7.9, 1.1 Hz, Ar-H, 2H), 7.15 – 7.11 (m, Ar-H,1H), 7.07 – 7.02 (m, Ar-H, 2H), 2.40 (d, *J* = 14.7 Hz, HC-H, 2H), 2.21 (d, *J* = 14.8 Hz, HC-H, 2H), 1.01 (s, CH_3, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.61, 165.98, 147.67, 147.26, 136.72, 136.66, 121.59, 121.36, 120.40, 119.18, 79.73, 75.44, 51.37, 29.85. HRMS (FT-ICR): Calculated $[C_{22}H_{25}N_3O_3]Na^+$: 402.1794. Found: 402.1783.

*meso,racemo-2,4,6-tri(2-pyridynyl)-2,4,6-heptanetriol•H_2O (**mrT**):* Yield 890 mg, 0.7% ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.57 – 8.47 (m, Ar-H, 1H), 8.20 – 8.11 (m, Ar-H, 1H), 8.01 – 7.91 (m, Ar-H, 1H), 7.69 (m, 1H), 7.55 (m, Ar-H, 1H), 7.29 (m, Ar-H, 1H), 7.23 – 7.13 (m, Ar-H, 4H), 6.79 – 6.71 (m, Ar-H, 2H), 2.89 (d, *J* = 14.6 Hz, CH_2, 1H), 2.59 (d, *J* = 14.7 Hz, CH_2, 1H), 2.48 (d, *J* = 14.7 Hz, CH_2, 1H), 2.13 (d, *J* = 14.6 Hz, CH_2, 1H), 1.25 (s, CH_3, 3H), 1.01 (s, CH_3, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.60, 164.84, 164.22, 147.61, 147.51, 147.12, 137.14, 135.79 (d, *J* = 4.9 Hz), 121.81, 120.87, 120.67, 120.60, 119.80, 119.46, 80.10, 75.90, 75.83, 52.79, 50.61, 33.09, 29.93, 29.85.

Attempted isolation of aD

An aliquot (ca. 50 mg) of crude reaction product (prior to distillation) was loaded on a 1 mm thick silica gel TLC plate and eluted with 1:1 ethyl acetate/hexane with 1% triethylamine. The third major band (poorly separated **aD** and **rD**) was scraped and extracted with acetone, and the resulting residue eluted a second time under the same conditions. The leading edge of the major band pair (**rD** trailing) was collected. This yielded **aD** with ca. 20% 2-acetylpyridine. While the two constituents separate very distinctly, obtaining a pure sample of **aD** was not possible as it partially degrades to 2-acetylpyridine under ambient conditions. NMR spectra of the mixture were compared to those of 2-acetylpyridine to identify the peaks of **aD**, listed below.

*3-hydroxy-1,3-di(pyridin-2-yl)butan-1-one (**aD**)*: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H, Ar-H), 8.40 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1H, Ar-H), 7.92 (dt, *J* = 7.9, 1.1 Hz, 1H, Ar-H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H, Ar-H), 7.71-7.63 (m, 2H, Ar-H), 7.45 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H, Ar-H), 7.08 (ddd, *J* = 7.1, 4.9, 1.5 Hz, 1H, Ar-H), 5.47 (s, 1H, OH), 4.29 (d, *J* = 16.6 Hz, 1H, CH_2), 3.56 (d, *J* = 16.7 Hz, 1H, CH_2), 1.61 (s, 3H, CH_3).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 201.87 (C=O), 166.02 (Ar), 153.54 (Ar), 148.90 (Ar), 148.05 (Ar), 137.18 (Ar), 136.75 (Ar), 127.35 (Ar), 122.07 (Ar), 121.75 (Ar), 119.45 (Ar), 74.91 , 48.74 , 29.97. HRMS (FT-ICR) calc. $[C_{14}H_{14}N_2O_2]H^+$: 243.1134 Found: 243.1129.

Preparation of complexes

*Preparation of Co_2(**mD**)$_2CO_3$•$2H_2O$ (**1**).* To a stirred solution of **mD** (62 mg, 0.24 mmol) in acetonitrile (2 mL), a solution of $CoCl_2.2H_2O$ (33 mg, 0.2 mmol) in acetonitrile was added dropwise. 2-4 drops of methanol were added to completely dissolve the reaction mixture. The

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reaction mixture was stirred for 15 min and afterwards a 30% H_2O_2 solution (0.03 mL) was added. The color of the solution changed to blue. After stirring for 20 min, K_2CO_3 (83 mg, 0.6 mmol) was added to the reaction mixture. The solution was stirred overnight and the color changed to yellow brown. The solvent was removed and the crude product was dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and brown crystals of **1** were grown by layering the filtrate with pentane at room temperature. Yield: 52 mg, 70%. ^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 8.96 (d, J = 5.8, Ar-H, 2H), 8.71 (d, J = 5.5 Hz, Ar-H, 2H), 7.59 (m, Ar-H, 2H), 7.53 (m, Ar-H, 2H), 7.25 (m, Ar-H, 2H), 7.04 – 6.99 (m, Ar-H, 4H), 6.60 (d, J = 7.9 Hz, Ar-H, 2H), 2.32 (d, J = 15.0 Hz, HC-H, 2H), 2.10 (d, J = 15.0 Hz, HC-H, 2H), 1.48 (s, CH_3, 7H), 1.36 (s, CH_3, 6H).

*Preparation of Cu(**mD**)$_2$ (**2**).* To a stirred solution of **mD** (51 mg, 0.2 mmol) in acetonitrile (2 mL), a solution of $Cu(OAc)_2$•H_2O (20 mg, 0.1 mmol) in acetonitrile was added dropwise. The reaction mixture was stirred for 20 min and K_2CO_3 (41 mg, 0.3 mmol) was added to the reaction mixture. The solution was stirred overnight. The final solution was light blue in color. The solvent was removed and the crude product dissolved in acetonitrile and filtered. The volume of the filtrate was reduced and blue crystals of **2** were grown by slow evaporation at room temperature. Yield: 29 mg, 50%.

*Preparation of Cu$_2$(**mD**)$_2$•2H$_2$O (**3**).* To a stirred solution of **mD** (62 mg, 0.24 mmol) in methanol (2 mL), a solution of $Cu(OAc)_2$•H_2O (40 mg, 0.2 mmol) in methanol was added dropwise. The reaction mixture was stirred for 20 min resulting in a blue solution. K_2CO_3 (83 mg, 0.6 mmol) was added to the reaction mixture and left to stir overnight. The final solution was dark blue in color. The solvent was removed and the crude product dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and purple crystals of **3** were grown by layering the filtrate with pentane at room temperature. Yield: 30 mg, 45%. HRMS (FT-ICR): Calculated $[C_{30}H_{34}CuN_4O_4]Na^+$: 600.1774. Found: 600.1156.

*Preparation of Cu$_2$(**rD**)$_2$•2H$_2$O (**4**).* To a stirred solution of **rD** (62 mg, 0.24 mmol) in methanol (2 mL), a solution of $Cu(OAc)_2$•H_2O (40 mg, 0.2 mmol) in methanol was added dropwise. The reaction mixture was stirred for 20 min resulting in a blue solution. K_2CO_3 (83 mg, 0.6 mmol) was added to the reaction mixture and left to stir overnight. The final solution was dark blue in color. The solvent was removed and the crude product dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and light purple crystals of **3** were grown by layering the filtrate with pentane at room temperature. Yield: 25 mg, 40%. HRMS (FT-ICR): Calculated $[C_{30}H_{32}Cu_2N_4O_4]H^+$: 639.1094. Found: 639.1085.

*Preparation of [Mn$_3$(**mD**)$_3$μ$_3$-O][BAr$_F$]•H$_2$O (**5**).* To a stirred solution of **mD** (62 mg, 0.24 mmol) in acetonitrile/methanol (6:1; 2 mL), a solution of $MnCl_2$-2 H_2O (32 mg, 0.2 mmol) in methanol was added dropwise. The reaction mixture was stirred for 20 min resulting in a red/brown solution. H_2O_2 (6 eq.) and K_2CO_3 (83 mg, 0.6 mmol) were added and the reaction mixture was stirred at room temperature for 2 hours. The solvent was removed and the residue was dissolved in dichloromethane, filtered, and stirred with excess $NaBArF_4$ in dichloromethane for 1 h. The mixture was filtered, reduced in volume and layered with pentane. Crystals of **5** formed as red plates after slow diffusion over several days at room temperature. Yield: <5%.

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*Preparation of Mn_4(**mD**)$_4CO_3$•10H_2O (**6**).* To a stirred solution of **mD** (62 mg, 0.24 mmol) in Acetonitrile/methanol (6:1; 2 mL), a solution of $MnCl_2$•2H_2O (32 mg, 0.2 mmol) in methanol was added dropwise. The reaction mixture was stirred for 20 min resulting in a red/brown solution. H_2O_2 (6 eq.) and K_2CO_3 (83 mg, 0.6 mmol) were added and the reaction mixture was heated to 45 ^oC and left to stir overnight. The solvent was removed and the residue was dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and brown crystals of **6** were grown by layering the filtrate with pentane at room temperature. Yield: 30 mg, 40%.

*Preparation of [Mn_2(**mD**)$_2$(H_2O)$_2$][NO_3]$_2$•6H_2O (**7**).* A solution of ***6*** in 0.1 M KNO_3 buffer was electrolyzed at 1 V vs. NHE using a platinum mesh working electrode for ~1 hour. Red crystals were grown by slow evaporation of the solution over several days.

*Preparation of [Mn_4(**mD**)$_4$(CH_3COO)$_2$][PF_6]$_2$ (**8**).* To a stirred solution of **mD** (62 mg, 0.24 mmol) in Acetonitrile/methanol (6:1; 2 mL), a solution of Mn(OAc)$_2$•4H_2O (49 mg, 0.2 mmol) in methanol was added dropwise. The reaction mixture was stirred for 20 min resulting in a red/brown solution. H_2O_2 (6 eq.) and K_2CO_3 (83 mg, 0.6 mmol) were added and the reaction mixture was stirred overnight at room temperature. The solvent was removed and the residue was dissolved in dichloromethane and filtered. Excess KPF_6 was added and the mixture was stirred for 1 hour and filtered. The volume of the filtrate was reduced and brown crystals of **8** were grown by layering the filtrate with pentane at room temperature. Yield: 20 mg, 22%.

*Preparation of Mn_3(**mmT**)$_2Cl_2$ (**9**) and Mn_2(**mmT**)$_2$ (**10**).* To a stirred solution of **mmT** (91 mg, 0.24 mmol) in Acetonitrile/methanol (6:1; 2 mL), a solution of $MnCl_2$•2H_2O (32 mg, 0.2 mmol) in methanol was added dropwise. The reaction mixture was stirred for 20 min resulting in a red/brown solution. H_2O_2 (6 eq.) and K_2CO_3 (83 mg, 0.6 mmol) were added and the reaction mixture was stirred overnight at room temperature. The solvent was removed and the residue was dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and crystals of **9** and **10** were grown by layering the filtrate with pentane at room temperature. No attempt was made to separate **9** and **10** in bulk from the crude mixture (formed in moderate yield), thus no yields were recorded.

*Preparation of Ni(**mD**)$_2$ (**11**).* To a stirred solution of **mD** (62 mg, 0.24 mmol) in acetonitrile (2 mL), a solution of $NiBF_4$•6H_2O (68 mg, 0.2 mmol) in acetonitrile was added dropwise. The reaction mixture was stirred for 20 min and K_2CO_3 (83 mg, 0.6 mmol) was added to the reaction mixture and left to stir overnight. The final solution was tan in color. The solvent was removed and the crude product dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and tan colored crystals of **11** were grown by layering the filtrate with pentane at low temperature. Yield: ~30 mg, 30%.

*Preparation of [Ni_2(**mD**)$_2$(CH_3COO)][CH_3COO] (**12**).* To a stirred solution of **mD** (62 mg, 0.24 mmol) in acetonitrile/methanol (3:1) (2 mL), a solution of Ni(OAc)$_2$•4H_2O (50 mg, 0.2 mmol) in acetonitrile/methanol (3:1) was added dropwise. The reaction mixture was stirred for 15 min and afterwards a 30% H_2O_2 solution (0.03 mL) was added. After stirring for another 20 min, $NaHCO_3$ (59 mg, 0.7 mmol) was added to the reaction mixture. The solution was stirred overnight at 65 °C. The solvent was removed and the crude product was dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and blue crystals of **12**

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were grown by slow evaporation of this solution layered with octane at room temperature. Yield: 38 mg, 50%.

Preparation of Co_2***(mmT)***$_2$$\bullet 2H_2O$ ***(13)***. To a stirred solution of **mmT** (76 mg, 0.2 mmol) in acetonitrile (2 mL), a solution of $Co(OAc)_2.2H_2O$ (49 mg, 0.2 mmol) in acetonitrile was added dropwise. 2-4 drops of methanol were added to completely dissolve the reaction mixture. The reaction mixture was stirred for 15 min and afterwards a 30% H_2O_2 solution (0.03 mL) was added. The color of the solution changed to brownish red. After stirring for 20 min, K_2CO_3 (83 mg, 0.6 mmol) was added to the reaction mixture, and the solution was stirred overnight. The solvent was removed and the crude product was dissolved in dichloromethane and filtered. The volume of the filtrate was reduced and brown crystals of **1** were grown were grown by slow evaporation of this solution layered with octane at room temperature. Yield: 15-20%.

Supporting Information

NMR and HRMS spectra, cyclic voltammograms, and crystallographic details are available free of charge via the internet at http://pubs.acs.org.

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[1] (a) Tsui, E. Y.; Kanady, J. S.; Agapie, T. Synthetic cluster models of biological and heterogeneous manganese catalysts for o_2 evolution. *Inorg. Chem*. **2013**, *52*, 13833. (b) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. N• reduction and hydrogenation to ammonia by a molecular iron-potassium complex. *Science* **2011**, *334*, 780. (c) Parent, A.R; Sakai, K. Progress in base-metal water oxidation catalysis. *ChemSusChem* **2014**, *7*, 2070. (d) Sharninghausen, L. S.; Sinha, S. B.; Shopov, D. Y.; Choi, B.; Mercado, B. Q.; Roy, X.; Balcells, D.; Brudvig, G. W.; Crabtree, R. H. High oxidation state iridium mono-μ-oxo dimers related to water oxidation catalysis. *J. Am. Chem. Soc*. **2016**, *138*, 15917. (e) Sharninghausen, L. S.; Mercado, B. Q.; Crabtree, R. H.; Balcells, D.; Campos, J. Gel-assisted crystallization of $[Ir_4(IMe)_7(CO)H_{10}]^{2+}$and $[Ir_4(IMe)_8H_9]^{3+}$ clusters derived from catalytic glycerol dehydrogenation. *Dalt. Trans.* **2015**, *44*, 18403.

[2] (a) Dempsey, J. L.; Esswein, A. J.; Manke, D. R.; Rosenthal, J.; Soper, J. D.; Nocera, D. G. Molecular chemistry of consequence to renewable energy. *Inorg. Chem.*, **2005**, *44*, 6879. (b) Clouston, L. J.; Bernales, V.; Carlson, R. K.; Gagliardi, L.; Lu, C. C. Bimetallic cobalt–dinitrogen complexes: impact of the supporting metal on n_2 activation. *Inorg. Chem*. **2015**, *54*, 9263. (c) Thomsen, J. M.; Huang, D. L.; Crabtree, R. H.; Brudvig, G. W. Iridium-based complexes for water oxidation. *Dalton Trans*. **2015**, *44*, 12452. (d) Limburg,J.; Vrettos, J. S.; Sands, L. M. L.; Rheingold, A. L.; Crabtree R. H.; Brudvig, G.W. A functional model for O-O bond formation by the O_2-evolving complex in photosystem II. *Science* **1999**, *283*, 1524.

[3] (a) Kärkäs, M. D.; Verho, O.; Johnston, E. V.; Åkermark, B. Artificial Photosynthesis: Molecular systems for catalytic water oxidation. *Chem. Rev*. **2014**, *114*, 11863. (b) Umena, Y.; Kawakami, K.; Shen, J. R.; Kamiya, N. Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. *Nature,* **2011**, 473, 55. (c) Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W. Molecular catalysts for water oxidation. *Chem. Rev*. **2015**, *115*, 12974. (d) McEvoy, J. P.; Brudvig, G. W. Water-splitting chemistry of photosystem II. *Chem. Rev*. **2006**, *106*, 4455.

[4] (a) Hagadorn, J. New binucleating ligands to support dizirconium organometallics. *Chem. Commun*., **2001**, 2144. (b) Peterson, S. M.; Helm, M. L.; Appel, A. M. Nickel complexes of a binucleating ligand derived from an SCS pincer. *Dalton Trans*., **2015**, *44*, 747. (c) Pankhurst, J. R.; Cadenbach, T.; Betz, D.; Finn, C.; Love, J. B. Towards dipyrrins: oxidation and metalation of acyclic and macrocyclic schiff-base dipyrromethanes. *Dalton Trans*., **2015**, *44*, 2066. (d) Veauthier, J. M.; Cho, W-S.; Lynch, V. M.; Sessler, J. L. Calix[4]pyrrole schiff base macrocycles. novel binucleating ligands for μ-oxo iron complexes. *Inorg. Chem.*, **2003**, *44*, 1220. (e) VanOrman, C. A.; Reddy, K. V.; Sayre, L. M.; Urbach, F. L. Dicopper(II) complexes with flexible binucleating ligands containing two tridentate coordination sites. *Polyhedron*, **2001**, *20*, 541.

[5] Okamura, M.; Kondo, M.; Kuga, R.; Kurashige, Y.; Yanai, T.; Hayami, S.; Praneeth, V. K. K.; Yoshida, M.; Yoneda, K.; Kawata, S.; Masaoka, S. A pentanuclear iron catalyst designed for water oxidation. *Nature* **2016**, *530*, 465.

View Article Online
DOI: 10.1039/C7NJ01845B

[6] (a) Michaelos, T.; Shopov, D. Y.; Sinha, S. B.; Sharninghausen, L. S.; Fischer, K.; Lant, H. M. C. A pyridine alkoxide chelate ligand that promotes both unusually high oxidation states and water-oxidation catalysis. *Acc. Chem. Res.* **2017**, DOI: 10.1021/acs.accounts.6b00652. (b) Schley, N. D.; Blakemore, J. D.; Subbaiyan, N. K.; Incarvito, C. D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W. distinguishing homogeneous from heterogeneous catalysis in electrode-driven water oxidation with molecular iridium complexes. *J. Am. Chem. Soc*. **2011**, *133*, 10473. (c) Hull, J. F., Balcells, D., Blakemore, J. D.; Incarvito C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. Highly active and robust Cp* iridium complexes for catalytic water oxidation. *J. Am. Chem. Soc*. **2009**, *131*, 8730. (d) Thomsen, J. M.; Sheehan, S. W.; Hashmi, S. M.; Campos, J.; Hintermair, U.; Crabtree, R. H.; Brudvig, G. W. Electrochemical activation of Cp* iridium complexes for electrode-driven water-oxidation catalysis. *J. Am. Chem. Soc*. **2014**, *136*, 13826.

[7] (a) Sinha, S. B.; Shopov, D. Y.; Sharninghausen, L. S.; Vinyard, D. J.; Brudvig, G. W.; Crabtree, R. H. a stable coordination complex of rh(iv) in an N,O-donor environment. *J. Am. Chem. Soc.* **2015**, *137*, 15692. (b) Shopov, D. Y.; Rudshteyn, B.; Campos, J.; Batista, V. S.; Crabtree, R. H.; Brudvig, G. W. Stable iridium(IV) complexes of an oxidation-resistant pyridine-alkoxide ligand: highly divergent redox properties depending on the isomeric form adopted. *J. Am. Chem. Soc.*, **2015**, *137*, 7243. (c) Shopov, D. Y. Rudshteyn, B.; Campos, J.; Vinyard, D. J.; Batista, V. S.; Brudvig, G. W.; Crabtree, R. H. A full set of iridium(IV) pyridine-alkoxide stereoisomers: highly geometry-dependent redox properties. *Chem. Sci*. **2017,** *8*, 1642.

[8] Sheehan, S. W.; Hintermair, U.; Thomsen, J. M.; Brudvig, G. W.; Crabtree, R. H. Iridium complexes for electrocatalysis. U.S. Patent 20150021194 A1, Jan 22, 2015.

[9] Wong, Y.-L.; Yang, Q.; Zhou, Z.-Y.; Lee, H. K.; Mak, T. C. W.; Ng, D. K. P. S. Synthesis, structure and oxo-transfer properties of dioxotungsten(VI) complexes with pyridine-based *NO*- and *NS*-bidentate ligands. *New J. Chem*. **2001**, *25*, 353.

[10] Taft, K. L.; Caneschi, A.; Pence, L. E.; Delfs, C. D.; Papaefthymiou, G. C.; Lippard, S. J. Iron and manganese alkoxide cubes. *J. Am. Chem. Soc.* **1993**, *115*, 11753

[11] Michaelos, T. K.; Lant, H. M. C.; Sharninghausen, L. S.; Craig, S. M.; Menges, F. S.; Mercado, B. Q.; Brudvig, G. W.; Crabtree, R. H. Catalytic oxygen evolution from manganese complexes with an oxidation-resistant N,N,O-donor ligand. *Chem Plus Chem* **2016**, *81*, 1129.