

# Nonclassical Oxygen Atom Transfer as a Synthetic Strategy: Preparation of an Oxorhenium(V) Complex of the Bis(3,5-di-*tert*-butyl-2-phenoxo)amide Ligand

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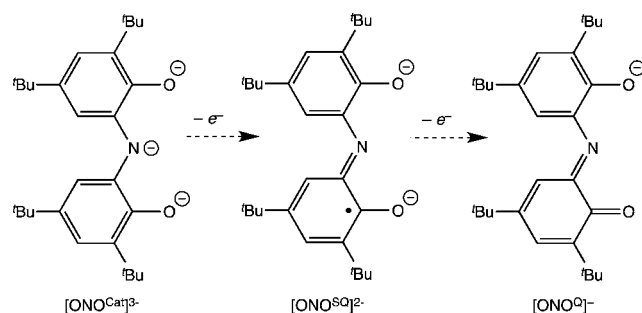
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## Supporting Information

**ABSTRACT:** Oxo(triphenylphosphine)[bis(3,5-di-*tert*-butyl-2-phenoxo)amido]rhenium(V) [(ONO<sup>Cat</sup>)ReO(PPh<sub>3</sub>)] is prepared by the reaction of iododioxobis(triphenylphosphine)rhenium(V) [ReO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>I] with lead bis(3,5-di-*tert*-butyl-1,2-quinone-1-(2-oxy-3,5-di-*tert*-butylphenyl)imine) [Pb(ONO<sup>Q</sup>)<sub>2</sub>]. In this reaction, the ONO ligand undergoes a two-electron reduction, with concomitant oxidation of PPh<sub>3</sub> to OPPh<sub>3</sub> and transformation of the dioxorhenium(V) fragment into a monooxorhenium(V) fragment, constituting a net nonclassical oxygen atom transfer. (ONO<sup>Cat</sup>)ReO(PPh<sub>3</sub>) adopts a square pyramidal geometry with an apical oxo group [*d*<sub>ReO</sub> = 1.6873(14) Å] and a highly folded ONO ligand [O–Re–O = 129.55(6)°]. The fully reduced, trianionic oxidation state of the ONO ligand is confirmed by spectroscopic and metrical data.

Redox-active ligands have received increasing attention as supporting ligands for transition-metal-mediated redox reactions in which the ligands share or bear the exclusive burden of changing oxidation state over the course of the reaction.<sup>1</sup> One useful ligand in such reactions is the 3,5-di-*tert*-butyl-1,2-quinone-1-(2-oxy-3,5-di-*tert*-butylphenyl)imine, or ONO, ligand (Scheme 1) first introduced by Stegmann and Scheffler as a ligand for group 14 metals.<sup>2</sup> It and its aza analogues have been used as supporting ligands in alcohol oxidation,<sup>3</sup> nitrene transfer,<sup>4</sup> and dioxygen reduction.<sup>5</sup> In many of these reactions, redox processes at the ligands are accompanied by bond making or breaking at the metal center, a phenomenon that we have

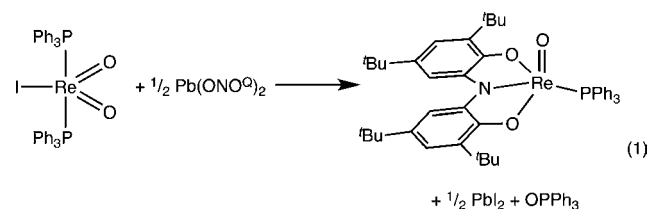
Scheme 1. Oxidation States of the ONO Ligand



recently termed “nonclassical” inner-sphere redox reactions in the particular context of oxygen atom transfer reactions.<sup>6</sup>

We were particularly interested in extending the chemistry of the ONO ligand into hitherto unknown rhenium complexes. A recent study of rhenium amidophenolates indicates that they have a rich redox chemistry,<sup>7</sup> with oxidation taking place nearly equally at the rhenium center and the amidophenolate ligand.<sup>8</sup> Similar rhenium catecholates undergo oxygen atom transfer chemistry with net redox changes solely at the metal center, although the accessibility of ligand oxidation has been proposed to play a role in facilitating the reactions.<sup>9</sup> We thus wished to explore whether the ONO ligand would promote ligand- or metal-centered redox events or whether both could be observed under proper circumstances. Here we report the preparation of oxorhenium(V) phosphine complexes of the ONO<sup>Cat</sup> ligand via a route that involves ligand-centered redox changes in a net nonclassical oxygen atom transfer.

In past studies, we have found that the lead(II) complex Pb(ONO<sup>Q</sup>)<sub>2</sub><sup>10</sup> is a mild and efficient reagent for the replacement of halides with the ONO ligand in chlorosilanes and -stannanes.<sup>11</sup> The lead reagent reacts analogously with the dioxorhenium(V) iodide complex ReO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>I<sup>12</sup> to give solid yellow PbI<sub>2</sub> and dark red (ONO)ReO(PPh<sub>3</sub>) (eq 1). The



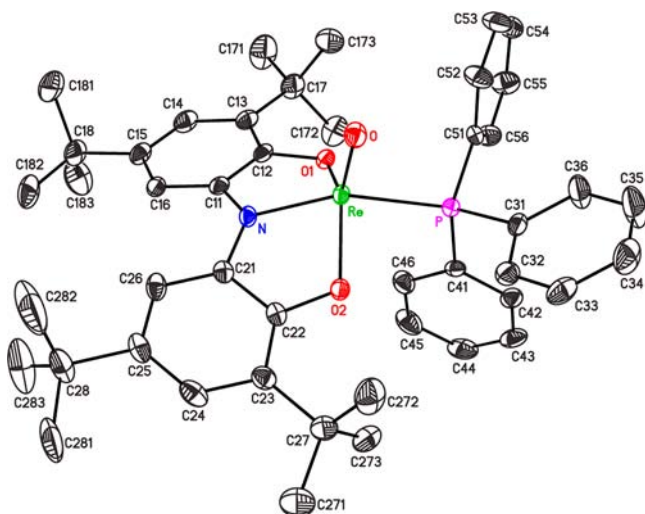
reaction proceeds in high yield, as judged by in situ <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, with only trace amounts of ONO- or PPh<sub>3</sub>-containing byproducts. A total of 1 equiv of triphenylphosphine oxide is detected by NMR. The air-sensitive rhenium complex can be isolated in moderate yield by precipitation from methanol after filtration through silica gel to remove OPPh<sub>3</sub>.

The formulation of the rhenium-containing product as (ONO)ReO(PPh<sub>3</sub>) is supported by NMR spectroscopy, which indicates that the compound is diamagnetic and mirror-symmetric and contains a single PPh<sub>3</sub> ligand. The presence of

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a terminal oxo group is indicated by the characteristic absorption in the IR spectrum at  $950\text{ cm}^{-1}$ , typical of oxorhenium(V) complexes with  $\pi$ -donor ligands (compare  $\text{MeN}[\text{CH}_2\text{CH}_2\text{NMe}_2]_2\text{ReO}(\text{CH}_3)$ ,  $\nu_{\text{ReO}} = 958\text{ cm}^{-1}$ ).<sup>13</sup> X-ray crystallography<sup>14</sup> (Figure 1 and Tables S1 and S2 in the



**Figure 1.** Thermal ellipsoid plot of  $(\text{ONO}^{\text{Cat}})\text{ReO}(\text{PPh}_3)$ , with hydrogen atoms and minor components of disordered *tert*-butyl groups omitted for clarity. Selected bond distances (Å) and angles (deg): Re–O, 1.6873(14); Re–O1, 1.9515(14); Re–O2, 1.9733(15); Re–N, 1.9628(16); Re–P, 2.4359(6); O1–C12, 1.384(2); O2–C22, 1.381(2); N–C11, 1.412(3); N–C21, 1.402(3); O–Re–P, 99.85(5); O–Re–N, 113.26(7); O–Re–O1, 114.06(7); O–Re–O2, 116.31(7); O1–Re–O2, 129.55(6).

Supporting Information, SI) indicates that the compound adopts a square pyramidal geometry typical of five-coordinate rhenium(V) oxo complexes, with an apical oxo group and significant displacement of the  $\text{ReO}$  moiety above the plane of the equatorial ligands. The ONO ligand adopts its usual *mer* geometry but displays an unusual degree of folding, with the  $\text{O1–Re–O2}$  angle of  $129.55(6)^\circ$  among the smallest observed in  $\text{M}(\text{ONO})$  complexes. For comparison, holo- and mer-leptic first-row transition-metal  $\text{M}(\text{ONO})_2$  complexes have  $\text{O–M–O}$  angles in the range of  $150.6\text{--}171.6^\circ$ ,<sup>15</sup>  $\text{W}(\text{ONO})_2$  has  $\text{O–M–O}$  angles of  $152.8^\circ$ ,<sup>16</sup> and monoligated  $(\text{ONO})\text{Ta}$  complexes have  $\text{OTaO}$  angles of about  $148^\circ$ .<sup>17</sup> Only  $\text{Pb}(\text{ONO})_2$ , with its highly distorted, almost  $\kappa^2$ , coordination of the ONO ligand, has smaller  $\text{O–M–O}$  angles ( $125.4^\circ$ ).<sup>10,11</sup> Despite distortion of the ONO ligand in  $(\text{ONO})\text{ReO}(\text{PPh}_3)$ , the nitrogen atom maintains a nearly planar geometry, with the angles around the nitrogen atom summing to  $358.7(3)^\circ$ .

While the ONO ligand may in general adopt one of three possible oxidation states (Scheme 1), in this case the chemical data unambiguously indicate an  $(\text{ONO}^{\text{Cat}})\text{ReO}(\text{PPh}_3)$  assignment. The observed square pyramidal geometry is typical of oxorhenium(V) complexes. In contrast, formulation of the compound as  $(\text{ONO}^{\text{Q}})\text{ReO}(\text{PPh}_3)$  would require an oxorhenium(III) moiety. Such compounds are rare, and known examples have a strong preference for pseudotetrahedral over square pyramidal geometry.<sup>18</sup> Formulation as an oxorhenium(IV)<sup>19</sup> complex of  $[\text{ONO}^{\text{SQ}}]^{2-}$  is likewise chemically unreasonable. Spectroscopic and structural data confirm the assignment as a fully reduced, aromatic ligand. The carbon atoms bonded to oxygen atoms resonate at  $\delta\ 169.83$  in the  $^{13}\text{C}\{^1\text{H}\}$  NMR (Figure

S3 in the SI), which is at the downfield end of the range observed for  $\text{ONO}^{\text{Cat}}$  complexes (compare  $[\text{ONO}^{\text{Cat}}]\text{Rh}(\text{PPh}_3)_2$ ,  $\delta\ 168.98$ <sup>20</sup>) but significantly upfield of  $\delta\ \sim 178$  observed for  $[\text{ONO}^{\text{Q}}]$  complexes.<sup>21</sup> The optical spectrum of the red compound (Figure S4 in the SI) displays intense ligand-to-metal charge-transfer bands in the ultraviolet tailing into the visible but no bands at longer wavelength characteristic of  $[\text{ONO}^{\text{Q}}]$  or  $[\text{ONO}^{\text{SQ}}]$  complexes.<sup>22</sup> Finally, X-ray crystallography, which reveals typical single-bond C–O and C–N distances and aromatic C–C distances, is indicative of a fully reduced ligand with little  $\pi$  donation to the metal.<sup>8</sup> Electrochemistry suggests a relatively electron-rich compound, with the onset of oxidation at  $+0.34\text{ V}$  vs ferrocene/ferrocenium (Figure S5 in the SI) compared to, for example,  $+0.63\text{ V}$  for  $\text{W}(\text{ONO}^{\text{Cat}})_2$ ,<sup>16</sup> although the comparison is complicated by the irreversibility of the oxidation for the rhenium complex and the possibility that it is metal-centered rather than ligand-centered.

In the synthesis, the ONO ligand is reduced by two electrons from the quinone oxidation state to the catecholate oxidation state. The two electrons originate from one of the phosphine ligands in  $\text{ReO}_2(\text{PPh}_3)_2$ , which is oxidized to triphenylphosphine oxide. The fact that the oxidation state of the ONO ligand is different in the reagent than it is in the final product is not in itself unusual in reactions of redox-active ligands. For example, *o*-benzoquinones are frequently used as starting materials for the formation of semiquinone or catecholate complexes.<sup>23</sup> Such redox shifts can be useful or essential synthetically, as in the recently reported reaction of  $\text{K}[\text{ONO}^{\text{Q}}]$  with  $[(1,5\text{-cyclooctadiene})\text{Rh}(\mu\text{-Cl})_2]$ , which allows the preparation of  $[\text{ONO}^{\text{Cat}}]\text{Rh}^{\text{III}}$  complexes without the need to attempt ligand substitution at an inert rhodium(III) center.<sup>20</sup> In most cases, however, the redox equivalents used to adjust the oxidation state are provided by the metal centers, as in the cases cited above, or by dioxygen, as in the aerobic self-assembly of  $\text{M}(\text{ONO})_2$  from ammonia and catechol.<sup>24</sup> The preparation of  $(\text{ONO}^{\text{Cat}})\text{ReO}(\text{PPh}_3)$  from  $\text{ReO}_2(\text{PPh}_3)_2$  and  $\text{Pb}(\text{ONO}^{\text{Q}})_2$  represents a novel example where the reducing equivalents come via atom transfer of a coordinated oxo group.

The net reaction is thus an example of nonclassical oxygen atom transfer, with reduction of a redox-active ligand accompanying cleavage of a rhenium–oxo bond and formation of a bond from oxygen to the phosphine that is oxidized. While the *net* reaction is nonclassical, it is by no means clear that the *mechanism* proceeds by nonclassical oxygen atom transfer. After metathesis of  $\text{ONO}^{\text{Q}}$  for iodide (presumably the first step in the reaction), one could envision that the  $(\text{ONO})\text{ReO}_2(\text{PPh}_3)$  [or possibly  $(\text{ONO})\text{ReO}_2$ ] formed could exist in several possible geometric isomers and might be reasonably formulated either as an  $(\text{ONO}^{\text{Q}})\text{Re}^{\text{V}}$  complex or as an  $(\text{ONO}^{\text{Cat}})\text{Re}^{\text{VII}}$  complex. Oxygen atom transfer from the former would constitute a genuine nonclassical oxygen atom transfer step. In contrast, oxygen atom transfer from the latter would constitute a sort of “bucket brigade” mechanism for oxygen atom transfer, where the rhenium center initially passes its electrons to the ONO ligand to form the rhenium(VII) dioxo complex and, in turn, receives electrons from phosphorus(III) via a classical oxygen atom transfer reaction. Which of these pathways is preferred, as well as details of the further reactivity of  $(\text{ONO}^{\text{Cat}})\text{ReO}(\text{PPh}_3)$ , is currently under investigation.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Synthetic, spectroscopic, and crystallographic details, table of bond distances and angles, NMR spectra, an optical spectrum, and a cyclic voltammogram of (ONO<sup>Cat</sup>)ReO(PPh<sub>3</sub>), and crystallographic information for (ONO<sup>Cat</sup>)ReO(PPh<sub>3</sub>) in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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- (14) Data were collected on a dark-red 0.19 × 0.13 × 0.12 mm<sup>3</sup> crystal grown from methanol, using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at  $T = 120(2)$  K: C<sub>46</sub>H<sub>53</sub>N<sub>3</sub>O<sub>3</sub>Pre,  $M = 887.08$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 10.1620(6)$  Å,  $b = 14.7652(9)$  Å,  $c = 28.6116(18)$  Å,  $Z = 4$ ,  $V = 4293.0(5)$ . Refinement of 479 parameters (all heavy atoms were anisotropic, all hydrogen atoms were in calculated positions, and one *tert*-butyl group [centered at C28] was disordered and modeled in two orientations) converged at  $R1 = 0.0204$ ,  $wR2 = 0.0381$  for 11313 unique observed reflections with  $I > 2\sigma(I)$  and at  $R1 = 0.0240$ ,  $wR2 = 0.0387$  for all 12039 independent reflections.
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