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Chemically Reversible Four-Electron Oxidation and Reduction Utilizing Two Inorganic Functional Groups

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Supporting Information

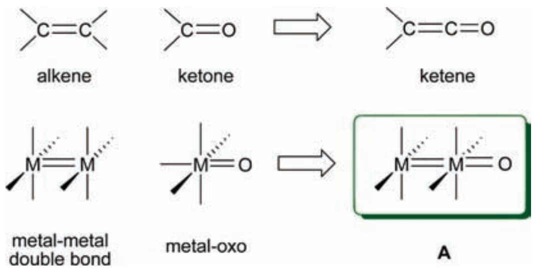
ABSTRACT: Four-electron oxidation of the quadruply bonded W_2(II,II) compound W_2(2,2′-dipyridylamide)$_4$, **1**, results in the formation of a novel, diamagnetic ditungsten terminal oxo compound $[W_2O(2,2'\text{-dipyridylamide})_4]^{2+}$, **2**. In contrast to the chemical inertness of mononuclear tungsten oxo species, **2** undergoes a four-electron reduction including oxygen-atom transfer in reactions with excess tri-*tert*-butylphosphine in acetonitrile to recover **1**. This unusual chemically reversible multielectron reactivity is ascribed to the cooperation of W—O and W—W multiple bonding.

Multielectron transfer reactions are very important in chemistry as well as in biological processes.[1,2] A major challenge in the chemical community is to improve the efficiency of multielectron reactions such as these. Recent successes in promoting multielectron redox processes in well-defined molecules have made use of multiple metal centers,[3] or single-metal atom centers that are able to span a large variety of oxidation states,[4] or coordination complexes with redox-noninnocent ligands.[5] New ways to facilitate multielectron transfer chemistry are of great significance, and we report here a novel molecule design that allows chemically reversible four-electron processes to occur via the combination of two inorganic functional groups in a single molecule.

Functional groups are used in organic chemistry to categorize and predict chemical reactivity. For example, compounds in Scheme 1 with carbon—carbon double bonds (alkenes) or carbon—oxygen double bonds (ketones) are known and expected to display certain chemical characteristics such as addition reactions in the former case, and reductions or nucleophilic additions in the latter case. Combining the alkene and ketone functional groups in one molecule results in the ketene structure, and ketenes are known to be much more reactive than either alkenes or ketones by themselves.

In the 1980s, Chisholm[6] and Holm[7] promoted the idea that metal—metal multiple bonds or metal—oxygen multiple bonds could be considered as 'inorganic functional groups' in consideration of the wealth of information known about their chemical reactivity. In principle, these inorganic functional groups could be combined to form compounds with a dimetallo-ketene type of structure (**A**, Scheme 1). Only recently has systematic work begun in our lab to investigate the chemistry of these new, exotic multifunctional molecules.[8] Redox chemistry is a common theme in the chemistry of both metal—metal and metal—ligand multiple bonds. Here we report that combining these two functional groups in one molecule allows chemically reversible four-electron oxidation and reduction processes to take place that are not possible in the component molecules themselves.

Scheme 1



Tungsten is recognized to form strong metal—metal multiple bonds and metal—oxygen multiple bonds in its low (II—IV) and high (IV—VI) oxidation states, respectively, rendering it a promising candidate for the formation of type **A** molecules. Recently, we reported the rich redox properties of the dinuclear quadruply bonded compound $W_2(dpa)_4$, **1**, (dpa = deprotonated form of 2,2′-dipyridylamine, see Figure 1),[9] and characterized its one-electron oxidized W_2^{5+} form. In the course of these studies, we found that oxidation of **1** with an excess of I_2 (>6 equiv) in the presence of adventitious water (reaction a in Figure 1) leads to the formation of the novel ditungsten terminal oxo complex $[W_2O(dpa)_4](I_3)_2$ (**2**(**I$_3$**)$_2$) containing one square-pyramidal $N_4W{\equiv}O$ group and a separate, eight-coordinate W ion. This dinuclear $\{W_2O\}^{6+}$ species results from a remarkable four-electron oxidation of **1**. Typically, overoxidation of W_2^{4+} species gives rise to thermodynamically stable polyoxotungstate ions or to edge-sharing bioctahedral species[10] neither of which are readily returned to the quadruply bonded W_2^{4+} state.[11] Thus, the isolation of a discrete terminal oxo complex here is unprecedented and results from the utilization of the tridentate dpa ligand. In order to study the $\{W_2O\}^{6+}$species in more detail, it was necessary to develop a reproducible, rational, stepwise synthetic approach that would avoid the presence of reactive I_3^- counterions.

The two-electron oxidation of **1** with two equivalents of ferrocenium triflate (FcOTf) (reaction b in Figure 1) furnishes the W_2^{6+} complex $[W_2(dpa)_4](OTf)_2$ (**3**). Oxidation of **3** with one equivalent of *m*-chloroperoxybenzoic acid (*m*-CPBA) (reaction c in Figure 1) was monitored via UV—vis spectroscopy and

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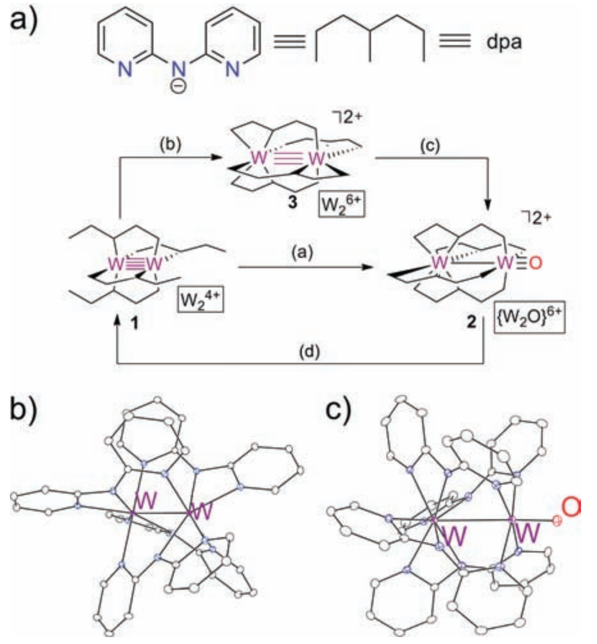


Figure 1. a) Reaction conditions: (a) 6.1 I_2, trace H_2O; (b) 2 FcOTf; (c) 1 *m*-CPBA; (d) xs. P^tBu_3, ~82 °C. c) Molecular structure of the dicationic dinuclear unit in **2** and b) in **3** with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

resulted in the clean formation of a species with an absorption maximum at 706 nm (Figure S1, Supporting Information [SI]). Addition of a source of the bulky counterion tetraphenylborate (BPh_4^-) made it possible to crystallize the oxidation product as $[W_2O(dpa)_4](OTf)(BPh_4)$ (**2(OTf)(BPh₄)**), which contains the desired $\{W_2O\}^{6+}$ moiety. Compounds **2** and **3** have been structurally characterized by X-ray diffraction and their purity was established by NMR spectroscopy, mass spectrometry, and elemental analysis. Compound **2** is indefinitely stable under inert atmosphere in the solid state as well as in solution. Exposure to air results in overoxidation to polyoxotungstate species. Compound **3** is stable for short times in solution at room temperature.

In the crystal structure of **3** (Figure 1) both W(III) ions are six coordinate with respect to the bridging/chelating dpa ligands with W−N distances ranging from 2.125[1] to 2.194[1] Å. The additional W−W interaction gives each W ion an effective coordination number of seven, in roughly pentagonal bipyramidal geometry. The W−W distance of 2.7156(2) Å is much longer than expected for a W−W triple bond, the highest possible bond order between two W(III) (d^3) ions, which are typically ~2.4 Å.[12] The molecular structure of **2** (Figure 1) features one square-pyramidal W ion with an axial W−O bond length of 1.696[2] Å and equatorial coordination at ~2.139[3] Å by four pyridine N-atoms from the dpa ligands. The short W−O distance is indicative of a W≡O triple bond, consistent with the formulation of W≡O triple-bonds in other square-pyramidal or octahedral tungsten−oxo complexes.[13] The second W ion is eight coordinate in a distorted square antiprismatic geometry ($d(W{-}N_a) = 2.162[2]$ Å; $d(W{-}N_{py}) = 2.198[2]$ Å). There is a relatively short W−W distance of 3.066[4] Å.

For compound **3**, the long W−W distance of 2.72 Å is incompatible with the interpretation of a strong W≡W triple bond. However, the ^1H NMR spectrum of **3** (Figure 2) displays eight sharp, equally intense resonances of expected multiplicity at 8.6−6.5 ppm in the aromatic region, consistent with molecular D_2 symmetry and diamagnetism of the W_2^{6+} unit. For the purpose of this work we will consider **3** to have an unusually long triple bond and note that, in analogy to other compounds with weak metal−metal bonds,[14] we suspect only weak pairing of the π-electrons and not full W−W π-bonds.[15]

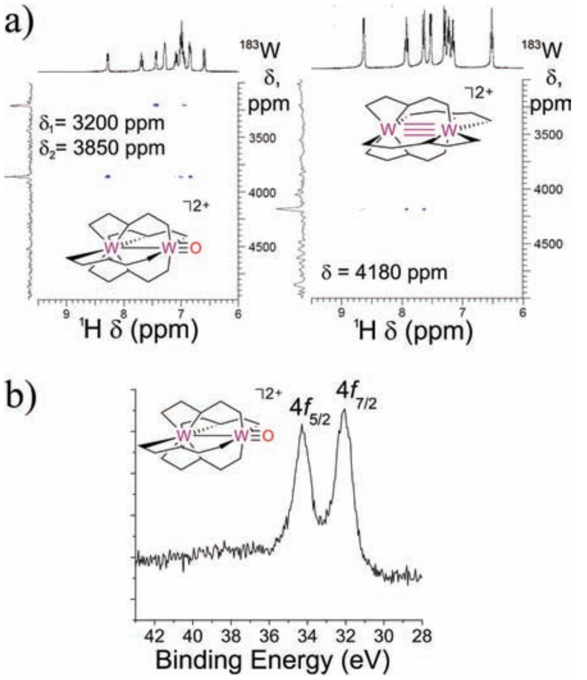


Figure 2. a) $^1H-^{183}W$ HMBC spectra of **2(BPh₄)(OTf)** (left) and **3** (right) measured in CD_3CN. b) XPS spectrum of **2**.

The solution ^1H NMR spectrum of **2** (Figure 2) features eight resonances at 8.3−6.6 ppm that can be assigned to the $[W_2O(dpa)_4]^{2+}$ molecule and are in agreement with its C_4 solid-state structure. More importantly, these results demonstrate that the $\{W_2O\}^{6+}$ unit is diamagnetic. The ^{17}O NMR spectrum of **2**, isotopically enriched with 10% ^{17}O, shows a resonance at 891 ppm for the oxo ligand. Though comparable data for W(IV)−oxo compounds are lacking, W(VI)−oxo complexes show characteristic ^{17}O chemical shifts from 700 to 800 ppm.[16] The spectral features of **2** are consistent with three formal oxidation-state assignments: (a) W(II)−W(VI)≡O with low-spin W(II) ($S = 0$), (b) W(III)−W(V)≡O with strong antiferromagnetic coupling, and (c) W(IV)W(IV)≡O. To gain information about the electron distribution in the $\{W_2O\}^{6+}$ unit we have employed ^{183}W NMR and X-ray photoelectron spectroscopy (XPS). Because the ^{183}W nucleus ($I = 1/2$; 14% natural abundance) has very low NMR sensitivity, it was not possible to observe ^{183}W signals for our compounds directly. However, $^1H-^{183}W$ HMBC (heteronuclear multiple bond correlation) 2D spectra were obtained for **2** and **3** (Figure 2a). For compound **3**, in which both W ions are unquestionably in the oxidation state +III, a single ^{183}W resonance at 4180 ppm was found. Compound **2** displays two resonances at 3200 ppm and 3850 ppm associated with the two inequivalent W nuclei of the $\{W_2O\}^{6+}$ moiety. This comparison allows us to exclude formulation (a) W(II)W(VI)O for the $\{W_2O\}^{6+}$ unit. However, there are not enough literature examples to unambiguously distinguish between oxidation-state assignments (b) and (c) based on the ^{183}W NMR results alone, and therefore XPS (X-ray photoelectron spectroscopy) was utilized

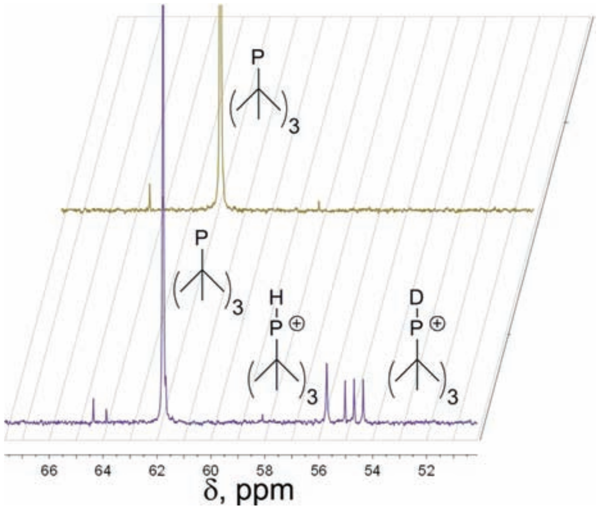
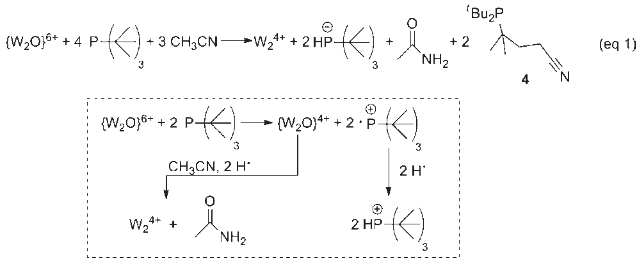


Figure 3. $^{31}P\{^1H\}$ NMR spectra before (top) and after (bottom) reaction (d) (see Figure 1) in CD_3CN.

as a complementary method. The binding energy of W 4f electrons is known to increase by ~0.9 eV with each unit increase in W oxidation state[17] and serves thereby as a sensitive probe for the oxidation state of W nuclei. The XPS spectrum of **2** (Figure 2 b) displays two signals at 32.1 and 34.3 eV. This peak pattern arises from $4f_{5/2}/4f_{7/2}$ spin−orbit splitting which causes the observed characteristic intensity ratio and peak separation of ~2.2 eV.[18] The absence of other peaks suggests that both W ions in **2** are in the same oxidation state, and we therefore conclude that assignment (c) is correct.

Mononuclear compounds with W≡O triple bonds show characteristic inertness toward O-atom transfer reactions because of the exceedingly strong W≡O bond, especially in the W(IV)≡O oxidation state. For example, whereas reaction of $W(VI)OCl_4$ with triphenylphosphine results in a 50% yield of $W(IV)Cl_4(PPh_3)_2$,[19] no such oxidation of tertiary phosphines by W(IV)≡O groups has been observed.[7] Furthermore, there are even examples of stable octahedral W(IV)≡O complexes that feature coordination of strongly nucleophilic and easily oxidized bisphosphines to the W(IV)≡O group, such as $[W(O)(F)(dppe)_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane)[20] and $[W(O)(Cl)(dmpe)_2]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane).[21] However, we reasoned that the thermodynamic price of cleaving the W≡O bond in **2** could be offset by the generation of strong W−W bonds in the reduced product. Therefore, we decided to investigate the reactivity of **2** toward tri-*tert*-butylphosphine (P^tBu_3), envisioning likely formation of **3** and the corresponding phosphine oxide, $O{=}P^tBu_3$, as products. Heating a mixture of **2** (~0.2 mM) and excess P^tBu_3 to ~85 °C in CH_3CN (reaction d in Figure 1) causes a color change from yellow-green to gray to blue to occur within 10 min (Figure S2, SI). Surprisingly, the UV−vis spectrum of the product mixture is identical to the reported spectral signature of **1** which contains the W_2^{4+} unit.[9] The presence of **1** was also confirmed by ^1H NMR. Thus, instead of a two-electron reduction resulting from simple oxygen atom transfer, the $\{W_2O\}^{6+}$ unit undergoes a remarkable four-electron reduction including oxygen atom transfer to yield the quadruply bonded compound **1**! This 4 e^- reaction pathway is not feasible for any mononuclear tungsten terminal oxo compounds and underlines the unique interplay between metal−metal and metal−ligand multiple bonds in **2**.

Scheme 2



In an effort to characterize the oxidation products, this reaction was conducted in deuterated acetonitrile (CD_3CN) and monitored by means of ^1H- and $^{31}P\{^1H\}$ NMR spectroscopy (Figures S3 (SI) and Figure 3). The product mixture, which was expected to contain phosphine oxide, instead contained the monocationic species $HP^tBu_3^+$ (55.7 ppm) and $DP^tBu_3^+$ (54.8 ppm) in approximately equal ratios. The presence of phosphonium ions implies the transient existence of highly reactive phosphinyl radicals ($\bullet P^tBu_3^+$) as a result of one-electron oxidation of P^tBu_3. These radicals may abstract an H/D-atom from other P^tBu_3 or solvent CD_3CN molecules. Surprisingly, no formation of OP^tBu_3 (64.6 ppm) could be observed, leaving the fate of the oxygen atom from **2** unexplained. The ^1H NMR spectrum in CD_3CN of the product mixture after the reaction was conducted in CH_3CN displays additional peaks that answer this question corresponding to H_2O (2.18 ppm) and acetamide (1.87, 5.56, 6.10 ppm), which is a hydrolysis product of acetonitrile.

We also observed the formation of a precipitate during this reaction, the qualitative composition of which was analyzed by MALDI-MS experiments. In addition to the slightly soluble **1**, the precipitate contains the final oxidation products of this reaction: the radical coupling products **4** of a carbon-centered $^tBu_2P[C(CH_3)_2(CH_2\bullet)]$ radical and solvent radicals •CHDCN or $\bullet CD_2CN$ which appear at 242.3 and 243.3 amu, respectively, in the mass spectrum. Thus, a balanced equation for this unusual four-electron redox reaction may be written as shown in Scheme 2 (eq 1).

There are many bizarre features of this reaction that point to intriguing mechanistic possibilities. First, the fact that no phosphine oxide is formed means that phosphine oxidation must occur via outer-sphere electron transfer. This is an electronic preference of the system rather than one prompted by the sterically encumbered P^tBu_3 substrate, because results with the less crowded P^nBu_3 also indicate phosphonium ion formation rather than phosphine oxide formation. Control experiments were also performed in which P^tBu_3 was oxidized with the one-electron oxidant $[N\text{-}(4\text{-bromophenyl})_3][OSO_2CF_3]$ or $Cu(OSO_2CF_3)_2$. The phosphonium ion is also observed in these reactions, indicating that it is a direct result of one-electron oxidation of P^tBu_3.

In our mechanistic hypothesis, Scheme 2, we therefore indicate outer-sphere electron transfer from P^tBu_3 to **2** as the first step in the reaction, producing two highly reactive intermediates: the phosphinyl radicals and a reduced ditungsten oxo species ($\{W_2O\}^{4+}$). The former species must abstract H atoms from P^tBu_3 or solvent, whereas the reactivity of the latter species is not predictable. A reduced Mo^{2+}-oxo species has recently been proposed by Long et al.[21] to be very basic, and in analogy we may expect the $\{W_2O\}^{4+}$ species to be a strong nucleophile. It could abstract H atoms or attack the nitrile C atom directly, ultimately leading to the formation of acetamide.

Rates of disappearance of **2** were measured in CH_3CN and CD_3CN, and the reactions were found to be faster in CD_3CN by a factor of ~2.1. This result rules out the possibility of H-atom abstraction from solvent by **2** and is consistent with a mechanism whereby outer-sphere reduction of **2** is rate limiting,[23] since the rates of electron-transfer reactions vary strongly with the properties of the solvent medium.

In summary, the W(IV) oxo group is historically notorious for its chemical inertness, but we show that it can be activated for new reactivity by the placement of a second W atom in its primary coordination sphere. The interplay between W—O and W—W multiple bonds leads to unexpected reactivity. Up to now, any metal—oxo compound that reacts with phosphines is known to do so via oxygen atom transfer yielding phosphine oxide products. The $\{W_2O\}^{6+}$ species does not follow this paradigm but instead promotes a series of radical reactions. Preliminary studies suggest that this novel reactivity could be used to oxidize hydrocarbons, which we are currently pursuing in our lab.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, detailed description of $^1H-^{183}W$ HMBC experiments, and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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