ORGANOMETALLICS

Reactivity of Organometallic Tantalum Complexes Containing a Bis(phenoxy)amide (ONO)^{3–} Ligand with Aryl Azides and 1,2-Diphenylhydrazine

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Supporting Information



The reactivity of tantalum dimethyl and diphenyl complexes (ONO^{cat})TaMe₂ (**2**) and (ONO^{cat})TaPh₂ (**3**) with aryl azides and 1,2diphenylhydrazine is reported. *p*-Tolyl azide inserts into a Ta–C bond of **2** or **3** to afford (ONO^{cat})TaMe(η^2 -MeNNN-*p*-C₆H₄Me) (**6**) or (ONO^{cat})TaPh(η^2 -PhNNN-*p*-C₆H₄Me) (7), respectively. In the presence of another 1 equiv of azide, another insertion occurs, affording the bis(triazenido) complexes (ONO^{cat})Ta(η^2 -MeNNN-*p*-C₆H₄Me)₂ (**4**) and (ONO^{cat})Ta(η^2 -PhNNN-*p*-C₆H₄Me)₂ (**5**). Complexes **2** and **3** also react with 1,2-diphenylhydrazine, resulting in the loss of 2 equiv of methane or benzene, respectively, along with ¹/₂ equiv of azobenzene. The tantalum-containing product was isolated as the pyridine adduct {(ONO^{cat})Ta(μ^2 -NPh)(py)}₂ (**8**), which implicates a tantalum(III) intermediate. The viability of this (ONO^{cat})Ta^{III} intermediate was proven by KC₈ reduction of (ONO^{cat})TaCl₂ (**1**) in THF, resulting in activation of a C–O bond of THF and formation of {(ONO^{cat})Ta(μ -O(CH₂)₃CH₂)}₂ (**10**), which was characterized by single-crystal X-ray diffraction studies.

■ INTRODUCTION

The synthesis and reactivity of transition-metal complexes with redox-active ancillary ligands has enjoyed a rebirth, thanks to reports of surprising reactivity derived from the cooperation between the metal and ligand valence orbitals. Late-transitionmetal complexes with ligands derived from catechol have potential application as cross-coupling catalysts, ${}^{1}H^{+}/H_{2}$ electrocatalysts, 2,3 and alcohol and amine oxidation catalysts.⁴⁻⁶ Similarly, midtransition-metal complexes with redox-active ligands have shown disparate reactivity patterns such as N2 activation^{7,8} and water oxidation.⁹⁻¹² Our research group has been focused on the development of early-transition-metal complexes with redoxactive ligands in the primary coordination sphere. This strategy has allowed us to demonstrate oxidative addition and group transfer reactivity at zirconium(IV) and tantalum(V) metal centers, despite formal d⁰ electron configurations at the metal.¹³⁻¹⁸ To further develop the chemistry of early transition metals with redox-active ligands, we targeted organometallic platforms as a way to exploit the reactivity of metal-carbon bonds alongside the redox reactivity imparted by the redox-active ligand set.

Organometallic complexes of the early transition metals are useful synthons for the preparation of metal alkoxo, oxo, amido, and imido complexes. Protonolysis of an M-R (R = alkyl, aryl) functionality with a primary amine can release R-H to give the corresponding amide; with a second M-R group this amide can react further to form a metal imide by 1,2-elimination of a second R-H equivalent. In cases where the metal—imido complex is low-coordinate, this second elimination is reversible and R-H bond activation has also been observed.^{19,20} Hydrazine derivatives also react with early-transition-metal organometallic complexes to give metal imido complexes.^{21,22}

Organoazides (RN₃) offer two common routes for the installation of nitrogen-donor ligands on early transition metals.^{23,24} If the metal center can be oxidized by two electrons, nitrene transfer to form a metal imido complex can occur.²⁵ For early-transitionmetal complexes this route is uncommon, though nitrene transfer reactions have been reported for low-valent vanadium.^{26,27} We have shown that ligand-based reducing equivalents are also competent for facilitating nitrene transfer from an organoazide to an early-transition-metal center. Hence, the reaction of PhN3 with $(NNN^{cat})TaCl_2 ((NNN^{cat})^{3-} = bis(2-isopropylamido-4-methy$ oxyphenyl)amide) resulted in the formation of (NNN^q)TaCl₂-(=NPh) with a two-electron oxidation of the redox-active $(NNN^{cat})^{3-}$ ligand to the quinonate $((NNN^{q})^{-})$ oxidation state.¹⁷ A second reaction pathway for organoazides with earlytransition-metal organometallic complexes is insertion into metalhydride or metal–carbon bonds.^{28–30} For example, $Cp_2^*Hf(H)_2$

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Received:
May 23, 2011

Published:
August 25, 2011
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reacts with phenyl azide to produce the triazenido complex $Cp_2^*Hf(H)(PhNNNH)$; however, upon heating, N_2 is lost to afford $Cp_2^*Hf(H)(NHPh)$, the product of formal nitrene insertion into the Hf–H bond.³¹

Herein we report the synthesis and reactivity of organometallic (ONO^{cat}) TaR_2 (R = Me (2), Ph (3); (ONO^{cat})^{3–} = N,Nbis(3,5-di-tert-butyl-2-phenoxide) amide) complexes with aryl azides and 1,2-diphenylhydrazine. Insertion of aryl azide into the Ta-C bonds of 2 and 3 are observed to form the corresponding mono-triazenido and bis-triazenido complexes. In all cases, the triazenido ligands appear to be bidentate. The reaction of 2 with 1,2-diphenylhydrazine initially affords the hydrazido complex (ONO^{cat})Ta(Me)(η^2 -PhNN(H)Ph) (9) with the loss of 1 equiv of methane. Heating solutions of 9 with pyridine resulted in the loss of another 1 equiv of methane, 1/2 equiv of PhNNPh, and the quantitative formation of $\{(ONO^{cat})Ta(\mu^2 -$ NPh)(py) $_{2}$ (8). Evidence suggests that the azobenzene is formed by reductive elimination from a (ONO^{cat})Ta(PhNNPh) species, implicating the generation of a reduced (ONO^{cat})Ta^{III} fragment under the reaction conditions. Independent generation of the putative tantalum(III) fragment by KC8 reduction of $(ONO^{cat})TaCl_2(1)$ in THF supported this contention, as C-O bond activation of THF was observed, resulting in the formation of { $(ONO^{cat})Ta(\mu - O(CH_2)_3CH_2)$ }₂ (10).

RESULTS AND DISCUSSION

Synthesis and Characterization of $(ONO^{cat})TaR_2$ Complexes. Tantalum dimethyl and diphenyl complexes of the redox-active $(ONO^{cat})^{3-}$ ligand were accessed by metathesis routes. The dichloride $(ONO^{cat})TaCl_2(OEt_2)$ (1) was treated with 2 equiv of MeLi in cold diethyl ether to afford $(ONO^{cat})TaMe_2$ (2) as a pale yellow powder in 90% yield after filtration to remove LiCl and subsequent solvent removal. As previously reported,¹⁴ $(ONO^{cat})H_3$ can be doubly deprotonated with nBuLi and then treated with $TaCl_2Me_3$ to afford 2 directly; however, the overall yield for the single-step route is only 60%. Dichloride 1 also provides access to the tantalum diphenyl analogue $(ONO^{cat})TaPh_2$ (3) as a red amorphous solid in 95% yield.

The NMR spectroscopic characterization of complexes 2 and 3 are consistent with five-coordinate, $C_{2\nu}$ -symmetric complexes in solution. The ¹H NMR spectrum of 2 reveals a symmetric $(ONO^{cat})^{3-}$ ligand with the aryl proton resonances appearing at 7.03 and 7.70 ppm and the ^tBu proton resonances appearing at 1.43 and 1.58 ppm. The two equivalent methyl ligands of 2 are readily identified by their chemical shifts of 0.77 ppm in the ¹H NMR spectrum and 59.7 ppm in the ¹³C NMR.³² The (ONO^{cat})³⁻ ligand of 3 shows nearly identical signatures in the ¹H NMR spectrum, with aromatic resonances at 7.04 and 7.70 ppm and ^tBu resonances at 1.44 and 1.58 ppm. The two equivalent phenyl ligands of 3 are readily identified by their ¹H NMR resonances, which show the appropriate ${}^{3}J_{HH}$ coupling pattern, at 7.02 (para), 7.20 (meta), and 8.18 (ortho) ppm. As expected, the ipso carbon of the phenyl ligands is readily observed at 202.9 ppm in the ¹³C NMR spectrum of 3.³³

Confirmation of the coordination geometry of **2** was obtained by single-crystal X-ray diffraction experiments. Crystals of **2** suitable for X-ray diffraction studies were grown from saturated pentane solutions containing a drop of benzene. Complex **2** crystallizes in the orthorhombic space group *Pnma* with a mirror plane containing the tantalum center, the carbon atoms of the two methyl ligands, and the nitrogen atom of the (ONO^{cat})^{3–}



Figure 1. ORTEP drawing of $(ONO^{cat})TaMe_2(2)$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $(ONO^{cat})TaMe_2$ (2)

Bond Distances/Å					
$T_{a}(1) - N(1)$	2.074(3)	C(1)-C(2)	1.394(4)		
Ta(1) = O(1) Ta(1) = C(20)	1.890(2) 2.122(5)	C(2) - C(3) C(3) - C(4)	1.388(4) 1.394(4)		
Ta(1) - C(21)	2.120(5) 1.381(4)	C(4)-C(5) C(5)-C(6)	1.393(5) 1.387(5)		
N(1) - C(2)	1.406(3)	C(1) - C(6)	1.384(4)		
Bond Angles/deg .					
C(20)-Ta(1)-C(21) N(1)-Ta(1)-C(20) N(1)-Ta(1)-C(21)	110.4(2) 116.86(18) 132.73(17)	O(1)-Ta(1)-O(1)' O(1)-Ta(1)-N(1)	149.44(13) 75.47(7)		

ligand. The molecular structure of **2** is shown as an ORTEP drawing in Figure 1; selected bond distances and angles are provided in Table 1. As expected, **2** is a five-coordinate, distorted-trigonal-bipyramidal complex. While the Ta–C bond distances are similar to those in the structurally analogous complex $[(OCO)TaMe_2]^+$ $((OCO)^{2-} = bis(2-oxyphenyl)carbene)$,³² the C–Ta–C bond angle in **2** is significantly smaller than 120° and the two N–Ta–C bond angles are quite different, consistent with a slight distortion toward square-pyramidal geometry about the metal center. The O–Ta–O angle is small, consistent with the limited bite angle afforded by two fused five-membered chelate rings of the $(ONO^{cat})^{3-}$ ligand. The C–C bond distances within the backbone of the $(ONO^{cat})^{3-}$ ligand are all 1.39(1) Å, consistent with an aromatic ring and the reduced catecholate form of the ligand.³⁴

Insertion of Organoazides into Ta–C Bonds. In an attempt to generate tantalum imido complexes in the presence of alkyl or aryl ligands, complexes 2 and 3 were treated with organic azides. Treatment of a benzene solution of 2 with 2 equiv of p-MeC₆H₄N₃ at 50 °C resulted in an immediate color change from yellow to red. There was no evidence for the liberation of Scheme 1

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Figure 2. ORTEP drawing of $(ONO^{cat})Ta(\eta^2-MeNNN-p-C_6H_4Me)_2$ (4). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

 N_2 during the course of the reaction. Solvent removal afforded modest yields of the double azide insertion product (ONO^{cat})-Ta(η^2 -MeNNN-*p*-C₆H₄Me)₂ (4), which was characterized in solution by NMR, IR, and UV—vis spectroscopy and in the solid state by single-crystal X-ray diffraction. Similarly, the addition of 2 equiv of *p*-MeC₆H₄N₃ to a benzene solution of 3 at 50 °C resulted in the formation of the analogous bis(triazenido) complex (ONO^{cat})Ta(η^2 -PhNNN-*p*-C₆H₄Me)₂ (5), as shown in Scheme 1.

The nature of the double azide insertion product was identified by X-ray diffraction experiments carried out on 4. Crystals of 4 suitable for X-ray diffraction studies were obtained by cooling saturated solutions of the complex in a mixture of toluene and pentane to -35 °C. Complex 4 crystallized in the monoclinic space group C2/c; the molecular structure is depicted as an ORTEP drawing in Figure 2, and selected metrical parameters are given in Table 2. Since 4 is C_2 -symmetric, the centrosymmetric space group requires a racemic mixture of isomers in the crystal ($\delta\delta$ and $\lambda\lambda$ isomers with regard to the triazenido ligands). The tantalum center is seven-coordinate, with the $(ONO^{cat})^3$ ligand occupying three meridional coordination sites as observed in the structure of 2; the two triazenido ligands of 4 occupy two coordination sites each. The metrical parameters for the $(ONO^{cat})^{3-}$ ligand fully support its assignment as the formally trianionic catecholate oxidation state of the ligand. Slightly longer Ta-O bond distances in 4 are consistent with the increase in coordination number from 5 in 2 to 7 in 4. The triazenido ligands are oriented with the methyl groups together and the tolyl groups

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(ONO^{cat})Ta(\eta^2-MeNNN-p-C_6H_4Me)_2$ (4)

Bond Distances/Å					
Ta(1)-N(1)	2.063(3)	C(1) - C(2)	1.395(3)		
Ta(1) - O(1)	1.9567(15)	C(2) - C(3)	1.402(3)		
Ta(1)-N(2)	2.1135(19)	C(3) - C(4)	1.391(4)		
Ta(1)-N(4)	2.288(2)	C(4) - C(5)	1.402(3)		
N(2)-N(3)	1.349(3) C(5)-C(6)		1.396(3)		
N(3) - N(4)	1.276(3) C(1)-C(6)		1.395(3)		
O(1) - C(2)	1.363(3)				
N(1) - C(1)	1.412(2)				
Bond Angles/deg					
N(1)-Ta(1)-N(2)	107.96(5)	O(1)-Ta(1)-O(1)'	148.73(9)		
N(1)-Ta(1)-N(4)	143.64(6)	O(1)-Ta(1)-N(1)	74.37(5)		
O(1)-Ta(1)-N(2)	97.87(7)	N(2)-Ta(1)-N(4)	93.11(8)		
O(1) - Ta(1) - N(4)	132.84(7)	N(2) - Ta(1) - N(2)'	144.07(11)		
N(2)-N(3)-N(4)	105.62(19)	N(4)-Ta(1)-N(4)'	72.72(11)		

pointed outward. The Ta–N bond distances to the triazenido ligands are very different at 2.29 Å for Ta(1)–N(4) and 2.11 Å for Ta(1)–N(2). This difference is well outside of the error associated with the measurement of the Ta–N distances and suggests that resonance structure A in eq 1 is the better π -bond description of the triazenido ligand. The N–N bond distances within the triazenido ligand further support this electronic picture, with a short N(3)–N(4) distance of 1.28 Å being consistent with an N=N double bond and a long N(2)–N(3) distance of 1.35 Å being consistent with an N–N single bond.^{35–37}



Solution NMR spectra suggest analogous C_2 -symmetric molecular structures for 4 and 5, as indicated in Scheme 1. The ¹H NMR spectrum for 4 shows only one methyl resonance for the triazenido ligand at 3.37 ppm and no resonances in the region associated with a tantalum-bound methyl ligand. Similarly, the resonance for the tantalum-bound methyl at 59.7 ppm in the ¹³C NMR spectrum of 2 is replaced by a diagnostic N-CH₃ resonance at 42.4 ppm in the ¹³C NMR of 4. The (ONO^{cat})³⁻ ligand is symmetric, and the tolyl groups of the triazenido ligands

Scheme 2



are equivalent in 4 on the NMR time scale. Similarly, the 1 H NMR spectrum of 5 shows resonances for the $(ONO^{cat})^{3-}$ ligand and for the tolyl groups of the triazenido ligand that are nearly identical with those of 4. The ipso carbon resonance for the tantalum-bound phenyl ligands of 3 disappears in the 13 C NMR spectrum of 5, and the phenyl protons are shifted upfield to 6.8, 7.0, and 7.5 ppm in the 1 H NMR spectrum of 5.

Treatment of tantalum dimethyl complex 2 or tantalum diphenyl complex 3 with 1 equiv of organoazide resulted in nearly quantitative formation of the monotriazenido complex. In the case of 2, the reaction with 1 equiv of p-MeC₆H₄N₃ afforded (ONO^{cat})-TaMe(η^2 -MeNNN-*p*-C₆H₄Me) (**6**) in nearly quantitative yield after 12 h at room temperature. Similarly, diphenyl complex 3 reacted to completion upon addition of 1 equiv of *p*-MeC₆H₄N₃ at 25 °C to afford (ONO^{cat})TaPh(η^2 -PhNNN-*p*-C₆H₄Me) (7). Addition of 2 equiv of p-MeC₆H₄N₃ to either 2 or 3 resulted only in the formation of the monoinsertion products after 12 h at 25 °C; however, when the mixtures were heated to 50 °C, a second insertion reaction occurred to afford the bis(triazenido) complexes 4 and 5, respectively. Complexes 6 and 7 were readily identified by their ¹H and ¹³C NMR spectra. The (ONO^{cat})³⁻ ligands in 6 and 7 are symmetric according to the ¹H NMR spectra, indicating approximate C_s symmetry on the NMR time scale. The proton resonance for the tantalum-bound methyl ligand of 6 is shifted downfield relative to 2 by 0.5 ppm (to 1.28 ppm). In the case of 7, the ¹³C NMR resonance for the ipso carbon of the phenyl ligand is barely shifted relative to 3, appearing at 202.4 ppm. Attempts to obtain quantitative insertion rate data under pseudo-first-order conditions were unsuccessful, as the initial insertion (to give 4 or 5) was too fast to monitor by NMR spectroscopy and the second insertion (to give 6 or 7) was complicated by secondary reactions with excess p-MeC₆H₄N₃. Thermolysis experiments aimed at forming a tantalum imide complex from 4, 5, 6, or 7 resulted in decomposition of the triazenido complex without measurable release of N₂ gas.

N–H Protonolysis Reactivity of (ONO^{cat})TaR₂. As previously reported, ¹⁴ 2 reacts with aniline derivatives to afford binuclear tantalum complexes with bridging arylimido ligands. The bridging anilide complex $[(ONO^{cat})Ta(\mu^2-NPh)(py)]_2(8)$ was prepared by heating a 1:1 solution of 2 and aniline in benzene at reflux for 8 h followed by addition of pyridine, as shown in Scheme 2. When the reaction between 2 and 1 equiv of aniline was conducted at room temperature, ca. 50% conversion to $[(ONO^{cat})-Ta(\mu^2-NPh)(NH_2Ph)]_2$ was observed with the remainder of 2 recovered. When aniline, pyridine, and 2 were combined in a single flask and heated, the pyridine adduct $(ONO^{cat})TaMe_2(py)$ was isolated without conversion to 8. The diphenyl complex 3 also reacted with aniline and pyridine to form 8 in high yields.

The initial reaction between 1,2-diphenylhydrazine and 2 resulted in the loss of 1 equiv of methane and the formation of a tantalum hydrazido complex formulated as (ONO^{cat})TaMe- $(\eta^2$ -NPhNHPh) (9). As depicted in Scheme 2, addition of 1,2diphenylhydrazine to a chilled pentane solution of 2 resulted in the immediate precipitation of 9 as a bright yellow powder in good yield. The presence of an intact Ta-CH₃ group in 9 was confirmed by single resonances at 0.98 and 44.2 ppm in the ¹H and ¹³C NMR spectra, respectively. A single N-H resonance was observed at 5.43 ppm in the ¹H NMR spectrum, and the corresponding vibration appeared at 3214 cm⁻¹ in the IR spectrum. Four resonances for the *tert*-butyl groups of the $(ONO^{ca\bar{t}})^{3-}$ ligand indicated a C_1 -symmetric molecule, consistent with η^2 hapticity of the hydrazido ligand. While 9 was stable in the solid state, solutions of the complex slowly released methane, precluding the isolation of X-ray-quality crystals for an absolute structural determination. Attempts to elucidate the orientation of the hydrazido ligand by 2-D NMR techniques were inconclusive. Given the modest stability of 9 to methane loss, we favor the isomer of 9 shown in Scheme 2, with the remaining N-H located trans to the Ta-Me bond.

The loss of methane from solutions of **9** is accelerated by the presence of stoichiometric quantities of ligands such as pyridine, THF, and even phosphines. Yellow benzene solutions of **9** containing 1 equiv of pyridine slowly turned reddish purple and afforded **8** as the final tantalum-containing product, along with $1/_2$ equiv of azobenzene, as summarized in Scheme 2. Solutions of diphenyl complex **3** and 1,2-diphenylhydrazine release 2 equiv of benzene at ambient temperature (30 °C) with no isolable intermediate analogous to **9**; however, the addition of pyridine to these reaction solutions afforded quantative yields of **8** and azobenzene, consistent with Scheme 2.

Generation and Reactivity of a (ONO^{cat})Ta^{III} Fragment. The formation of 8 and azobenzene as the terminal products

from reactions of 2 or 3 with 1,2-diphenylhydrazine suggests the intermediacy of a tantalum(III) fragment. Equations 2-5 summarize the series of reactions needed to convert 2 equiv of 9 into 8 and azobenzene. In eq 2, elimination of methane from 9 would form a species with the composition (ONO^{cat})Ta(N₂Ph₂), consistent with the observed reactivity of 9 in solution. Three plausible formulations for the (ONO^{cat})Ta(N₂Ph₂) species would be as a $Ta^V - (diazenido)^{2-}$ complex, a $Ta^{IV} - (diazenido)^{-}$ complex, or a $Ta^{III} - (diazene)$ complex. Regardless of the electronic formulation of this species, loss of the neutral diazene PhN=NPh would afford a (ONO^{cat})Ta^{III} fragment, as shown in eq 3. Such a tantalum(III) species would be expected to be strongly reducing, and its addition to an intact (ONO^{cat})Ta(N₂Ph₂) species (eq 4) would assemble the bimetallic tantalum imido core of 8. Final trapping of the bimetallic tantalum imido core by pyridine (eq 5) would be consistent with the preparation of 8 from 2 and aniline as presented above.

$$2 (ONO^{cat})Ta(\mu^{2}-NPh-NHPh) \longrightarrow 2 (ONO^{cat})Ta(\eta^{2}-N_{2}Ph_{2}) + 2 CH_{4} (2) (ONO^{cat})Ta(\eta^{2}-N_{2}Ph_{2}) \longrightarrow (ONO^{cat})Ta^{III} + PhN=NPh (3) (ONO^{cat})Ta(\eta^{2}-N_{2}Ph_{2}) + (ONO^{cat})Ta^{III} \longrightarrow [(ONO^{cat})Ta(\mu^{2}-NPh)]_{2} (4) [(ONO^{cat})Ta(\mu^{2}-NPh)]_{2} + 2 py \longrightarrow [(ONO^{cat})Ta(\mu^{2}-NPh)(py)]_{2} (5)$$

Equations 3 and 4 represent the key redox reactions leading to the formation of 8 and azobenzene and implicate a (ONO^{cat}) ${\rm Ta}^{\rm III}$ intermediate. To test the plausibility of such a tantalum(III) species, KC₈ reductions of 1 were examined in various solvents. The reduction of 1 with 2 equiv of KC_8 in THF resulted in the formation of a yellow-orange solution. The tantalum-containing product was a tantalum(V) complex containing a ring-opened THF molecule, $[(ONO^{cat})Ta{\mu_2-O(CH_2)_3CH_2}]_2$ (10), obtained in modest yields after recrystallization from pentane (Scheme 3). The ¹H NMR spectrum of **10** showed a symmetric (ONO^{cat})³⁻ ligand with aromatic and ^tBu resonances that are shifted downfield slightly relative to those of 2. The ring-opened THF molecule gave rise to four well-defined resonances in the ¹H NMR spectrum at 4.74 (triplet), 2.48 (quintet), 1.86 (multiplet), and 1.25 ppm (triplet). The diagnostic¹¹³C NMR resonance for the metal-bound methylene carbon was observed at 74.3 ppm.^{38–40} For reactions carried out in THF, the presence of a stoichiometric amount or excess azobenzene had no effect on the outcome of the reaction, and 10 was the only product observed.

A single-crystal X-ray structure of 10 revealed the dimeric nature of the ring-opened THF product. Figure 3 shows 10 as an ORTEP drawing, and Table 3 gives selected metrical parameters for the primary coordination sphere of the tantalum center. The complex crystallizes in the monoclinic space group $P2_1/n$ with two crystallographically unique, but chemically equivalent, molecules of 10 in the asymmetric unit. The bimetallic complex is best described as an edge-sharing bioctahedron with the oxygen atoms of the ring-opened THF molecules occupying the bridging positions. The $(ONO^{cat})^{3-}$ ligands are planar and parallel to one another in the dimer. All bond distances within the (ONO^{cat})³⁻ ligands are consistent with their assignment to the catecholate oxidation state. The ring-opened THF molecules chelate to a single tantalum center to form a six-membered ring that sits in a boat conformation with a Ta-C distance longer than that observed in the structure of dimethyl complex 2. The bridging oxygen atoms are nearly trigonal planar, having a sum of angles of 359°. Surprisingly, the Ta–O distance within the six-membered chelate ring is longer $(Ta(1)-O(3) \approx 2.13 \text{ Å})$ than the Ta-O





Figure 3. ORTEP drawing of $[(ONO^{cat})Ta{\mu^2-O(CH_2)_3CH_2}]_2$ (10). Thermal ellipsoids are drawn at the 50% probability level. A crystallographically distinct but chemically equivalent second molecule of 10, pentane solvent molecules, and hydrogen atoms have been omitted for clarity.

distance to the adjacent metal center $(Ta(1)-O(3)' \cong 2.08 \text{ Å})$, even though the latter Ta-O bond is located opposite the strongly trans influencing alkyl of the ring-opened THF molecule.

When 1 was reduced with potassium graphite in the absence of THF, the putative $(ONO^{cat})Ta^{III}$ fragment could be trapped with azobenzene. To avoid the reaction of the $(ONO^{cat})Ta^{III}$ fragment with THF, 1 was treated with KC₈ in cold toluene followed by $^{1}/_{2}$ equiv of PhN=NPh. When it was warmed to room temperature, the solution was reddish purple, consistent with the formation of the bimetallic tantalum imido core. Addition of pyridine to the solution afforded 8 in 77% isolated yield, indicating that two $(ONO^{cat})Ta^{III}$ fragments are capable of the four-electron reduction of dizobenzene.

CONCLUSIONS

The reaction of tantalum dimethyl and diphenyl complexes 2 and 3 with aryl azides to form triazenido complexes was unexpected but not unprecedented. The related tantalum complex

Table 3. Selected Bond Distances	(Å)) and	Angles	(deg)	for
$[(ONO^{cat})Ta{\mu_2-O(CH_2)_3CH_2}]_2$	(1	0)	e		

Bond Distances/Å					
Ta(1) - N(1) Ta(1) - O(1)	2.064(6)	Ta(2) - N(2) Ta(2) - O(4)	2.080(6)		
Ta(1) = O(1) Ta(1) = O(2)	1.923(3) 1.938(5)	Ta(2) = O(4) Ta(2) = O(5)	1.937(0) 1.938(5)		
Ta(1)-O(3) Ta(1)-O(3)'	2.130(5) 2.083(5)	Ta(2)-O(6) Ta(2)-O(6)'	2.143(5) 2.064(6)		
Ta(1) - C(32)	2.171(9)	Ta(2) - C(64)	2.155(9)		
Bond Angles/deg					
O(3)-Ta(1)-O(3)'	68.2(2)	O(6) - Ta(2) - O(6)	68.1(3)		
O(3)-Ta(1)-C(32)	82.3(3)	O(6) - Ta(2) - C(64)	82.3(3)		
Ta(1) - O(3) - Ta(1)'	111.8(2)	Ta(2) - O(6) - Ta(2)'	111.9(3)		

[NNN^{cat}] TaCl₂ reacts smoothly with aryl azides: the donation of two electrons from the redox-active ligand allows reduction of the azide and formation of a tantalum—imido bond. In the case of **2** and **3**, the aryl azide must insert into the Ta—C bond faster than the two-electron oxidation that leads to N₂ extrusion and formation of the imido ligand. While azide insertions to give triazenido species have been observed for hydride complexes of the early transition metals,³⁵ the analogous alkyl complexes have been shown to be robust to azide insertion,^{28,29,36} a direct reflection of the much lower migratory aptitude of methyl versus hydride ligands. In the case of **2** and **3**, the migration must be relatively facile, as it quantitatively beats out nitrene transfer to the tantalum center.

Another interesting feature of the (ONO^{cat}) Ta platform is the apparent accessibility of the tantalum(III) oxidation state. As expected, 1,2-diphenylhydrazine reacts with 2 or 3 by sequential protonolysis reactions to lose methane or benzene. The expected product of these reactions was a (ONO^{cat}) Ta(PhNNPh) complex, but instead reductive elimination of azobenzene occurred to liberate the putative (ONO^{cat}) Ta^{III} fragment. In the reaction with 1,2-diphenylhydrazine, the reduced fragment can be trapped by a second (ONO^{cat}) Ta(PhNNPh) to break the N–N bond and form imido dimer 8. The reactivity of the (ONO^{cat}) Ta^{III} fragment was further illustrated by its ability to cleave a C–O bond of THF to afford 10, a reaction that is observed for highly reduced complexes of the early transition metals^{39,41,42} but is unreported for tantalum(III).^{43,44}

Finally, two (ONO^{cat})Ta^{III} fragments react with azobenzene in the absence of THF to give 8, highlighting the ability of this platform to mediate four-electron reactivity. Previous results showed that the four-electron oxidation of 8 resulted in the extrusion of azobenzene with the formation of (ONO^{cat})TaCl₂-(py).¹⁴ Taken together, these two reactions indicate that the (ONO)Ta platform remains intact through an overall fourelectron series with minimal changes to the molecular geometry: (ONO^{cat})Ta^{III}, (ONO^{cat})Ta^V, (ONO^q)Ta^V ((ONO^q)⁻ = 3,5di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butyl-phenyl)imine). Such a multielectron sequence is rare in mononuclear transition-metal complexes⁴⁵ but in this case is enabled through the cooperation between a redox-active ligand and a tantalum metal center.

EXPERIMENTAL PROCEDURES

General Considerations. All compounds and reactions reported below are both air and moisture sensitive. All manipulations were carried out using standard vacuum-line, Schlenk-line, and glovebox techniques. Solvents were sparged with argon before being deoxygenated and dried by passage through Q5 and activated alumina columns, respectively. To test for effective oxygen and water removal, aliquots of each solvent were treated with a few drops of a purple solution of sodium benzophenone ketyl radical in THF. 1,2-Diphenylhydrazine was purchased from Alfa Aesar and sublimed to remove traces of azobenzene before use. Aryl azides^{46,47} and (ONO^{cat})TaCl₂(OEt₂) (1)¹⁴ were synthesized by literature procedures.

Spectroscopic Measurements. NMR spectra were collected on Bruker Avance 600 and 500 MHz spectrometers in dry, degassed C_6D_6 or CDCl₃. ¹H NMR spectra were referenced to tetramethylsilane (TMS) using the residual protio impurities of the solvent; ¹³C NMR spectra were referenced to TMS using the natural-abundance ¹³C impurities of the solvent. All chemical shifts are reported using the standard δ notation in parts per million; positive chemical shifts are to a higher frequency from the given reference. Infrared spectra were recorded as KBr pellets with a Perkin-Elmer Spectrum One FTIR spectrophotometer. Electronic absorption spectra were recorded with a Perkin-Elmer Lambda 800 UV/vis spectrophotometer in 1 cm path length cells at 25 °C.

X-ray Data Collection and Reduction. X-ray diffraction data for 4 and $10 \cdot 2.6C_5H_{12}$ were collected for single crystals mounted on a glass fiber and held in place with Paratone oil using a Bruker CCD platform diffractometer equipped with a CCD detector. Measurements were carried out at at 143 K using Mo K α (λ = 0.71073 Å) radiation, which was wavelength-selected with a single-crystal graphite monochromator. X-ray diffraction data for 2 were collected on a Bruker D8 platform diffractometer equipped with an APEX CCD detector at UC San Diego. Measurements were carried out at 208 K using Mo K α (λ = 0.710 73 Å) radiation, which was wavelength-selected with a single-crystal graphite monochromator. The SMART program package was used to determine unit-cell parameters and for data collection. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. Analytical scattering factors for neutral atoms were used throughout the analyses. Hydrogen atoms in 2, 4, and 10 · 2.6C₅H₁₂ were generated in calculated positions and refined using a riding model. ORTEP diagrams were generated using ORTEP-3 for Windows.⁴⁸ Diffraction data for 2, 4, and $10 \cdot 2.6C_5H_{12}$ are shown in Table 4.

(ONO^{cat})TaMe₂ (2). Compound 2 was prepared by an alternative method to the previously published procedure.¹⁴ A 20 mL scintillation vial equipped with a stir bar was charged with a red solution of 1 (0.419 g, 0.559 mmol, 1 equiv) in diethyl ether (18 mL). The solution was frozen in a liquid-nitrogen cold well, and then immediately upon thawing it was treated with a 1.37 M solution of MeLi in diethyl ether (0.839 mL, 1.15 mmol, 2 equiv). The mixture was then stirred as it was warmed to ambient temperature (30 °C). After it was stirred for 3 h, the mixture was filtered and the volatiles were removed under reduced pressure. The resulting yellow-brown residue was treated with 3 mL of pentane and chilled (-35 °C) so that 2 could be isolated by filtration as a yellow powder. Yield: 0.278 g (78%). Characterization data for 2 prepared by this method matched the data previously reported for the complex.¹⁴

(ONO^{cat})Ta(Ph)₂ (3). A 20 mL scintillation vial equipped with a stir bar was filled with a red solution of 1 (0.164 g, 0.20 mmol, 1 equiv) in diethyl ether (15 mL) and frozen in a liquid-nitrogen-filled cold well. To the recently thawed solution was added solid PhLi (0.037 g, 0.44 mmol, 2.2 equiv), and the mixture was then stirred as it was warmed to ambient temperature. After it was stirred for 16 h, the dark red solution was filtered to remove LiCl, and the filtrate was dried under reduced pressure. The resulting dark red residue was titurated with pentane (5×5 mL) to remove diethyl ether and extracted with cyclopentane (10 mL). The solution was concentrated down (~3 mL) and cooled to -35 °C to induce 3 to precipitate as a dull red powder that was isolated by filtration and dried under vacumm. Yield: 0.168 g (92%).

Table 4. Crystal Data Collection and Refinement Parameters
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	$(ONO^{cat})TaMe_2(2)$	$(ONO^{cat})Ta(\eta^2-(p-tolyl)NNNMe)_2$ (4)	$[(ONO^{cat})Ta(O(CH_2)_3CH_2)]_2 (10 \cdot 2.6C_5H_{12})$
empirical formula	$C_{30}H_{46}NO_2Ta$	$C_{44}H_{60}N_7O_2Ta$	$C_{77}H_{127}N_2O_6Ta_2$
formula wt	633.63	899.94	1539.91
cryst syst	orthorhombic	monoclinic	monoclinic
space group	Pnma	C2/c	$P2_{1}/n$
<i>a,</i> Å	11.752(3)	19.9660(15)	18.4766(14)
b, Å	26.728(8)	17.1104(13)	17.3171(13)
c, Å	9.396(3)	12.9627(10)	23.2598(18)
α, deg	90	90	9
β , deg	90	101.5030(10)	94.7570(10)
γ, deg	90	90	90
<i>V</i> , Å ³	2951.5(15)	4339.2(6)	7416.6(10)
Ζ	4	4	4
F(000)	1288	1848	3189
no. of rflns collected	17 455	16 377	81 444
no. of indep rflns (R_{int})	3634 (0.0437)	4743 (0.0218)	17 181 (0.0557)
R1 $(I > 2\sigma_I)^a$	0.0320	0.0224	0.0654
wR2 (all data) ^a	0.0757	0.0572	0.1554
a R1 = $\Sigma F_{o} - F_{c} / \Sigma F_{o} $	$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]]$	$]/\Sigma[w(F_o^2)^2]]^{1/2}$; GOF = $[\Sigma w(F_o - F_c)^2/$	$\left[\left(n-m\right)\right]^{1/2}.$

Anal. Calcd for C₄₀H₅₀NO₂Ta: C, 63.40; H, 6.65; N, 1.85. Found: C, 60.67; H, 6.90; N, 1.83. ¹H NMR (600 MHz; C₆D₆; 298 K; δ /ppm): 8.18 (d, ³J_{HH} = 6.6, 4H, aryl H), 7.70 (d, ⁴J_{HH} = 1.8, 2H, aryl H), 7.20 (t, ³J_{HH} = 7.8 Hz, 4H, aryl H), 7.04 (d, ⁴J_{HH} = 1.8 Hz, 2H, aryl H), 7.02 (t, ³J_{HH} = 7.8 Hz, 2H, aryl H), 1.58 (s, 18H, ^fBu), 1.44 (s, 18H, ^fBu). ¹³C NMR (128 MHz; C₆D₆; 298 K; δ /ppm): 202.9 (aryl C), 154.5 (aryl C), 148.3 (aryl C), 145.6 (aryl C), 136.9 (aryl C), 134.4 (aryl C), 131.7 (aryl C), 115.4 (aryl C), 110.7 (aryl C), 35.0 (C(CH₃)₃), 34.7 (C(CH₃)₃), 32.0 (C(CH₃)₃), 30.4 (C(CH₃)₃). UV/vis (C₆H₆; $\lambda_{max}/nm (\epsilon/M^{-1} cm^{-1})$): 295 (52 500). (ONO^{cat})Ta(η^2 -MeNNN-*p*-C₆H₄Me)₂ (4). A 25 mL Straus tube

equipped with a stir bar was charged with a yellow solution of 2(0.141 g)0.22 mmol, 1 equiv) and N₃(*p*-C₆H₄Me) (0.059 g, 0.44 mmol, 2 equiv) in benzene (10 mL). The solution was stirred at 50 °C for 1 h as the yellow-orange solution darkened to red. The solvent was removed under vacuum, and the resulting residue was washed with pentane to give 4 as a dull red powder (yield 0.119 g, 60%). X-ray-quality crystals of 4 were grown from chilled $(-35 \,^{\circ}\text{C})$ saturated pentane solutions. Anal. Calcd for C44H60N7O2Ta: C, 58.72; H, 6.72; N, 10.89. Found: C, 57.42; H, 6.92; N, 10.80. ¹H NMR (600 MHz; C_6D_6 ; 298 K; δ /ppm): 7.88 (s, 2H, aryl H), 7.37 (d, ³*J*_{HH} = 8.4 Hz, 2H, aryl H), 7.12 (s, ³*J*_{HH} = 1.8 Hz, 2H, aryl H), 6.78 (d, ³*J*_{HH} = 8.4 Hz, 2H, aryl H), 3.37 (s, 6H, N-CH₃), 1.95 (s, 6H, N(p-C₆H₄-CH₃), 1.44 (s, 18H, ^tBu), 1.40 (s, 18H, ^tBu). ¹³C NMR (128 MHz; C₆D₆; 298 K; δ/ppm): 156.4 (aryl C), 145.1 (aryl C), 143.9 (aryl C), 134.9 (aryl C), 130.5 (aryl C), 129.9 (aryl C), 119.1 (aryl C), 118.3 (aryl C), 117.3 (aryl C), 110.4 (aryl C), 42.4 (N-CH₃), 35.0 $(C(CH_3)_3)$, 34.6 $(C(CH_3)_3)$, 32.2 $(C(CH_3)_3)$, 29.8 $(C(CH_3)_3)$, 20.8 (Ar-CH₃). UV/vis (C₆H₆; λ_{max}/nm (ϵ/M^{-1} cm⁻¹)): 300 (24000).

(ONO^{cat})Ta(η^2 -PhNNN-*p*-C₆H₄Me)₂ (5). A 25 mL Straus tube equipped with a stir bar was charged with a red solution of 3 (0.106 g, 0.14 mmol, 1 equiv) and N₃(*p*-C₆H₄Me) (0.039 g, 0.28 mmol, 2 equiv) in benzene (10 mL). The solution was stirred at 50 °C for 1 h. The solvent was stripped under vacuum, and the resulting dark red residue was suspended in 5 mL of pentane before it was chilled to -35 °C. Compound 5 was isolated as a dull red-purple solid by filtration (yield 0.140 g, 97.7%). Anal. Calcd for C₅₄H₆₄N₇O₂Ta: C, 63.33; H, 6.30; N, 9.57. Found: C, 61.90; H, 6.00; N, 9.10. ¹H NMR (600 MHz; C₆D₆; 298 K; δ/ppm): 7.94 (s, 2H, aryl H), 7.53 (br, 7H, aryl H), 7.14 (s, 2H, aryl C), 6.98 (m, 4H, aryl H), 6.80 (m, 7H, aryl H), 1.92 (s, 6H, N(*p*-C₆H₄-CH₃), 1.42 (s, 18H, ^tBu), 1.26 (s, 18H, ^tBu). ¹³C NMR (128 MHz; $C_6 D_6; 298 \text{ K}; \delta/\text{ppm}): 156.6 \text{ (aryl C), } 145.4 \text{ (aryl C), } 143.3 \text{ (aryl C), } 135.4 \text{ (aryl C), } 130.2 \text{ (aryl C), } 129.7 \text{ (aryl C), } 129.0 \text{ (aryl C), } 128.7 \text{ (aryl C), } 127.1 \text{ (aryl C), } 119.1 \text{ (aryl C), } 110.2 \text{ (aryl C), } 34.8 \text{ (} C(CH_3)_3\text{), } 34.2 \text{ (} C(CH_3)_3\text{), } 31.8 \text{ (} C(CH_3)_3\text{), } 29.3 \text{ (} C(CH_3)_3\text{), } UV/\text{vis} \text{ (} C_6H_6\text{; } \lambda_{\text{max}}/\text{nm} \text{ (} \varepsilon/\text{M}^{-1} \text{ cm}^{-1}\text{))}: 309 \text{ (} 29521\text{), } 478 \text{ (} 16243\text{).}$

 $(ONO^{cat})TaMe(\eta^2-MeNNN-p-C_6H_4Me)$ (6). A 20 mL scintillation vial equipped with a stirbar was charged with a yellow solution of 2 (0.133 g, 0.209 mmol, 1 equiv) in benzene (15 mL) and stirred as N_3 -(p-C₆H₄Me) (0.028 g, 0.21 mmol, 1 equiv) was slowly dripped into the solution at ambient temperature. After the mixture was stirred for 12 h, the solvent was removed under reduced pressure and the resulting orange residue triturated with pentane $(3 \times 5 \text{ mL})$ to give 6 as a dull orange powder (yield 0.160 g, 99%). Anal. Calcd for C₃₇H₅₃N₄O₂Ta: C, 57.96; H, 6.97; N, 7.31. Found: C, 57.60; H, 6.90; N, 7.28. ¹H NMR (600 MHz; C₆D₆; 298 K; δ /ppm): 7.81 (s, 2H, aryl H), 7.17 (d, ³J_{HH} = 10.2 Hz, 2H, aryl H), 7.06 (\bar{s} , 2H, aryl H), 6.62 (d, ${}^{3}J_{HH} = 10.2$, 2H, aryl H), 3.18 (s, 3H, N-CH₃), 1.88 (s, 3H, N(*p*-C₆H₄-CH₃), 1.46 (s, 18H, ^tBu), 1.42 (s, 18H, ^tBu), 1.28 (s, 3H, Ta-CH₃). ¹³C NMR (128 MHz; C₆D₆; 298 K; δ/ppm): 156.0 (aryl C), 145.8 (aryl C), 145.5 (aryl C), 144.3 (aryl C), 134.6 (aryl C), 134.0 (aryl C), 130.0, (aryl C), 116.7 (aryl C), 116.3 (aryl C), 110.8 (aryl C), 56.5 (Ta-CH₃), 42.4 (N-CH₃), 35.1 (C(CH₃)₃), 34.7 (C(CH₃)₃), 32.0 (C(CH₃)₃), 29.8 (C(CH₃)₃), 20.7 (Ar-CH₃). UV/vis (C₆H₆; λ_{max}/nm (ϵ/M^{-1} cm⁻¹)): 292 (18 800).

(ONO^{cat})TaPh(η^2 -PhNNN-*p*-C₆H₄Me) (7). A 20 mL scintillation vial equipped with a stirbar was charged with a dark red solution of 3 (0.130 g, 0.172 mmol, 1 equiv) in benzene (10 mL) and stirred as N₃-(*p*-tolyl) (0.023 g, 0.172 mmol, 1 equiv) was slowly dripped into the solution at ambient temperature. The reaction mixture was then stirred for 12 h, after which time the solvent was stripped under vacuum and the resulting residue was suspended in 5 mL of pentane before cooling to -35 °C. Compound 7 was isolated by filtration as a dark red powder and dried under vacuum. Yield: 0.148 g (99%). Anal. Calcd for C₄₇H₅₇N₄O₂Ta: C, 63.36; H, 6.45; N, 6.29. Found: C, 62.56; H, 6.71; N, 5.36. ¹H NMR (600 MHz; C₆D₆; 298 K; δ /ppm): 8.10 (d, ³J_{HH} = 6.6 Hz, 2H, aryl H), 7.80 (d, ⁴J_{HH} = 1.8 Hz, 2H, aryl H), 7.16 (d, ³J_{HH} = 7.8 Hz, 2H, aryl H), 7.06 (d, ⁴J_{HH} = 1.8 Hz, 2H, aryl H), 7.01 (t, ³J_{HH} = 8.4 Hz, 2H, aryl H), 6.79 (t, ³J_{HH} = 7.8 Hz, 1H, aryl H), 6.75 (d, ³J_{HH} = 7.8 Hz, 2H, aryl H), 6.68, (d, ³J_{HH} = 8.4 Hz, 1H, aryl H), 1.93

(s, 3H, (p-C₆H₄-CH₃), 1.40 (s, 18H, ^tBu), 1.38 (s, 18H, ^tBu). ¹³C NMR (128 MHz; C₆D₆; 298 K; δ /ppm): 202.4 (aryl C), 156.6 (aryl C), 146.8 (aryl C), 145.9 (aryl C), 145.2 (aryl C), 144.3 (aryl C), 135.9 (aryl C), 134.9 (aryl C), 134.1 (aryl C), 130.5 (aryl C), 129.8 (aryl C), 129.5 (aryl C), 129.2 (aryl C), 129.0 (aryl C), 125.8 (aryl C), 119.1 (aryl C), 118.5 (aryl C), 117.9 (aryl C), 111.1 (aryl C), 35.0 (C(CH₃)₃), 34.7 (C(CH₃)₃), 31.9 (C(CH₃)₃), 30.0 (C(CH₃)₃), 20.9 (N(p-C₆H₄-CH₃). UV/vis (C₆H₆; λ _{max}/nm (ϵ /M⁻¹ cm⁻¹)): 293 (24200), 415 (3150).

[(ONO^{cat})Ta(μ -NPh)(py)]₂ (8). Method A. A 50 mL roundbottom flask equipped with a stirbar was charged with a toluene slurry (10 mL) of KC₈ (0.034 g, 0.25 mmol, 1.9 equiv) and frozen in a liquidnitrogen-filled cold well. As the slurry thawed, a recently thawed red solution of 1 (0.100 g, 0.13 mmol, 1 equiv) in toluene (10 mL) was added rapidly and the mixture was stirred for 10 min before an orange solution of PhNNPh (0.012 g, 0.06 mmol, 0.5 equiv) in toluene (5 mL) was slowly dripped in. The solution was stirred for 1 h as it was slowly warmed to ambient temperature. The graphite was removed by filtration to give a purple-red solution that was treated with pyridine (0.011 mL, 0.13 mmol, 1 equiv) and concentrated (\sim 2 mL) before 20 mL of pentane was added and the solution was cooled to -35 °C, resulting in the precipitation of 8 as a purple-brown solid that was isolated by filtration and dried under vacuum. Yield: 0.077 g (77%).

Method B. A 50 mL Schlenk flask equipped with a stirbar and a reflux condenser was charged with a yellow solution of 2 (0.315 g, 0.49 mmol, 1 equiv) and aniline (0.045 mL, 0.49 mmol, 1 equiv) in benzene (20 mL). The solution was heated to reflux and stirred for 8 h. The purple-red solution was cooled to room temperature for 1 h before pyridine (0.040 mL, 0.49 mmol, 1 equiv) was added via syringe, resulting in the development of a purple-brown color. After it was stirred for 12 h, the mixture was concentrated down (\sim 4 mL) and 15 mL of pentane was cannula-transferred into the flask, resulting in the precipitation of 8 as a purple-brown solid that was isolated by filtration and dried under vacuum. Yield: 0.210 g (65%). Anal. Calcd for C₇₈H₁₀₀N₆O₄Ta₂: C, 60.54; H, 6.51; N, 5.43. Found: C, 60.34; H, 6.71; N, 5.40. ¹H NMR (500 MHz; CDCl₃; 298 K; δ /ppm): 8.25 (d, ${}^{3}J_{HH}$ = 5 Hz, 4H, aryl H), 7.37 $(t, {}^{3}J_{HH} = 7.5 \text{ Hz}, 2\text{H}, \text{aryl H}), 6.95 (s, 4\text{H}, \text{aryl H}), 6.88 (t, {}^{3}J_{HH} = 6.5 \text{ Hz},$ 4H, aryl H), 6.63 (s, 4H, aryl H), 6.55 (t, ${}^{3}J_{HH} = 7.5$ Hz, 4H, aryl H), 6.26 (d, ³*J*_{HH} = 7.5 Hz, 4H, aryl H), 6.24 (t, ³*J*_{HH} = 7.5 Hz, 4H, aryl H), 1.55 (s, 36H, ^tBu), 1.22 (s, 36H, ^tBu). ¹³C NMR (77 MHz; CDCl₃; 298 K; δ/ ppm): 157.0 (aryl C), 155.6 (aryl C), 147.7 (aryl C), 142.4 (aryl C), 142.3 (aryl C), 134.1 (aryl C), 127.0 (aryl C), 124.4 (aryl C), 123.7 (aryl C), 114.8 (aryl C), 110.3 (aryl C), 34.7 (C(CH₃)₃), 34.5 (C(CH₃)₃), 31.7 (C(CH₃)₃), 30.6 (C(CH₃)₃). UV/vis (toluene; λ_{max} /nm (ϵ / $M^{-1} cm^{-1}$): 298 (46000), 354 (20600), 445 (7800).

(ONO^{cat})TaMe(η^2 -PhNNHPh) (9). A 20 mL scintillation vial was charged with a cold $(-35\ ^\circ C)$ yellow solution of 2 (0.200 g, 0.32 mmol, 1 equiv) in pentane (15 mL) before it was treated with solid 1,2diphenylhydrazine (0.058 g, 0.32 mmol, 1 equiv), resulting in effervescence. The solution was shaken for 5 min as a bright yellow precipitate formed that was isolated by filtration. The precipitate was washed with pentane and identified as 9 (yield 0.228 g, 90%). Anal. Calcd for C41H54N3O2Ta: C, 61.41; H, 6.79; N, 5.24. Found: C, 60.81; H, 6.88; N, 5.33. ¹H NMR (600 MHz; C₆D₆; 298 K; δ/ppm): 7.96 (s, 2H, aryl H), 7.11 (s, 2H, aryl H), 6.93 (br s, 4H, aryl H), 6.81 (br s, 4H, aryl H), 6.69 (br s, 2H, aryl H), 5.43 (s, 1H, N–H), 1.56 (s, 9H, ^tBu), 1.51 (s, 9H, ^tBu), 1.49 (s, 9H, ^tBu), 1.39 (s, 9H, ^tBu), 0.98 (s, 3H, Ta-CH₃). ¹³C NMR (128 MHz; C₆D₆; 298 K; δ/ppm): 155.7 (aryl C), 155.3 (aryl C), 148.6 (aryl C), 145.9 (aryl C), 145.5 (aryl C), 144.6 (aryl C), 144.5 (aryl C), 143.4 (aryl C), 134.6 (aryl C), 134.3 (aryl C), 129.7 (aryl C), 129.4 (aryl C), 125.4 (aryl C), 122.6 (aryl C), 117.5(aryl C), 116.9 (aryl C), 115.5 (aryl C), 115.3 (aryl C), 110.6 (aryl C), 110.5 (aryl C), 44.2 (Ta-CH₃), 35.1 (C(CH₃)), 34.8 (C(CH₃)), 34.6 (C(CH₃)), 32.2 (C(CH₃)), 32.2 (C(CH₃)), 30.2 (C(CH₃)), 30.0 (C(CH₃)). IR (KBr; $\nu_{\rm NH}/\rm{cm}^{-1}$): 3214. UV/vis (C₆H₆; λ_{max} /nm (ϵ /M⁻¹ cm⁻¹)): 295 (15 000).

 $(ONO^{cat})Ta(\eta^2-O(CH_2)_3CH_2)$ (10). A 50 mL round-bottom flask equipped with a stirbar was charged with a slurry of KC_8 (0.098 g, 0.73 mmol, 2.2 equiv) in THF (10 mL) and frozen in a liquid-nitrogen-filled cold well. As the slurry thawed, a recently thawed red solution of 1 (0.248 g, 0.33 mmol, 1 equiv) in THF (20 mL) was rapidly added and the mixture was stirred as it was warmed to ambient temperature for 1 h. The graphite was removed by filtration to give an orange-red solution that was dried under reduced pressure. The resulting orange residue was dissolved in pentane and cooled to -35 °C to give **10** as a yellow-orange solid that was isolated by filtration and dried under vacuum (yield 0.145 g, 65%). Anal. Calcd for C₆₄H₉₆N₂O₆Ta₂: C, 56.88; H, 7.16; N, 2.07. Found: C, 55.52; H, 7.35; N, 2.24. ¹H NMR (600 MHz; C_6D_6 ; 298 K; $\delta/$ ppm): 7.83 (s, 2H, aryl H), 7.11 (s, 2H, aryl H), 4.74 (t, ³*J*_{HH} = 4.8 Hz, 2H, OCH₂-), 2.48 (quin, ${}^{3}J_{HH}$ = 5.9 Hz, 2H, -CH₂-), 1.86 (m, ${}^{3}J_{HH}$ = 6.6 Hz, 2H, $-CH_2-$), 1.60 (s, 18H, ^tBu), 1.46 (s, 18H, ^tBu), 1.25 (quin, ³J_{HH} = 5.4 Hz, 2H, Ta-CH $_2-$). ¹³C NMR (128 MHz; C₆D₆; 298 K; δ /ppm): 155.7 (aryl C), 145.1 (aryl C), 144.9 (aryl C), 134.9 (aryl C), 116.7 (aryl C), 110.7 (aryl C), 74.8 (O-CH₂), 74.3 (Ta-CH₂), 35.1 (C(CH₃)₃, 34.9 (C(CH₃)₃, 32.1 (C(CH₃)₃), 32.0 (CH₂), 30.5 (CH₂), 26.4 ((C(CH₃)₃). UV/vis $(C_6H_6; \lambda_{max}/nm (\epsilon/M^{-1} cm^{-1}))$: 300 (15 000), 410 (2300).

Protonolysis of (ONO^{cat})TaR₂ (R = Me (2), Ph (3)) with 1,2-Diphenylhydrazine. A 100 mL Schlenk flask equipped with a stirbar and a reflux condenser was charged with 10 mL of an orange-red solution of 2 (0.113 g, 0.14 mmol, 1 equiv), 1,2-diphenylhydrazine (0.026 g, 0.14 mmol, 1 equiv), and pyridine (0.011 mL, 0.14 mmol, 1 equiv), and the mixture was then refluxed and stirred for 6 h. The solution was cooled for 1 h before an aliquot was removed from the solution and placed in a 1 mL volumetric flask with 100 μ L of an internal standard (biphenyl) and diluted to 1 mL with benzene. The remaining red-purple solution was concentrated (~2 mL) and treated with 20 mL of pentane. The resulting dark purple-brown precipitate was isolated by filtration and identified as 8 (yield 0.095 g, 87%).

A similar procedure was performed with 3 (0.060 g, 0.08 mmol, 1 equiv), 1,2-diphenylhydrazine (0.015 g, 0.08 mmol, 1 equiv), and pyridine (0.007 mL, 0.08 mmol, 1 equiv) to give 8 (yield 0.055 g, 88%).

Decomposition of (ONO^{cat})**TaMe**(η^2 -**PhNNHPh**). A 100 mL Straus tube equipped with a stirbar was charged with a bright yellow solution of 9 (0.113 g, 0.141 mmol, 1 equiv) in benzene (10 mL), and pyridine (0.011 mL, 0.14 mmol, 1 equiv) was slowly dripped into the solution, resulting in a rapid color change to red. The solution was stirred at 65 °C for 6 h, resulting in a color change of the solution to purple-red. The solution was cooled for 1 h before an aliquot was removed from the solution and placed in a 1 mL volumetric flask with 100 μ L of an internal standard (biphenyl) and diluted to 1 mL with benzene. The sample was analyzed by GC/MS to determine the yield of aryl diazene. The remaining red-purple solution was concentrated (~2 mL) and treated with 20 mL of pentane. The resulting dark purple-brown precipitate was isolated by filtration and identified as 8 (yield 0.090 g, 83%).

ASSOCIATED CONTENT

Supporting Information. CIF files giving X-ray crystallographic data for 2, 4, and $10 \cdot 2.6C_5H_{12}$ as well as figures giving ¹H NMR spectra for all new complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We thank Dr. Joe Ziller (UCI), Dr. Arnie Rheingold, and Dr. Antonio DiPasquale (UCSD) for assistance with X-ray crystallography. The NSF CAREER Program (No. CHE-0645685) funded this work. A.F.H. is a Camille Dreyfus Teacher-Scholar.

REFERENCES

(1) Smith, A. L.; Hardcastle, K. I.; Soper, J. D. J. Am. Chem. Soc. 2010, 132, 14358–60.

- (2) Ringenberg, M. R.; Kokatam, S. L.; Heiden, Z. M.; Rauchfuss, T. B. J. Am. Chem. Soc. **2008**, 130, 788–789.
- (3) Ringenberg, M. R.; Nilges, M. J.; Rauchfuss, T. B.; Wilson, S. R. Organometallics **2010**, *29*, 1956–1965.
- (4) Chaudhuri, P.; Hess, M.; Weyhermuller, T.; Wieghardt, K. Angew. Chem., Int. Ed. **1999**, 38, 1095–1098.
- (5) Chaudhuri, P.; Hess, M.; Müller, J.; Hildenbrand, K.; Bill, E.; Weyhermüller, T.; Wieghardt, K. J. Am. Chem. Soc. **1999**, *121*, 9599–9610.
- (6) Paine, T. K.; Weyhermüller, T.; Wieghardt, K.; Chaudhuri, P. Dalton Trans. 2004, 2092–101.
- (7) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. J. Am. Chem. Soc. 2004, 126, 13794–13807.
- (8) Bart, S. C.; Chłopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* 2006, 128, 13901–12.
- (9) Muckerman, J. T.; Polyansky, D. E.; Wada, T.; Tanaka, K.; Fujita, E. Inorg. Chem. 2008, 47, 1787–802.
- (10) Tsai, M. K.; Rochford, J.; Polyansky, D. E.; Wada, T.; Tanaka, K.; Fujita, E.; Muckerman, J. T. *Inorg. Chem.* **2009**, *48*, 4372–4383.
- (11) Boyer, J. L.; Rochford, J.; Tsai, M. K.; Muckerman, J. T.; Fujita, E. Coord. Chem. Rev. 2010, 254, 309–330.
- (12) Wada, T.; Muckerman, J. T.; Fujita, E.; Tanaka, K. Dalton Trans. 2011, 40, 2225–33.
- (13) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. Inorg. Chem. 2005, 44, 5559–61.
- (14) Zarkesh, R. A.; Ziller, J. W.; Heyduk, A. F. Angew. Chem., Int. Ed. 2008, 47, 4715–8.
- (15) Blackmore, K. J.; Sly, M. B.; Haneline, M. R.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2008**, *47*, 10522–32.
- (16) Ketterer, N. A.; Fan, H.; Blackmore, K. J.; Yang, X.; Ziller, J. W.; Baik, M. H.; Heyduk, A. F. J. Am. Chem. Soc. 2008, 130, 4364–74.
- (17) Nguyen, A. I.; Blackmore, K. J.; Carter, S. M.; Zarkesh, R. A.; Heyduk, A. F. J. Am. Chem. Soc. **2009**, 131, 3307–3316.
- (18) Nguyen, A. I.; Zarkesh, R. A.; Lacy, D. C.; Thorson, M. K.; Heyduk, A. F. *Chem. Sci.* **2011**, *2*, 166–169.
- (19) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. J. Am. Chem. Soc. 1988, 110, 8729–8731.
- (20) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. J. Am. Chem. Soc. 1988, 110, 8731-8733.
- (21) Zambrano, C. H.; Fanwick, P. E.; Rothwell, I. P. Organometallics 1994, 13, 1174–1177.
- (22) Arney, D. S. J.; Burns, C. J. J. Am. Chem. Soc. 1995, 117, 9448–9460.
- (23) Cenini, S.; Gallo, E.; Caselli, A.; Ragaini, F.; Fantauzzi, S.; Piangiolino, C. *Coord. Chem. Rev.* **2006**, 250, 1234–1253.
- (24) Nugent, W. A.; Haymore, B. L. Coord. Chem. Rev. 1980, 31, 123–175.
- (25) Wigley, D. E. Prog. Inorg. Chem. 1994, 42, 239–482.
- (26) Gambarotta, A. J. Organomet. Chem. 1984, 270, C49-C52.
- (27) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. J. Am. Chem. Soc. **1985**, *107*, 7945–7952.
- (28) Chiu, K. W.; Wilkinson, M. G. Polyhedron 1984, 3, 79-85.
- (29) Luker, T.; Whitby, R. J.; Webster, M. J. Organomet. Chem. 1995, 492, 53–57.
- (30) Evans, W. J.; Walensky, J. R.; Ziller, J. W.; Rheingold, A. L. Organometallics 2009, 28, 3350–3357.
- (31) Hillhouse, G. L.; Bercaw, J. E. Organometallics 1982, 1, 1025–1029.
- (32) Watanabe, T.; Matsuo, T.; Kawaguchi, H. *Inorg. Chem.* 2006, 45, 6580–2.

- (33) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, 9, 963–968.
- (34) Bhattacharya, S.; Gupta, P.; Basuli, F.; Pierpont, C. G. Inorg. Chem. 2002, 41, 5810–5816.
- (35) Hillhouse, G. L.; Goeden, G. V.; Haymore, B. L. Inorg. Chem. 1982, 21, 2064–2071.
- (36) Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L.; Winter, C. H. Polyhedron **1997**, *16*, 4017–4022.
- (37) Barrett, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Kociok-Köhn, G.; Procopiou, P. A. *Inorg. Chem.* **2008**, 47, 7366–76.
- (38) Matsunaga, M. T.; Hillhouse, G. L.; Rheingold, A. L. J. Am. Chem. Soc. 1993, 115, 2075–2077.
- (39) Bradley, C. A.; Veiros, L. F.; Pun, D.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. J. Am. Chem. Soc. **2006**, *128*, 16600–12.
- (40) Beweries, T.; Jäger-Fiedler, U.; Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 3000–3004.
- (41) Bradley, C. A.; Veiros, L. F.; Chirik, P. J. Organometallics 2007, 26, 3191–3200.
- (42) Wong, E. W.; Walsby, C. J.; Storr, T.; Leznoff, D. B. *Inorg. Chem.* **2010**, *49*, 3343–50.
- (43) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. Organometallics 1986, 5, 2162–2164.
- (44) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. J. Am. Chem. Soc. **1988**, 110, 4964–4977.
- (45) Betley, T. A.; Peters, J. C. J. Am. Chem. Soc. 2004, 126, 6252-6254.
- (46) Smith, P. A. S.; Brown, B. B. J. Am. Chem. Soc. 1951, 73, 2438–2441.
- (47) Barral, K.; Moorhouse, A. D.; Moses, J. E. Org. Lett. 2007, 9, 1809–11.
- (48) Farrugia, L. J. J. Appl. Crystallogr. 1997, 30, 565–565.