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Redox-Active Ligands

Four-Electron Oxidative Formation of Aryl Diazenes Using a Tantalum Redox-Active Ligand Complex**

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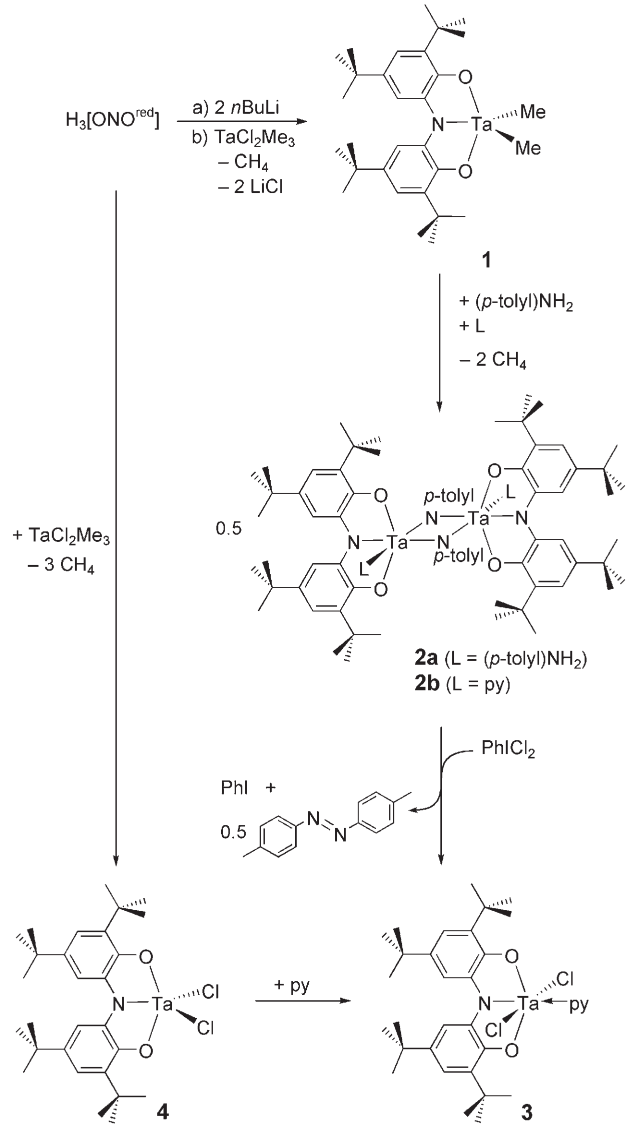
Transition-metal complexes capable of mediating multielectron transformations are critical components for a variety of small-molecule transformations. For example, the oxidation of C–H bonds[1] and the reduction of protons to H_2[2] are both two-electron transformations. The oxidation of water to O_2 is a four-electron process[3] and the reduction of nitrogen to ammonia is an overall six-electron process.[4] The design of metal complexes to promote or catalyze these multielectron reactions usually relies on one or more transition-metal ions capable of two-electron changes in a formal oxidation state. An alternative strategy is to incorporate redox-active ligands into the metal coordination sphere to supply reducing or oxidizing equivalents during a multielectron transformation.[5]

Herein, we report the use of a tridentate redox-active ligand, *N,N*-bis(3,5-di-*tert*-butyl-2-phenoxide)amide ($[ONO^{red}]^{3-}$),[6] coordinated to tantalum, to effect the four-electron oxidative formation of aryl diazenes. In its reduced form, $[ONO^{red}]^{3-}$ is a planar, tridentate ligand that coordinates to transition metals in a meridional geometry. The organometallic synthon $TaMe_3Cl_2$[7] has been used to prepare $[ONO^{red}]TaMe_2$ (**1**), which was then converted into the bridging imido dimer $\{[ONO^{red}]Ta[\mu\text{-}N(p\text{-tolyl})]L\}_2$ (**2a**, L = NH_2(*p*-tolyl); **2b**, L = pyridine (py); Scheme 1). Oxidation of **2b** resulted in the quantitative elimination of (*p*-tolyl)N=N(*p*-tolyl). To the best of our knowledge, this is the first example of N=N double bond formation and organic diazene elimination from a tantalum(V) bridging imido dimer. Oxidation studies of the related complex $[ONO^{red}]TaCl_2$ (**4**) with $PhICl_2$ suggest that the redox-active ligand plays the pivotal role of collecting oxidizing equivalents within the tantalum coordination sphere. The work presented herein highlights a new strategy for the design of metal complexes capable of multielectron oxidation reactions.

The bridging imido complexes **2a** and **2b** were prepared via dimethyl complex **1** (Scheme 1). Double deprotonation of $H_3[ONO^{red}]$ with *n*BuLi (2 equiv) followed by treatment with $TaCl_2Me_3$ afforded **1** in 49 % yield following recrystallization from pentane. The ^1H and ^{13}C NMR spectra of **1** showed diagnostic resonances for the $[ONO^{red}]^{3-}$ ligand. The methyl ligands of **1** resonated at $\delta = 0.77$ and 59.7 ppm in the ^1H and ^{13}C NMR spectra, respectively.

The methyl ligands of **1** are susceptible to protonolysis by anilines, which results in the formation of bimetallic complexes with two bridging imido ligands. As shown in Scheme 1, benzene solutions of **1** heated to reflux with two equivalents of NH_2(*p*-tolyl) resulted in the formation of



Scheme 1. Synthesis and oxidation chemistry of $\{[ONO^{red}]Ta[\mu\text{-}N(p\text{-tolyl})]L\}_2$ (**2**).

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{[ONO^{red}]Ta[μ-N(*p*-tolyl)][NH$_2$(*p*-tolyl)]}$_2$ (**2a**), which was characterized both in solution and in the solid state. The ^{1}H NMR spectrum of **2a** showed separate resonances for the bridging imido ligands and the neutral toluidine ligands, thus indicating that there is no exchange on the NMR timescale. The N-H protons of the coordinated toluidine were observed as a sharp singlet at $\delta = 4.48$ ppm in the ^{1}H NMR spectrum. The addition of pyridine to **2a** resulted in displacement of the coordinated toluidine and formation of the pyridine adduct, {[ONO^{red}]Ta[μ-N(*p*-tolyl)](py)}$_2$ (**2b**). The ^{1}H and ^{13}C NMR data for **2b** are congruent with the data for **2a**, which indicates similar metal coordination environments.

X-ray diffraction studies of **2a** revealed an edge-sharing bioctahedral structure (Figure 1).[8a] Dimeric tantalum complexes with bridging imido ligands are rare, and often contain Ta^{IV} centers and a formal metal–metal bond.[9] For d^0 Ta^V complexes, although dimers with bridging imido ligands are known,[10] terminal imido ligands are often observed.[11,12]

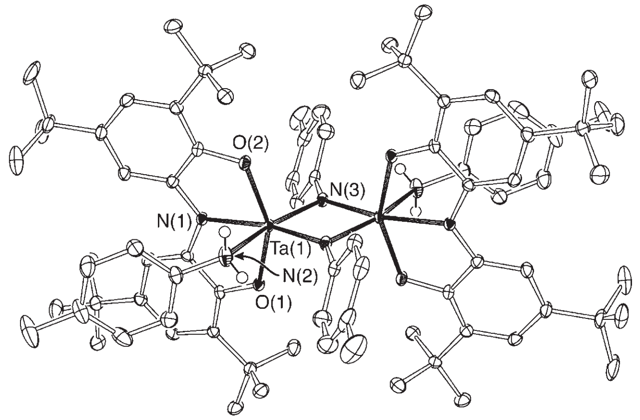


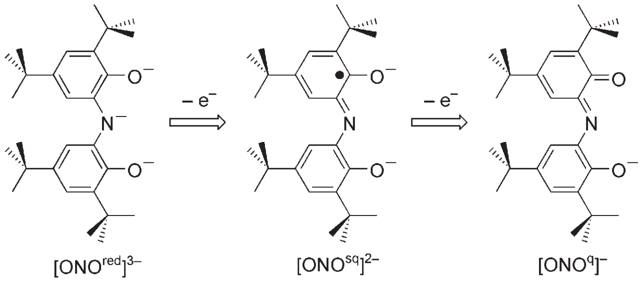
Figure 1. ORTEP diagram for {[ONO^{red}]Ta[μ-N(*p*-tolyl)][NH$_2$(*p*-tolyl)]}$_2$ (**2a**). Thermal ellipsoids are shown at 50% probability. Solvent molecules and hydrogen atoms have been omitted for clarity.

In **2a**, one [ONO^{red}]$^{3-}$ ligand coordinates in a meridional fashion to each tantalum(V) center. The two bridging imido ligands occupy *cis* coordination sites on each metal leaving the sixth coordination site for the neutral toluidene donor ligand. There is a slight asymmetry in the imide Ta−N bond lengths, which are 2.0164(17) and 2.0349(16) Å. The shorter distance corresponds to the Ta−N(imide) bond *trans* to the toluidene ligand, whereas the longer distance corresponds to the Ta−N(imide) bond *trans* to the amide nitrogen atom of the [ONO^{red}]$^{3-}$ ligand. The separation between the bridging imide nitrogen atoms is 2.6 Å, which is outside of the normal N−N bonding distance but within the van der Waals radii ($2 \times r_{\mathrm{vdW}} =$ 3.1 Å). The Ta–Ta distance is 3.0947(3) Å, which is outside of the normal metal–metal distance for a Ta^{IV}−Ta^{IV} bond (2.80–2.90 Å),[13] thus suggesting that **2a** is best described as a Ta^V dimer with no metal–metal bond.

Oxidation of **2b** with PhICl$_2$ resulted in the elimination of the azo product (*p*-tolyl)N=N(*p*-tolyl). Addition of two equivalents of PhICl$_2$ to a solution of **2b** in diethyl ether at room temperature caused a color change from dark purple to red as the reaction went to completion overnight.[14] After removal of the solvent, a ^{1}H NMR spectrum of the crude residue revealed the formation of (*p*-tolyl)N=N(*p*-tolyl), which was confirmed by GC–MS analysis. The metal-containing product, [ONO^{red}]TaCl$_2$(py) (**3**), was isolated as a red solid by recrystallization from toluene at −35 °C. As shown in Scheme 1, complex **3** was prepared independently by addition of pyridine to the five-coordinate tantalum dichloride complex [ONO^{red}]TaCl$_2$ (**4**).

Monitoring of the oxidation reactions of **2b** by GC–MS revealed the formation of one equivalent of aryl diazene per equivalent of bridging imido dimer **2b**. These oxidation reactions required two equivalents of PhICl$_2$, which corresponded to an overall four-electron oxidation of **2b**. Attempts to isolate and characterize oxidation intermediates from the reaction of **2b** with one equivalent of PhICl$_2$ were not successful; however, in such reactions the formation of substoichiometric aryl diazene was always observed.

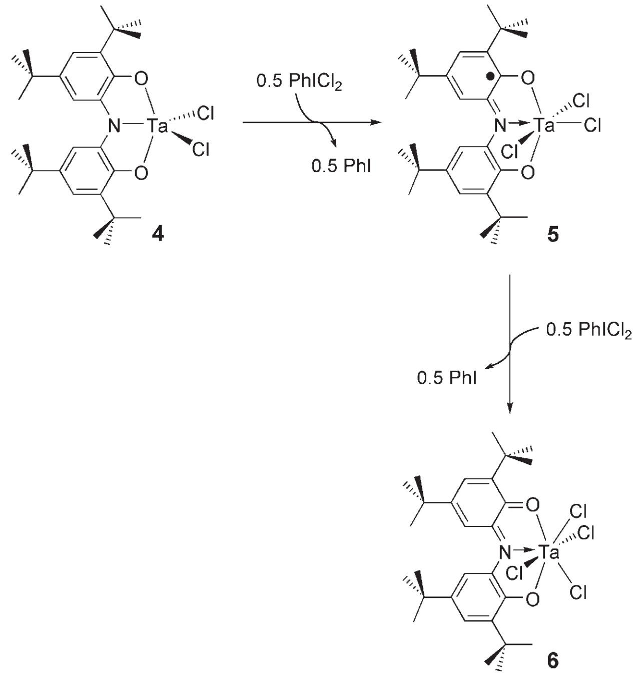
A key aspect to evaluate for the oxidation of **2b** is the role of the redox-active [ONO^{red}]$^{3-}$ ligand. As shown in Scheme 2, the [ONO^{red}]$^{3-}$ ligand can be oxidized by one electron to give the dianionic, semi-quinonate ligand [ONO^{sq}]$^{2-}$, or by two electrons to give the monoanionic, quinonate ligand [ONO^q]$^-$.[15] These ligand oxidation states could store single-electron oxidizing equivalents prior to the elimination of the aryl diazene.



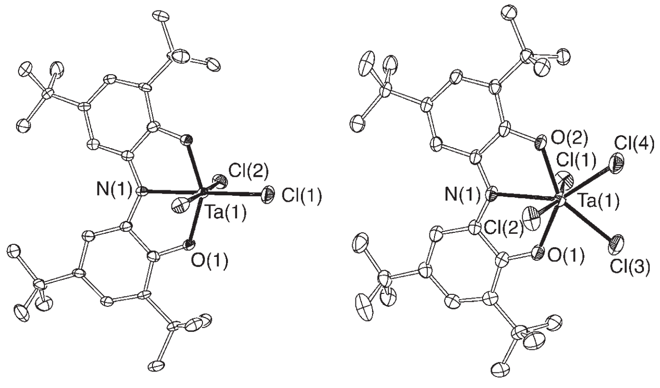
Scheme 2. Oxidation states of the [ONO] ligand platform.

Tantalum complexes of both [ONO^{sq}]$^{2-}$ and [ONO^q]$^-$ were prepared by halogen oxidation of **4**. According to Scheme 3, complex **4** reacted rapidly with 0.5 equivalents of PhICl$_2$ to afford the open-shell, radical product [ONO^{sq}]TaCl$_3$ (**5**) as a blue microcrystalline solid. The presence of an unpaired electron in **5** was confirmed by solution EPR spectroscopy. A multiple-line EPR signal at $g = 1.979$ (3522 G) was observed for solutions of **5** in diethyl ether at 298 K, consistent with the ligand-centered radical interacting with the tantalum nucleus ($I = 7/2$). Similar EPR features were observed for an octahedral Co^{III} complex with a single [ONO^{sq}]$^{2-}$ ligand.[16] X-ray-quality crystalline blocks of **5** were obtained from cold diethyl ether; the structure of **5** is presented as an ORTEP diagram in Figure 2.[8b]

When a 1:1 ratio of PhICl$_2$ to **4** was used, a two-electron oxidation resulted in the formation of [ONO^q]TaCl$_4$ (**6**) as a dark green microcrystalline solid. As indicated in Scheme 3, complex **6** is a closed-shell, diamagnetic compound that was characterized readily by ^{1}H NMR spectroscopy. Four *tert*-



Scheme 3. Oxidation reactions of [ONO^{red}]TaCl$_2$ (**4**) with PhICl$_2$.



5 **6**

Figure 2. ORTEP diagrams for [ONO^{sq}]TaCl$_3$ (**5**) and [ONO^{q}]TaCl$_4$ (**6**). Thermal ellipsoids are shown at 50% probability. Solvent molecules and hydrogen atoms have been omitted for clarity.

butyl resonances and four aromatic resonances were observed in the spectrum, which suggests distinct quinone and phenol portions of the [ONO^{q}]$^-$ ligand as shown in Scheme 1. Crystalline **6** for X-ray diffraction studies was obtained from diethyl ether; the solid-state structure of **6** is presented in Figure 2.[8c]

Radical complex **5** is a six-coordinate, pseudo-octahedral tantalum(V) complex in the solid state. The tantalum atom of **5** sits in a special position and as a result, only half of the [ONO^{sq}]$^{2-}$ ligand is unique. The one-electron-oxidized [ONO^{sq}]$^{2-}$ ligand is planar leaving three meridional coordination sites for the chloride ligands. The Ta–Cl bond lengths are 2.312(5) and 2.3686(14) Å, with the shorter distance observed for the chloride ligand *trans* to the nitrogen donor. The distances associated with the [ONO^{sq}]$^{2-}$ ligand are consistent with oxidation of the ligand: notably, the Ta–N distance in **5** is long at 2.222(13) Å.

The tantalum center of **6** is seven-coordinate in the solid state with approximate pentagonal bipyramidal geometry (Figure 2). The formation of **6** requires two-electron oxidation of the redox-active ligand, and bond lengths within the [ONO^{q}]$^-$ ligand are consistent with a symmetric, oxidized ligand. Both rings of the [ONO^{q}]$^-$ ligand of **6** have similar bond lengths, which suggests that the two rings of the ligand are equivalent; however, this proposal is inconsistent with both the ^{1}H NMR data discussed above and the ^{13}C NMR data, which show distinct C–O and C=O carbon resonances at $\delta = 155$ and 182 ppm, respectively. In a structural study of lead complexes with the [ONO^{q}]$^-$ ligand, the quinone character was localized, giving a localized quinone–phenol structure for the ligand, which was discernable in the ligand C–C and C–O bond lengths.[17] We suspect that the bond lengths observed for the [ONO^{q}]$^-$ ligand of **6** reflect averaged values resulting from both orientations of the [ONO^{q}]$^-$ ligand in the solid state.[18]

Strategies for storing multiple oxidizing or reducing equivalents in a single coordination complex are not well developed, despite the importance of such strategies in small-molecule oxidation and reduction reactions. The oxidation-induced elimination of (*p*-tolyl)N=N(*p*-tolyl) from **2b** is an overall four-electron process that results in the formation of an N=N double bond. We believe that two factors facilitate this reaction. First, the Ta$_2$N$_2$ core of **2b** may play a key role in organizing the nitrogen atoms for bond formation upon oxidation.[19] Second, the redox-active [ONO^{red}]$^{3-}$ ligand of **2b** can collect single-electron oxidation equivalents until the four-electron elimination of the diazene can occur. The halogen reactions resulting in the formation of **5** and **6** from **4** support the idea that the [ONO^{red}]$^{3-}$ ligand platform can participate in such oxidation reactions when coordinated to tantalum(V).[20] In a similar manner, one- and two-electron oxidations of complexes related to **2b** may lead to insight into the nature of N–N bond formation and by extension O–O bond formation. Further studies are required to probe the nature of these intermediate oxidation states. Nevertheless, the structure and reactivity of **2b** represent a new paradigm for tackling multielectron reactions in which oxidation leads to bond formation.

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[8] Compound **2a**: $C_{102}H_{130}N_6O_4Ta_2$, $M_r = 1866.02$, monoclinic, $P2_1/n$, $a = 14.7449(15)$, $b = 20.492(2)$, $c = 15.3737(16)$ Å, $\beta = 99.830(2)°$, $V = 4577.1(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.354$ Mg m^{-3}, $\mu = 2.443$ mm^{-1}, $R1 = 0.0193$ [$I > 2\sigma_I$], $wR2 = 0.0437$, GOF = 1.063. Compound **5**: $C_{28}H_{40}Cl_3NO_2Ta$, $M_r = 709.91$, orthorhombic, $Fdd2$, $a = 18.800(5)$, $b = 27.302(7)$, $c = 12.013(3)$ Å, $V = 6166(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.529$ Mg m^{-3}, $\mu = 3.849$ mm^{-1}, $R1 = 0.0330$ [$I > 2\sigma_I$], $wR2 = 0.0795$, GOF = 1.069. Compound **6**: $C_{28}H_{40}Cl_4NO_2Ta$, $M_r = 745.36$, monoclinic, $P2_1/n$, $a = 11.7269(15)$, $b = 19.453(3)$, $c = 14.4343(18)$ Å, $\beta = 104.292(2)°$, $V = 3190.8(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.552$ Mg m^{-3}, $\mu = 3.804$ mm^{-1}, $R1 = 0.0337$ [$I > 2\sigma_I$], $wR2 = 0.0872$, GOF = 1.079. CCDC-678271 (**2a**), 678272 (**5**), and 678273 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] In the case of **2a** and **2b**, variable-temperature NMR spectroscopy and mass spectrometry both suggest that the Ta_2N_2 core is preserved in solution with no evidence for a monomer–dimer equilibrium.

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[14] The use of other oxidants, such as Ag[BPh_4] or PhI$(OAc)_2$, did not lead to formation of the diazene product, which suggests that oxidation potential and Ta−Cl bond formation play a role in the efficacy of the oxidation reaction.

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[18] In other words, the quinone and phenol portions of the ligand in **6** pack similarly resulting in arbitrary “up” or “down” orientation of the molecule at each site.

[19] Crossover experiments in which mixtures of **2b** and phenylimido analogue {[ONO^{red}]Ta[μ-NPh](py)}$_2$ were oxidized yielded all three diazene products. These results suggest that although the Ta_2N_2 core of **2b** is stable in solution (see reference [12]), upon oxidation, equilibrium is established between a tantalum imide dimer and a putative tantalum imide monomer.

[20] This conclusion is further supported by preliminary electrochemical data for **2b**, **3**, and **4**, which show multiple oxidation events; however, electrochemical studies have been hampered by the irreversibility of these processes.