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N−N Bond Cleavage of Mid-Valent Ta(IV) Hydrazido and Hydrazidium Complexes Relevant to the Schrock Cycle for Dinitrogen Fixation

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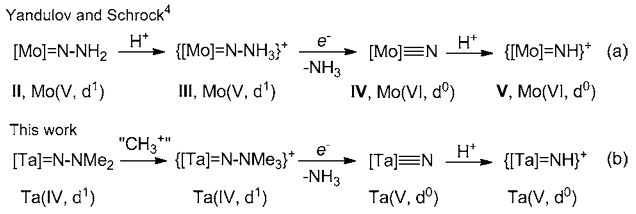
S *Supporting Information*

ABSTRACT: Chemical reduction of the Ta(V) hydrazido chloride **1** generates the open-shell, mononuclear Ta(IV) hydrazido complex **2**, which upon N-methylation yields the corresponding structurally characterized Ta(IV) hydrazidium **6**. Chemical reduction of **6** results in N−N bond cleavage to generate a cis/trans mixture of the [Ta(V),Ta(V)] bis(μ-nitrido) product **7** in tetrahydrofuran and the mononuclear Ta(V) parent imide **8** in toluene. These results serve to establish an important foundation for the pursuit of a group-5 metal variant of the Schrock cycle for dinitrogen fixation.

The development of molecularly well-defined transition-metal complexes that can mediate the energy-efficient conversion of dinitrogen to ammonia, also known as "dinitrogen fixation", ultimately requires finding viable solutions to the problem of chemically cleaving the strong N≡N triple bond in N_2 (bond dissociation energy = 226 kcal mol^{-1}) within a sequence of transformations that constitute a complete catalytic cycle.[1−3] In 2003, Yandulov and Schrock[4] successfully realized this goal using the Mo(III, d^3) triamidoamine dinitrogen complex $[(ArNCH_2CH_2)_3N]Mo(\kappa^1\text{-}N_2)$ [Ar = 3,5-(2,4,6-$^{i}Pr_3$-$C_6H_2)_2C_6H_3$] (**I**) in conjunction with multiple equivalents of reagents to deliver the required number of electrons and protons to reduce coordinated N_2 to 2 equiv of free NH_3 in a nonaqueous solvent (heptane).[5] As presented in eq (a) in Chart 1, the key N−N bond-cleaving steps of what is now commonly called the "Schrock cycle" proceed through protonation of Mo(V, d^1) hydrazido intermediate **II** to generate the corresponding Mo(V) hydrazidium species **III**, which upon one-electron reduction disproportionates to produce a Mo(VI, d^0) nitride (**IV**) and 1 equiv of NH_3. Protonation of **IV** yields the cationic parent imide **V**, which is then converted back to **I** through additional electron and proton additions under a N_2 atmosphere to complete the catalytic cycle (not shown).

An important question raised by the success of the Schrock cycle is whether a similar catalytic cycle can be implemented using other transition metals, and given a wealth of previously established dinitrogen chemistry, it seems reasonable to look toward the group-5 metals (V, Nb, and Ta) to achieve this feat.[6−8] To date, however, the number of well-characterized group-5 metal hydrazides remains very small, particularly for second-row Nb and third-row Ta.[9−11] Indeed, to the best of our knowledge, *no mid-valent group-5 metal hydrazido or hydrazidium complexes that would be relevant for evaluating the Schrock cycle have ever been prepared and characterized, including an evaluation of pathways leading to N−N bond cleavage.* Herein we report the synthesis, solid-state structures, and preliminary chemical reactivity profiles of Ta(IV, d^1) hydrazido and hydrazidium complexes that are supported by the monocyclopentadienyl (η^5-C_5R_5)/guanidinate $\{\eta^2\text{-}[N(R')C(NR''_2)N(R''')]\}$ (**C$_P$G**) ligand environment. Significantly, the latter of these engages in one-electron reduction and facile N−N bond cleavage chemistry with the generation of a Ta(V, d^0) nitride and cationic Ta(V, d^0) parent imide according to eq (b) in Chart 1. With these results, strong evidence now exists to support the adoption of the **C$_P$G** ligand platform as a viable foundation upon which to pursue the development of a catalytic group-5 metal variant of the Schrock cycle.

Chart 1



Following a path similar to that taken by us to obtain the first example of a mononuclear Ta(IV, d^1) imido complex, $Cp^*Ta[N(^iPr)C(NMe_2)_2N(^iPr)][N(^tBu)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$),[12] we obtained the desired initial target of the present work in straightforward fashion via the route shown in Scheme 1.[12,13] Treatment of $Cp^*Ta[N(^iPr)C(NMe_2)N(^iPr)]Cl_3$ with 2 equiv of lithium 1,1-dimethylhydrazide ($LiNHNMe_2$) in Et_2O at −30 °C provided an excellent yield of the Ta(V) hydrazido complex $Cp^*Ta[N(^iPr)C(NMe_2)N(^iPr)](\kappa^1\text{-}NNMe_2)(Cl)$ (**1**) as a yellow crystalline material. Chemical reduction of **1** employing KC_8 in tetrahydrofuran (THF) at −30 °C then provided an 85% yield of a paramagnetic, dark-red crystalline material for which an elemental analysis was fully consistent with that expected for the Ta(IV) hydrazido complex $Cp^*Ta[N(^iPr)C(NMe_2)N(^iPr)](\kappa^1\text{-}NNMe_2)$ (**2**) (Scheme 1). In further agreement with this assigned formal oxidation state of **2**, an isotropic X-band EPR spectrum recorded in toluene solution at 25 °C displayed an eight-line pattern for a single unpaired electron strongly coupled to a ^{181}Ta center, with $g_{iso} = 1.962$ and $A_{iso}(^{181}Ta) = 160$ G.[13]

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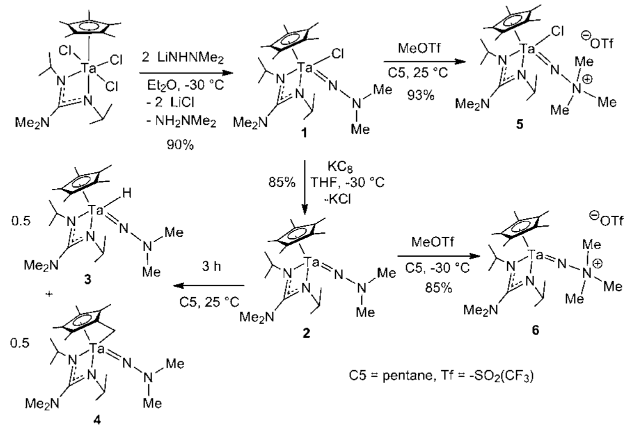
Scheme 1



Unequivocal structural proof for both **1** and **2** was provided by single-crystal X-ray analyses, and Figure 1 and Table 1 present the solid-state molecular structures and selected geometric parameters obtained from these data.[13] Comparison of **1** with **2** revealed small structural perturbations for the Ta═N−NMe$_2$ framework, the potentially most significant of these being a slight elongation of the N(1)−N(2) bond length that occurs with a concomitant small increase in pyramidalization of the *β*-nitrogen, N(2) (Table 1). These structural differences appear to be consistent with an increase in the ground-state contribution of the hydrazido resonance structure **A** over the 1,1-diazene structure **B** as the electron density of the metal increases in going from the Ta(V, d^0) center of **1** to the Ta(IV, d^1) center of **2**.[9d,e]

$$\underset{\mathbf{A}}{M^{z}{=}N{-}NR_2} \leftrightarrow \underset{\mathbf{B}}{M^{z-2}{-}N{=}NR_2}$$

Compound **2** proved to be unstable in concentrated pentane solution at 25 °C, and over the course of 3 h, it decomposed to provide two new diamagnetic products as determined by ^{1}H NMR spectroscopy.[13] Fractional crystallization from pentane at −30 °C and single-crystal X-ray analyses were able to establish their identities as the Ta(V) hydrazido hydride complex **3** and the Ta(V) hydrazido "tuck-in" complex **4** (Scheme 1 and Table 1; see the Supporting Information for complete crystal structure data).[13,14] Although detailed mechanistic studies have not been pursued, it is reasonable to assume that **3** and **4** arise from intermolecular H-atom abstraction from a Cp* methyl group by **2** (directly generating **3**) and subsequent metal−carbon bond formation between the Ta(IV) center and the resulting η^5-$C_5Me_4CH_2$ fragment (to produce **4**). Finally, this low thermal stability displayed by **2** could be taken as a prognosticator of chemical reactivity; however, the formal Ta-N double bond of this compound proved to be remarkably inert in solution toward a variety of reagents, including H$_2$, H$_3$SiPh, and CO.[11f,15] Attempts to develop a preparative route to **3** through the reaction of **2** with H-atom donors (e.g., 1,3-cyclohexadiene, triphenylmethane, tributyltin hydride, and 9,10-dihydroanthracene) were also unsuccessful.

Table 1. Selected Geometric Parameters for 1−6[13]

cmpd	Ta(1)−N(1) (Å)	N(1)−N(2) (Å)	Ta(1)−N(1)−N(2) (deg)	$\sum\theta_{N(2)}$ (deg)
1	1.7853(14)	1.375(2)	176.54(13)	333.44[a]
2	1.781(3)	1.398(5)	171.2(3)	330.40[a]
3	1.790(2)	1.385(3)	177.8(2)	332.80[a]
4	1.7955(13)	1.3898(19)	167.86(12)	331.88[a]
5	1.7989(13)	1.4119(18)	163.63(11)	329.05[b]
6	1.806(2)	1.417(3)	172.8(2)	328.34[b]

[a] Sum of the angles N(1)−N(2)−C(20), N(1)−N(2)−C(21), and C(20)−N(2)−C(21). [b] Sum of the angles C(20)−N(2)−C(21), C(20)−N(2)−C(22), and C(21)−N(2)−C(22).

Addition of 1 equiv of methyl trifluoromethanesulfonate (MeOTf) to pentane solutions of **1** and **2** at 25 °C and −30 °C, respectively, provided excellent yields of the corresponding Ta(V) and Ta(IV) hydrazidium complexes **5** and **6**, respectively.[11a,f,13] Although paramagnetic **6** also proved to be thermally unstable, it could nonetheless be isolated in analytically pure form through recrystallization from a toluene/pentane solvent mixture at −30 °C, which yielded dark-purple single crystals.[13] Elemental and spectroscopic analyses of both compounds, including an X-band EPR isotropic spectrum [$g_{iso} = 1.921$ and $A_{iso}(^{181}Ta) = 157$ G] in the case of **6**, provided initial support for the structures depicted in Scheme 1, and these were further confirmed through single-crystal X-ray analyses.

The solid-state molecular structures and selected geometric parameters of **5** and **6** are presented in Figure 1 and Table 1, respectively, and a common feature of both is that no close contacts are observed between the oxygen atoms of the OTf$^-$ anion and either the metal center or the quaternized *β*-nitrogen of the hydrazidium fragment.[13] Somewhat surprisingly, comparison of the Ta(1)−N(1) and N(1)−N(2) bond lengths for **5** and **6** revealed that virtually no perturbation occurs in going from the formal Ta(V, d^0) metal center in the former to the Ta(IV, d^1) center in the latter, while the Ta(1)−N(1) bond lengths in these

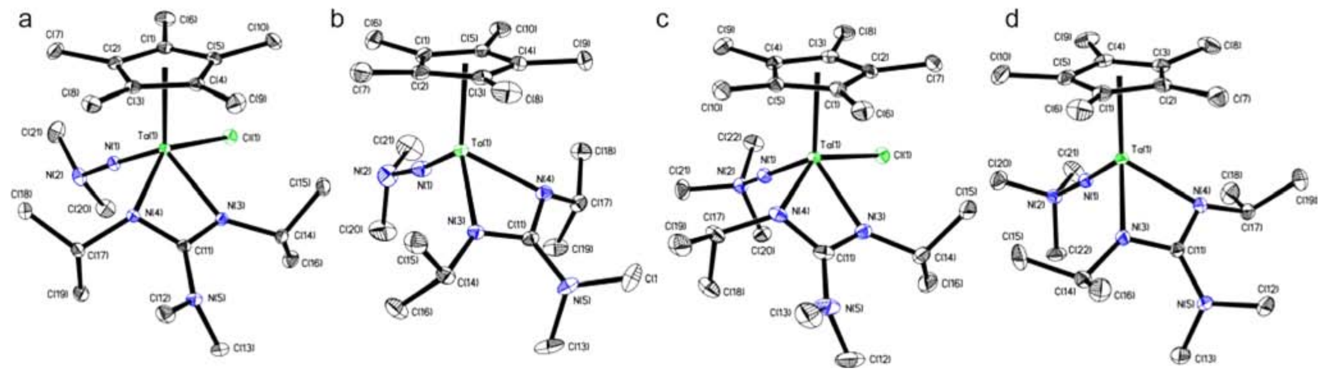
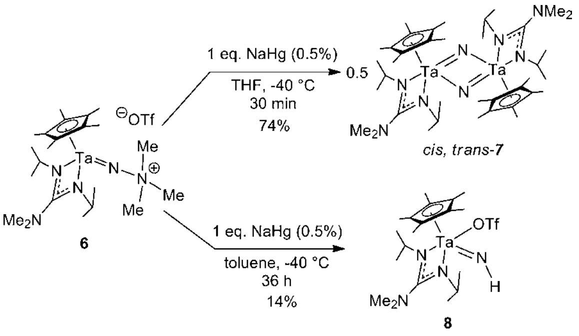


Figure 1. Molecular structures (30% thermal ellipsoids) of (a) **1**, (b) **2**, (c) **5**, and (d) **6**. H atoms and the triflate anions of **5** and **6** have been removed for clarity.[13]

cationic complexes are slightly elongated vis-à-vis the corresponding values obtained for **1** and **2**. It is possible that the origin of this structural difference between the hydrazido and hydrazidium complexes is due largely to an increase in nonbonded steric interactions within the supporting ligand environment upon methylation of the β-nitrogen rather than being electronic in nature (e.g., structure **A** vs structure **B**).

Scheme 2

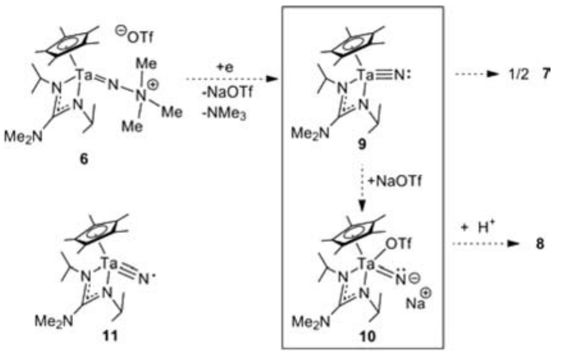


Investigations into reductive cleavage of the N–N bond in group-4 and group-6 metal hydrazidium complexes have been reported previously.[16] As Scheme 2 shows, chemical reduction of a deep-red solution of **6** in THF (dried and freshly vacuum-transferred from NaK alloy) using 1 equiv of 0.5% sodium amalgam (NaHg) at −40 °C produced within 30 min a yellow solution from which the diamagnetic [Ta(V),Ta(V)] bis(μ-nitrido) complex $[\{Cp^*Ta[N(^iPr)C(NMe_2)N(^iPr)](\mu\text{-}N)\}_2$ (**7**) was obtained in nearly quantitative yield as a mixture of cis and trans isomers that could be separated through differences in benzene solubility.[13] Figure 2 presents the solid-state molecular structures of *cis*-**7** and *trans*-**7** as obtained from single-crystal X-ray analyses along with selected geometric parameters. In this respect, the Ta_2N_2 four-membered rings in the two isomers are very similar to the analogous rings in the closely related amidinate complexes previously reported by us, namely, *cis*- and *trans*-$[\{Cp^*Ta[N(^iPr)C(Me)N(^iPr)](\mu\text{-}N)\}_2$, which are the products of the thermal N–N bond cleavage that occurs upon isomerization of the corresponding dinuclear "end-on-bridged" dinitrogen complex $\{Cp^*Ta[N(^iPr)C(Me)N(^iPr)]\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N)$ in solution above 0 °C.[8a,13,17]

Surprisingly, when the THF solvent was replaced with freshly dried toluene (vacuum-transferred from NaK alloy), chemical reduction of **6** with 1 equiv of 0.5% NaHg at −40 °C took a completely different path, as evidenced by isolation of the colorless Ta(V) parent imido complex $Cp^*Ta[N(^iPr)C(NMe_2)N(^iPr)](NH)(OTf)$ (**8**) in 14% yield (Scheme 2), which notably occurred in the absence of any spectroscopic evidence for concomitant formation of **7**. Both ^1H and ^{19}F NMR spectra confirmed the production of C_1-symmetric **8** to be both reproducible and scalable, and analytically pure crystalline material was obtained through recrystallization from pentane at −30 °C.[13] The solid-state molecular structure of **7** obtained from single-crystal X-ray analysis (Figure 2) displays a Ta(1)–N(1) bond length of 1.771(3) Å, and the triflate group is engaged in a strong bonding interaction with the Ta center with a Ta(1)–O(1) bond length of 2.1655(19) Å.

The isolation of *cis*- and *trans*-**7** through chemical reduction of **6** is consistent with transient generation of the terminal Ta(V) nitrido species **9** followed by dimerization (Scheme 3).[8,17,19]

Scheme 3



While the mechanistic origins of the structurally intriguing parent imide product **8**[16a,18] are less clear, we speculate that a lower rate of reduction in toluene leads to a lower solution concentration of **9**, thereby providing the opportunity for other reaction pathways to compete with bimolecular dimerization, such as protonation of a Ta(V) imide anion (e.g., **10**) with adventitious proton sources (Scheme 3).[20,21] At this preliminary stage, we also cannot rule out the possible intermediacy of a formal Ta(IV) nitridyl species (e.g., **11**) that then engages in H-atom abstraction along a path leading to **8**.[18g,22]

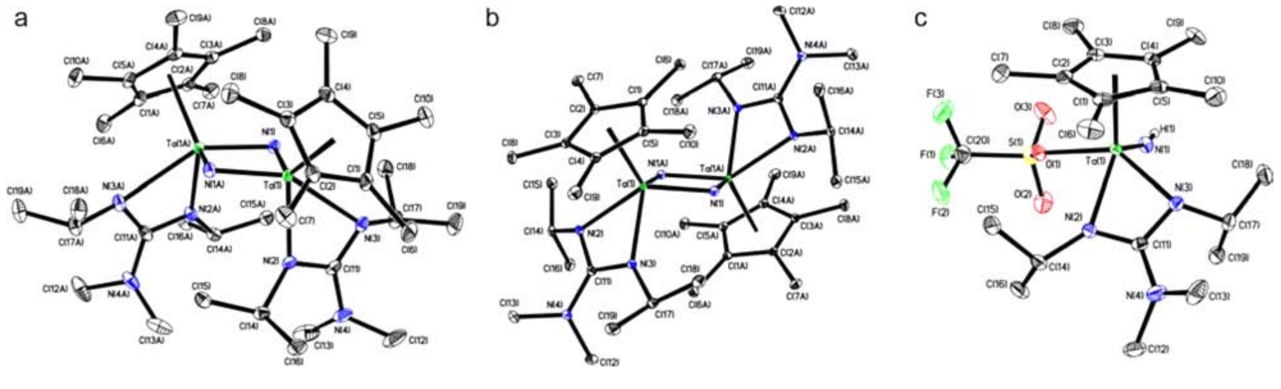


Figure 2. Molecular structures (30% thermal ellipsoids) of (a) *cis*-**7**, (b) *trans*-**7**, and (c) **8**. H atoms, except for H(1) in **8**, which is represented by a sphere of arbitrary size, have been removed for clarity. For *cis*-**7**: Ta(1)–N(1), 1.889(2) Å; Ta(1A)–N(1), 1.926(2) Å; N(1)–Ta(1)–N(1A), 84.75(10)°; N(1)···N(1A), 2.572 Å; Ta(1)–N(1)–Ta(1A), 95.00(10)°. For *trans*-**7**: Ta(1)–N(1), 1.8805(14) Å; Ta(1A)–N(1), 1.9550(14) Å; N(1)···N(1A), 2.592 Å; N(1)–Ta(1)–N(1A), 85.02(6)°; Ta(1)–N(1)–Ta(1A), 94.98(6)°.[13]

In conclusion, the results of the present study serve to establish an important precedent for the primary N−N bond-cleaving steps for a group-5 metal variant of the Schrock cycle, at least in terms of the relevant mid-valent metal hydrazide, hydrazidium, and parent imide intermediates presented in Chart 1. Through systematic manipulation of nonbonded steric interactions associated with the C_PG ligand environment, we are currently seeking to obtain kinetically stabilized derivatives of **9**−**11** that are amenable to more detailed investigations, including the elucidation of high-yielding pathways to protonated intermediates similar in nature to **8**.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. 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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