

Reactivity of Diazoalkanes with Tantalum(V) Complexes of a Tridentate Amido-Bis(phenolate) Ligand

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Summary: While a dimethyltantalum(V) complex of the $[ONO^{cat}]^{3-}$ ligand $([ONO^{cat}]H_3 = N,N-bis(3,5-di-tert-butyl-tert-but$ 2-phenol)amine) reacted with diazoalkane to afford products of insertion into the Ta-Me bond, the dichlorotantalum(V) complex [ONO^{cat}]TaCl₂(OEt₂) reacted with 2 equiv of Ph_2CN_2 to form the ketazine adduct $[ONO^{cat}]TaCl_2(\eta^2(N,N'))$ - $Ph_2C=NN=CPh_2$). When Ph_2CN_2 was added to the dichloride in neat styrene, catalytic carbene transfer was observed to form the corresponding cyclopropane

Interactions of diazoalkanes with transition-metal complexes lead to varied reactivity, depending on the electronic properties of the diazoalkane and the formal charge on the metal center.¹ Addition of diazoalkanes to electron-rich transition-metal complexes has proven to be a useful strategy for the generation of transition-metal carbene functionalities.² Studies carried out on the reaction of diazoalkanes with various copper(I) complexes revealed N2 expulsion from the diazoalkane to generate a putative copper carbene that then transfers the carbene fragment to unsaturated carbon-carbon double bonds, generating cyclopropanes.³

Given the importance of metal valence electrons in stabilizing the carbene and alkylidene resonance structures shown in eq 1, we hypothesized that a redox-active ligand might allow us to generate reactive metal-carbene functionalities for formally d⁰ transition metal complexes. By incorporating a redox-active ligand in a d⁰ metal coordination sphere, we have been able to realize halogen oxidative addition⁴ and carbon-carbon reductive elimination⁵ reactions at Zr(IV) centers, despite formal d⁰ electron counts. More recently, we developed the chemistry of a redox-active tris(amide) ligand with tantalum(V) and showed that the ligand could act as a two-electron reservoir, enabling the transfer of a nitrene group from an organic azide to the tantalum center to form a new tantalum imide;⁶ however, sterics seemed to preclude an analogous reaction to form the tantalum alkylidene from the corresponding diazoalkane.⁷ To reduce the steric demands of the redox-active ligand, we turned to the tridentate $[ONO^{cat}]^{3-}$ ligand platform $([ONO^{cat}]H_3 = N, N-bis(3, 5-di$ tert-butyl-2-phenol)amine),8 which also displays two-electron reactivity on coordination to tantalum(V).

$$[M^n] \xleftarrow{R}_{R'} \xleftarrow{M^{n+2}} \xleftarrow{R}_{R'} (1)$$

The tantalum(V) dimethyl complex $[ONO^{cat}]TaMe_2$ (1) reacted with diazoalkane to afford the product of 1,1-insertion into the tantalum-methyl bond, as has been observed for other d⁰ metal alkyls.¹⁰ Hence, the addition of 1 equiv of Ph₂CN₂ to 1 resulted in the formation of [ONO^{cat}]TaMe- $\{\eta^2(N,N')$ -NMeN=CPh₂ $\}$ (2) in nearly quantitative yields, as shown in Scheme 1. Compound 2 was characterized by NMR and IR spectroscopy. Equal-intensity singlet resonances at 2.78 and 1.30 ppm in the ¹H NMR spectrum are indicative of N-CH₃ and Ta-CH₃ groups, respectively. The IR spectrum shows a diagnostic stretch for the hydrazonato ligand at 1164 cm⁻¹. When 2 equiv of Ph₂CN₂ was added to 1, the double-insertion product $[ONO^{cat}]Ta\{\eta^2(N,N')\}$ -NMeN=CPh₂ $_{2}$ (3) was obtained as a dark red microcrystalline product. The ¹H NMR spectrum of **3** did not show a Ta-CH₃ resonance, but instead, a singlet at 2.94 ppm integrating as six protons was consistent with two N-CH3 groups of equivalent hydrazonato ligands.

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To circumvent the insertion of diazoalkane into the Ta-CH₃ bond, reactivity studies were conducted between various diazoalkanes and the dihalide complex [ONO^{cat}]-TaCl₂(OEt₂) (**4a**). The addition of 2 equiv of Ph₂CN₂ to a dark red solution of **4a** resulted in the liberation of 1 equiv of N₂ gas and the formation of a green solution from which [ONO^{cat}]TaCl₂(η^2 -Ph₂C=NN=CPh₂) (**5**) was isolated as a green solid in 76% recrystallized yield (Scheme 1). Substoichiometric ratios of Ph₂CN₂ to **4a** afforded mixtures of **5** and unreacted **4a** with no evidence for an intermediate species. Complex **5** also was prepared by the addition of 1 equiv of Ph₂C=NN=CPh₂ to a solution of **4a**.

X-ray diffraction studies on a single crystal of 5 showed a tantalum(V) metal coordinated to a reduced $[ONO^{cat}]^{3-1}$ ligand, with the ketazine ligand acting as a neutral donor ligand. As shown in Figure 1, 5 adopts a pseudo-pentagonalbipyramidal structure with axial chloride ligands and the ketazine and [ONO^{cat}]³⁻ ligands occupying the equatorial plane. Bond distances within the [ONO^{cat}]Ta framework are consistent with the fully reduced or catecholate form of the ligand.⁹ Specifically, short Ta-O and Ta-N bond distances of 1.94 and 2.02 Å, respectively, are consistent with tantalum-phenoxide and tantalum-anilide interactions. Similarly, long C-O (1.36 Å) and C-N (1.41 Å) distances and aromatic C-C distances (1.40 Å average) argue against oxidation of the ligand to the semiquinonate $([ONO^{sq})^{2^{-}})$ or quinonate ([ONO^q]⁻) oxidation states. The Ta-N distance for the ketazine ligand is long at 2.33 Å, consistent with a dative N→Ta interaction, and the N-N distance is lengthened only slightly from that of the free ketazine.¹¹ The C=N distance of 1.30 Å is consistent with a formal double bond, as is the C=N stretch at 1525 cm^{-1} in the IR spectrum and the imine carbon resonance at 172.5 ppm in the ¹³C NMR spectrum.

Complex **5** acts as a precatalyst for the formation of ketazine from 2 equiv of diazoalkane.¹² The coordinated ketazine in **5** could be displaced by strong donor ligands such as pyridine,

Figure 1. ORTEP drawing of $[ONO^{cat}]TaCl_2(\eta^2-Ph_2C=NN=CPh_2)$ (5). Ellipsoids are shown at the 50% probability level. A toluene molecule has been omitted for clarity.

affording the free ketazine and $[ONO^{cat}]TaCl_2(py)$ (4b, L = py), which is unreactive toward additional diazoalkane. Alternatively, excess Ph₂CN₂ also displaced the ketazine in 5, allowing for catalytic turnover. In a typical experiment, addition of 30 equiv of Ph₂CN₂ to a benzene solution of 5 resulted in effervescence, indicative of the release of N₂ from the diazoalkane. Monitoring reaction mixtures by ¹H NMR spectroscopy revealed complete consumption of Ph2CN2 under these conditions; however, the reaction is strongly inhibited by the ketazine product. The addition of excess ketazine to the reaction effectively stopped catalytic turnover. Similarly, reactions carried out with more than a 30:1 ratio of Ph₂CN₂ to 5 stalled without complete consumption of the diazoalkane. Preliminary kinetics experiments suggest a complicated rate law for the conversion of Ph₂CN₂ to Ph₂C=NN=CPh₂; however, the coupling reaction appears to be general, as reactions carried out with PhHCN₂, diazofluorenone, (Me₃Si)HCN₂, and ethyl diazoacetate resulted in similar reaction times and quantitative conversions to the corresponding ketazine products.¹³

The reaction to form a ketazine from 2 equiv of diazoalkane can be considered a carbene transfer from one diazoalkane to another with concomitant loss of 1 equiv of N_2 . To test this hypothesis, 5 was treated with excess Ph₂CN₂ in neat styrene as the solvent. As shown in the Supporting Information, after 6 h at 300 K, complete consumption of the diazoalkane was accompanied by 78% conversion to 1,1,2-triphenylcyclopropane and only 22% to Ph₂C=NN=CPh₂. Cooling the reaction mixture to 273 K effectively stopped all consumption of Ph₂CN₂, while heating itn to 338 K resulted in a decreased yield of the cyclopropane product and a corresponding increase in ketazine yield. Reactions carried out in mixtures of styrene and benzene also resulted in decreased yields of the cyclopropane and increased yields of ketazine. Results similar to those for the cyclopropanation of styrene were obtained for diazofluorenone and (Me₃Si)HCN₂; however, all attempts to effect carbene transfer to less reactive olefins such as cyclohexene, 1-vinylcyclohexene, and α -methylstyrene failed, resulting only in the formation of the corresponding ketazine.

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While 4a and 5 both function as precatalysts for the cyclopropanation of an activated olefin such as styrene, less reactive substrates failed to give the desired carbene transfer product. Moreover, control reactions with Rothwell's tantalum(V) complex, $TaCl_2(OR)_3$ (R = 2,6-diphenylphenoxide),¹⁴ showed reactivity analogous with that of diazoalkanes, yielding the ketazine product in benzene or the cyclopropane product in neat styrene.¹⁵ The modest reactivity displayed by 4a and 5, which is paralleled by TaCl₂(OR)₃, suggests that the redoxactive $[ONO^{cat}]^{3-}$ ligand in **4a** and **5** is not playing a key role to enable the formation of a Ta=CR2 species and subsequent carbene transfer to substrate. Instead, it is likely that the tantalum center is acting as a simple Lewis acid to activate a diazoalkane for nucleophilic attack according to the simple mechanism shown in eq 2. A rate-determining bimolecular reaction between a tantalum-diazoalkane adduct and free diazoalkane would lead to ketazine formation with liberation of N2. Free ketazine would strongly inhibit this bimolecular reaction by shifting the pre-equilibrium away from the tantalumdiazoalkane adduct.



This interpretation suggests that the diazoalkanes do not oxidize the $[ONO^{cat}]^{3-}$ ligand to form the putative tantalum

carbene species [ONOq]TaCl2(=CPh2). Oxidation of the ONO ligand platform from the [ONO^{cat}]³⁻ form to the [ONO^q]⁻ form results in a stark color change from burgundy to green,⁹ and during the reactions of **2a** with the various diazoalkanes studied here, no spectroscopic evidence for the formation of a green [ONO^q]Ta species was obtained. Instead of a redox mechanism for diazoalkane activation, coordination of the diazoalkane to 2a should enhance the electrophilic character of the diazoalkane, enabling nucleophilic attack by a substrate: either another diazoalkane or an activated olefin. That a diazoalkane oxidation of 2a could be thermodynamically unfavorable is entirely consistent with our previous report of PhN=NPh reductive elimination from the dimer of [ONO^q]TaCl₂-(=NPh)⁹ and highlights the differing reducing powers of the redox-active [ONO^{cat}]³⁻ and [NNN^{cat}]³⁻ ligand platforms. In the tantalum chemistry of the latter ligand, the reaction with diazoalkane gave a product that was best described as [NNN^q]TaCl₂(=NN=CPh₂),⁶ with an oxidized redox-active ligand and a reduced hydrazido group. In effect, the highly reducing [NNN^{cat}]³⁻ ligand quenched the electrophilic character of the diazoalkane, shutting it down for further reactivity. In this way it is intriguing to consider how strongly the electronic properties of the redox-active ligand modulate the reactivity at a metal center, and this points toward a strategy for tuning the metal's reactivity with a given substrate.

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Supporting Information Available: Text and tables giving detailed experimental procedures and cyclopropanation yields and a CIF file giving complete crystallographic details for **5**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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