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Extreme π-Loading as a Design Element for Accessing Imido Ligand Reactivity. A CCC-NHC Pincer Tantalum Bis(imido) Complex: Synthesis, Characterization, and Catalytic Oxidative Amination of Alkenes

Theodore R. Helgert,[†,‡,⊥,#] Xiaofei Zhang,[†,#] Hannah K. Box,[†,#] Jason A. Denny,[†] Henry U. Valle,[†] Allen G. Oliver,[§] Gopalakrishna Akurathi,[†] Charles Edwin Webster,*[,†] and T. Keith Hollis*[,†,‡]

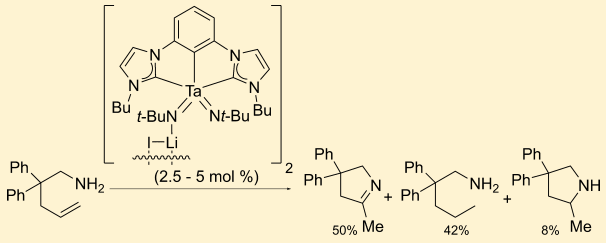
[†]Department of Chemistry and Center for Computational Sciences, Mississippi State University, Mississippi State, Mississippi 39762, United States

[‡]Department of Chemistry and Biochemistry, The University of Mississippi, Oxford, Mississippi 38655, United States

[§]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

Supporting Information

ABSTRACT: A rare Ta bis(imido) complex, which has unique reactivity, was prepared by manipulating the coordination sphere of a CCC-NHC pincer Ta complex. The reaction of lithium *tert*-butylamide with complex **1** yielded (1,3-bis(3′-butylimidazol-2′-yl-1′-idene)-2-phenylene)bis(*tert*-butylimido)tantalum(V) (**2**) as a lithium iodide bridged dimer, as determined by the X-ray structure. Complex **2** catalytically cyclized α,ω-aminoalkenes to effect an oxidative amination of alkenes (dehydrogenation by C−H activation) and produced a cyclic imine, an equivalent of reduced substrate, and varying proportions of hydroamination. Various additives and concentration impact the catalytic results. Computational and experimental observations have led to an initial mechanistic hypothesis. Based upon it, precatalyst **2** appears to be the first example of a bifunctional catalyst (MH-NHR) that is highly selective for nonpolar C═C bonds in preference to polar C═X bonds for outer-sphere hydrogenation.



INTRODUCTION

Metal−ligand multiple bonds are becoming ubiquitous in modern chemistry and play critical roles as both ancillary and reactive moieties.[1] Much fundamental inorganic chemistry work continues in the area,[2] including the recent example of a single, double, and triple M−N bond in one complex.[3] A few of the many applications that have become especially noteworthy include olefin metathesis,[4] dihydroxylation,[5] epoxidation,[6] aziridination,[7] and aminohydroxylation[8] for the synthesis of complex and biologically active compounds and functional materials.

The selective functionalization of unactivated C−H bonds, such as in methane to methanol, is of critical importance for developing sustainable energy resources.[9] C−H bond activiation remains one of the Holy Grails of modern organometallic research.[10] Parallel efforts in C−H activation have led to the achievement of selective borylation of aliphatic and arene hydrocarbons[11] and alkane dehydrogenation/transfer hydrogenation yielding alkenes.[12]

Recently a number of workers in the field have reexamined the "π-loading" hypothesis.[13] This strategy, which leads to a systematic approach to developing complexes for the activation of C−H bonds, was proposed by Wigley,[14] examined by Cundari,[15] and exploited by others.[13b,16] Work in the area of early transition metal imido complexes has been and continues to be an area of interest.[17] The metal−ligand multiple-bond chemistry of Ta[18] contains such notable examples as the first alkylidene carbene,[19] N_2,[20] and CO_2 activation.[21] C−H activation with Ta═NR complexes of sterically congested substituents was extensively studied,[22] and these iconic reports provide a detailed kinetic and thermodynamic analysis of Ta.[23] More recently, group 5 imido and bis(imido)s have been exploited for hydrogenation[13c] and hydroamination.[24]

The availability of three in-plane vacant orbitals in d^0 bent metallocene fragments, Cp_2M, can be traced back to Ballhausen and Dahl's analysis in 1961 and to Lauher and Hoffmann's construction in 1976.[25] The incredible versatility of this chemical fragment across the periodic table and with different types of reactivity has generated much interest in drawing the isolobal analogy between the bent Cp_2M fragment and the bent bis(imido) fragment, $(RN)_2M$ (Figure 1).[26] Recently, this analogy has been exploited in the design of group 5 bis(imido) complexes and their reactivity by Bergman and Arnold.[13c,27] These three frontier orbitals (Figure 1) are aligned in a meridional fashion. It was hypothesized a ligand that could

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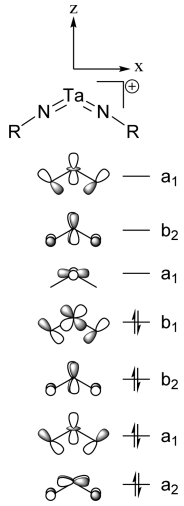


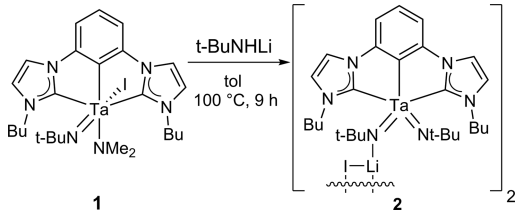
Figure 1. Isolobal frontier orbitals of a bent d^0 $[(RN)_2Ta]^+$ fragment that is analogous to a bent Cp_2M fragment.

interact with all three orbitals and maintain its geometric integrity would push up the energy of the $(RN)_2M$ fragment orbitals and make them accessible for chemical reactivity. Thus, the π-loading aspect of the complex would be maximized as it is fully coordinatively saturated and there are no more orbital interactions to be gained, which is termed "extreme π-loading".[28] A pincer-type ligand that is rigidly meridional and contains three strong donors (such as the monoanionic CCC-NHC pincer ligands with two NHC donors) might be ideally suited and produce more reactive imido groups. We have been exploiting CCC-NHC pincer ligands that are rigidly meridional and contain an anionic central donor and two NHC donors,[29] for which we recently reported the first examples for Ta.[30] We report herein the synthesis, characterization, and molecular structure of $[(^{Bu}C^{i}C^{i}C^{Bu})Ta(N^{t}Bu)_2{\cdot}LiI]_2$,[31] **2**, determined by X-ray crystallography, and its initial reactivity with α,ω-aminoalkenes that resulted in oxidative amination (OA), which involved a C−H bond activation and transfer hydrogenation reduction of an alkene.

RESULTS AND DISCUSSION

Synthesis. Following a slight modification of the procedure by Wigley,[32] complex **1** was treated with lithium *tert*-butylamide in toluene at 100 °C for 9 h (Scheme 1). The most obvious

Scheme 1. Synthesis of Ta(V) Bis(imido) Dimer 2



change in the ^{1}H NMR spectrum of the product was the loss of the diastereotopic dimethylamido signals at δ 4.24 and 3.89 for starting complex **1**. The signal corresponding to the methylene group adjacent to the nitrogen ($-NCH_2Pr$) shifted from a diastereotopic multiplet at δ 4.13 in **1** to a pseudotriplet at δ 4.18 in **2**. A signal at δ 1.06 with an integration of 18H corresponded to the two *tert*-butylimido ligands in the ^{1}H NMR spectrum of **2**. The ^{13}C NMR spectrum contained a carbene peak at δ 201.8 and an aryl (Ta−C) signal at δ 170.3. These data were consistent with the synthesis of a CCC-NHC pincer Ta bis(imido) complex, which was confirmed by X-ray analysis.

An ORTEP plot of complex **2** is presented in Figure 2 along with selected metric data. X-ray quality crystals of complex **2**

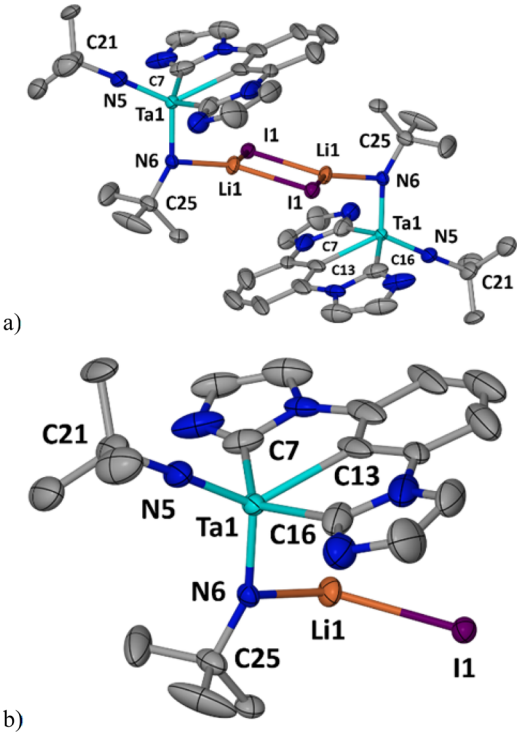


Figure 2. ORTEP representations of **2** with the *n*-butyl groups and hydrogens omitted for clarity of (a) the molecular dimer and (b) the asymmetric unit. Thermal ellipsoids are shown at 50% probability. Bond distances (Å): Ta1−N5 = 1.799(6); Ta1−N6 = 1.856(4); Ta1−C7 = 2.248(8); Ta1−C13 = 2.260(7); Ta1−C16 = 2.307(8). Angles (deg): N5−Ta1−N6 = 116.8(2); C7−Ta1−C13 = 68.7(4); C13−Ta1−C16 = 69.4(4); C7−Ta1−C16 = 137.7(3); Ta1−N5−C21 = 176.8(6); Ta1−N6−C25 = 151.0(5).

were grown by layering hexanes onto the reaction solution of **1** and lithium *tert*-butylamide. A distorted trigonal bipyramidal geometry along with the tridentate binding of the CCC-NHC pincer ligand was confirmed by X-ray analysis. The NHC carbon donors occupied coordination sites trans to each other, which yielded a $C^{NHC}-Ta-C^{NHC}$ bond angle of 137.7° due to the length of the Ta−C bonds. With lengths of 2.248(8) and 2.307(8) Å, the Ta−NHC bonds were similar (±0.02 Å) to the bond lengths of the previously reported Ta NHC complexes.[30f,33] At 2.260(7) Å the $Ta-C^{aryl}$ bond was similar to other aryl ligands flanked by neutral donors with values of 2.250(2), 2.248(5), and 2.270(3) Å.[30f,34] The non-lithium iodide bound imido ligand had a Ta−N bond length of 1.799(5) Å, while the imido ligand bound to Li had a Ta−N bond length of 1.856(5) Å. Regardless of binding to Li, both imido bond lengths were similar to the imido bond lengths of Wigley's Ta bis(imido) (±0.1 Å) complexes.[32] Also the Li−I bond was 2.705(11) Å, shorter than the sum of ionic radii of Li^+ and I^- (0.90 + 2.20 = 2.90 Å).[35]

The DFT geometry-optimized structure of **2** compares well to that determined by X-ray crystallography. The resulting

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molecular orbitals of the complex revealed that the HOMO of the dimer is, in fact, a mostly N-centered (~45%) π-type orbital of the imido ligand as illustrated in Figure 3a. Thus, the goal of

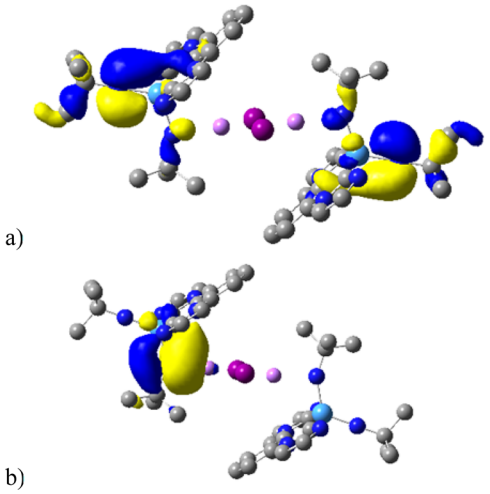


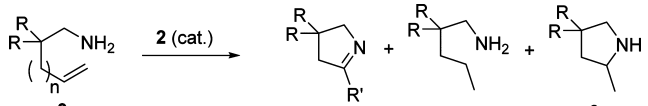
Figure 3. Illustration of select molecular orbitals of **2** with *n*-butyl groups and hydrogens omitted for clarity. (a) HOMO of **2**. (b) Localized molecular orbital illustrating the interaction between Li and N.

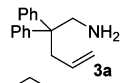
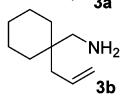
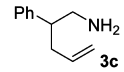
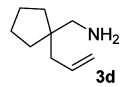
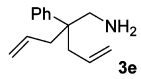
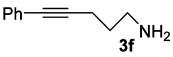
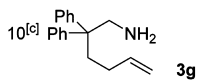
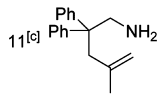
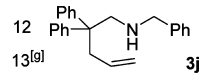
"extreme π-loading", making the imido orbitals the frontier and, therefore reactive orbitals, was achieved. HOMO−1 is the degenerate partner of that depicted in Figure 3a. A Boys localized molecular orbital indicates the bonding between the Li and N as illustrated in Figure 3b.[36]

VT-NMR of **2** from −70 to 95 °C on a 500 MHz NMR in THF-d_8 did not give sharp signals at low or high temperature (see Figure S36) for the pseudotriplet (δ 4.18) corresponding to the −N−CH_2Pr protons. The monomer−dimer equilibrium, exchange of the lithium iodide between imidos, coordination of THF, decomplexation, and dynamic tumbling issues all combined to complicate the system. Recourse to DFT computation indicated that the free energy of activation for LiI exchange between the imidos was 16.7 kcal/mol with THF coordinated (see Figure S54).

Catalysis. A Ta imido complex has been reported to catalyze the hydroamination (HA) of alkynes.[37] Intramolecular HA substrates (Table 1) were on hand since their reactivity under the influence of CCC-NHC pincer Ta monoamido complex **1** had been evaluated without observing any reactivity.[30f] When bis(imido) complex **2** was combined with the diphenyl-substituted substrate **3a** (Table 1, entry 1, method A) and heated in toluene, a mixture of products was obtained with no starting material remaining after 12 h at 120 °C. After some work deconvoluting the data, the major products were determined to be the cyclic imine (pyrroline), **4a** (R = Ph, R′ = Me) from oxidative amination and the "saturated" product **5a** (R = Ph), which resulted from hydrogenation of the alkene in the substrate. Thus, a net transfer oxidation/reduction process had occurred with reduction of ~1 equiv of starting material (**3**) for each equivalent of oxidized product **4**. Careful examination of the data revealed the presence of a small amount (~8%) of cyclic amine **6a** from hydroamination. Interestingly, the amount of HA product **6** (~8%) plus the amount of reduction product **5** (42%) matched the amount of OA product **4** (50%). The spectral data of the products (^{1}H NMR, ^{13}C NMR, and high-resolution mass spectral data; see the SI) matched the literature reports for the products using the diphenyl-substituted substrate.[38] A variety of late transition metal catalysts have been reported to catalyze the oxidative amination of vinyl arenes.[39] However, the oxidative amination of unactivated alkenes at the more substituted position as the major product was found in only one prior report by Mitsudo[38a] and as a minor side product.[40]

Table 1. Scope of Catalytic Oxidative Amination Activity of Complex 2 at 2.5 and 5 mol %



Entry	Substrate	t [h]	Conversion [%][a]	4 [%][a]	5 [%][a]	6 [%][a]
1[b]	 3a	12	100	50[d]	42	8
2[c]		16	100	39[d]	37	24
3[b]	 3b	16	100	51[d]	42	7
4[c]		24	100	39[d]	30	30
5[b]	 3c	12	100	50[d]	42	8
6[c]		40	100	29[d]	22	49
7[c]	 3d	24	100	33[d]	30	36
8[c]	 3e	16	100	55[d]	26	19
9[e]	 3f	16	100	100[f]	--	--
10[c]	 3g	48h, NR				
11[c]	 3h	48h, NR				
12 13[g]	 3j	48h, NR				

[a]Determined by ^{1}H NMR analysis. [b]Method A: toluene-d_8 at 120 °C [**3**] = 0.023 M, [**2**] = 0.0011 M (5 mol %). [c]Method B: benzene-d_6 at 80 °C [**3**] = 0.21 M, [**2**] = 0.005 M (2.5 mol %). [d]R′ = Me. [e]10 mol % **2** used. [f]R′ = Bn. [g]With 1.0 equiv of benzyl amine.

Examination of additional substrates (**3b** and **3c**) was carried out under method A conditions. The major products observed were again OA **4** and reduction **5** with minor amounts of hydroamination **6** as listed in Table 1, entries 3 and 5. Again, the amount of OA vs (reduction + HA) was 1:1, as observed in entry 1. These data could imply a competitive reduction process that transfers the hydrogen selectively to the alkene over the more polar C═N double bond, after formation of the OA product **4** (Scheme 2, **13** to **7**). This type of selectivity is the reverse of normal selectivity.[41] While these results were interesting and seemed to have mechanistic implications, for practicality attempted optimization using less catalyst, less-expensive C_6D_6, lower temperatures, and higher substrate concentrations (method B: Table 1, entries 2, 4, 6, 7, 8) led to a considerably different outcome. Thus, when method B was employed in the catalytic trials, two significant observations were made. First, significantly more hydroamination product **6** was observed, as may be noted in entries 2 (24%), 4 (30%), 6 (49%), 7 (36%), and 8 (19%). Second, and most importantly, the ratio of OA to (reduction + HA) is no longer 1:1.

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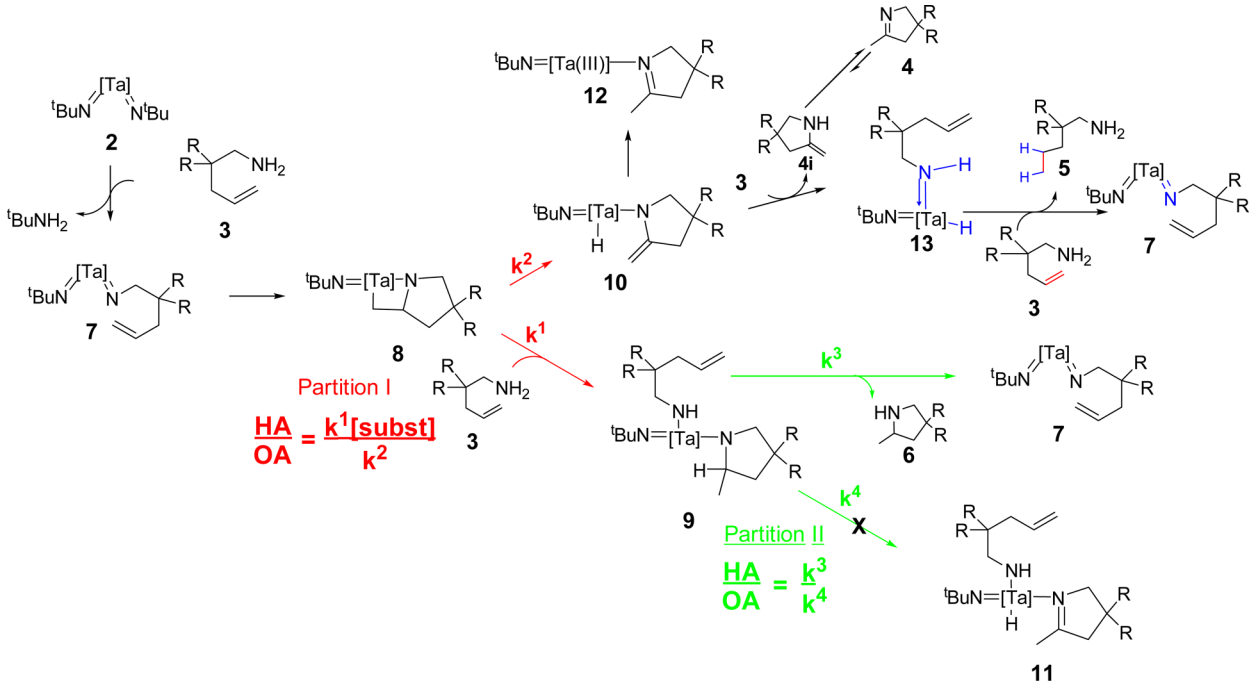
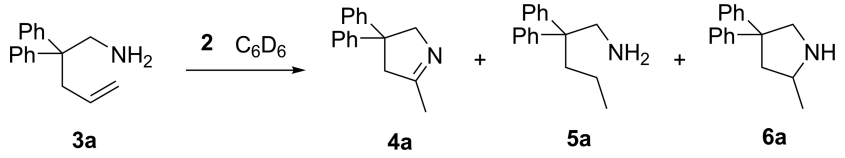
Scheme 2. Working Hypothesis for a Proposed Catalytic Pathway[a]

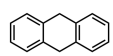
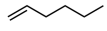


[a][Ta] = (^{Bu}C^{i}C^{i}C^{Bu})Ta.

Table 2. Catalytic Oxidative Amination Activity of Complex 2 with Additives and at Various Concentrations



3a 4a 5a 6a

Entry	[2]	[3a]	Additive[a]	T [°C]	t [h]	Conversion [%][b]	4a [%][b]	5a [%][b]	6a [%][b]
1	0.005	0.21	--	80	16	100	39	37	24
2	0.005	0.21	--	60	16	100	37	32	31
3	0.005	0.21	--	100	2	77	47	45	8
4	0.005	0.21	--	100	4	92	45	43	11
5	0.005	0.21	--	100	10	99	46	41	13
6	0.0005	0.021	--	100	10	100	57	38	5
7	0.0005	0.21	--	100	18	0	--	--	--
8	0.005	0.021	--	100	10	100	71	25	4
9	0.0005	0.021		100	10	97	51	40	9
10	0.0005	0.021		100	10	78	52	44	3
11	0.0005	0.021		100	10	11	~50 [c]	~50 [c]	0[c]
12[d]	0.0012	0.022		120	14	100	46	41	13

[a]The concentration of additive was 0.063 M. [b]Determined by ^{1}H NMR analysis. [c]At low conversion greater accuracy was not obtained, and HA product was not detected. [d]Entry 12 was carried out in tol-d_8.

Subjecting the substrate to reaction conditions in the presence of LiI gave no reaction.

The substrates evaluated are collected in Table 1 for convenient viewing of the results. Thus far, complex **2** was found to have activity for the formation of pyrroline rings. The OA was found to occur with substrates containing a spirocyclohexane (Table 1, entries 3 and 4), a spirocyclopentane (entry 7), a phenyl (entries 5 and 6), and a diallyl substituent (entry 8). No signals for these substrates were observed in the ^{1}H NMR spectrum after catalysis. A signal

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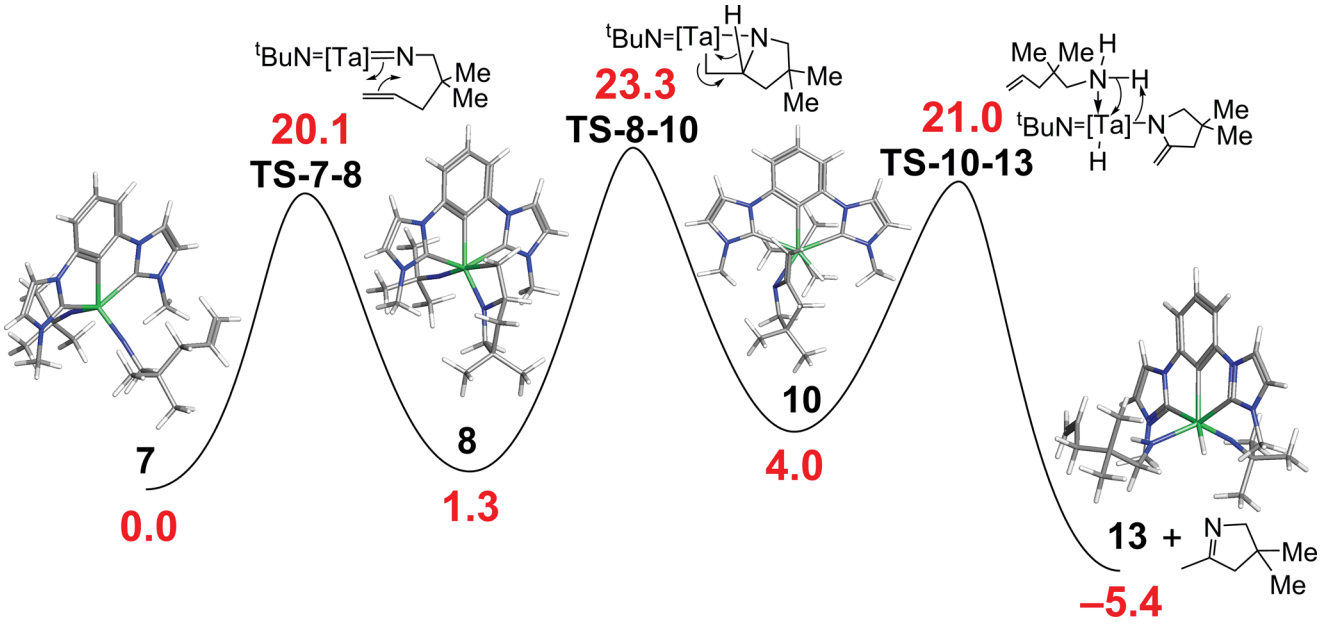

Figure 4. Schematic representation of the free energy diagram (kcal mol^{-1}, in red) for the proposed pathway from **7** to **8** to **10** to **13** from DFT computations. The diagrammatic structures represent the computed transition states. The *n*-butyl groups of complex **2** and the phenyl groups of **3a** were replaced with methyl groups for the computations.

around δ 173 was observed in the ^{13}C NMR spectra of all these substrates (entries 1−8) after catalysis. These data were consistent with pyrroline formation. The mass spectrum of the substrate with the phenyl and allyl substituent at the C-2 position of the substrate (entry 8) had signals at 200.1, 202.1, and 204.1, which is consistent with the $[M + H^+]^+$ products of catalysis as suggested. The mass spectrum of the spirocyclohexyl-substituted substrate (entry 4) had a signal at 152.1, which corresponded to the cyclic imine product. Complex **2** catalyzed the cyclization of an amino-alkyne substrate to produce the cyclic imine (entry 9). Furthermore, no reactivity was observed in substrates that would form a six-membered ring (entry 10), had an internally substituted double bond (entry 11), or had a secondary amine (Table 1, entries 12 and 13).

Inspired by the uncommon activity of complex **2**, the catalysis was investigated more carefully and for mechanistic insight using **3a** (Table 2) under a variety of conditions related to method B. The OA reaction is favored under a variety of conditions. It benefits from high temperature (entries 1−3) and short reaction times (entries 3−5). Most importantly, it was found that the lower the concentration of the substrate, the higher the proportion of OA (entries 5, 6, and 8). As seen in entry 7 at 0.21 M substrate and 0.0005 M **2**, no reaction was observed. This concentration dependence provides insight into the mechanism of the reaction (*vide infra*). The addition of 9,10-dihydroanthracene had little effect on the overall rate of reaction and minimal impact on the ratio of products (entries 6 vs 9). This observation and the lack of observable anthracene (entry 9) are consistent with the absence of radicals during the reaction. The presence of a sacrificial alkene *tert*-butylethylene (tbe) impeded the reaction (78% vs 100% in 10 h, entries 10 vs 6) with little impact on the product ratios. The steric congestion of tbe was considered as a possible issue. Therefore, 1-hexene was evaluated as a sacrificial hydrogen acceptor. 1-Hexene dramatically reduced the rate of reaction (11% vs 100%, entries 11 vs 6), but OA and reduced-alkene products were observed, ∼1:1. At this low conversion HA product was not detectable. Significantly, under slightly altered conditions complete conversion was obtained in the presence of 1-hexene (entry 12). With complete conversion, it was possible to identify all three products **4a**, **5a**, and **6a**, but no reaction of the 1-hexene was observed. Thus, presumably the high selectivity for the alkene of the substrate is due to an interaction with the amino group in **3a** or an as yet unidentified reaction pathway.

Computational and Mechanistic Analysis. The experimental data in Tables 1 and 2 combined with computations (substrate **3a** was modeled as the dimethyl analogue to simplify the computations) led to a working hypothesis for a proposed catalytic cycle as depicted in part in Scheme 2 and Figure 4. The lack of reactivity of 2° amines with and without the presence of benzylamine (Table 1, entries 12 and 13)[42] implicates the formation of a Ta imido. Partitioning between the OA (k^2) vs the HA (k^1) pathways can occur at intermediate **8**, which contains an azatantallacyclobutane. At this point the HA/OA ratio will be dependent upon k^1[subst]/k^2, i.e., the ratio **9**:**10**. The conversion from **8** to **10** involves a C−H activation at the α-carbon that is similar to that of hydroaminoalkylation.[24,43] Alternatively, if **8** is converted to **9**, partitioning can occur at **9** via path k^3 or k^4. If partitioning occurred here, the ratio of products would be dependent only on the ratio of k^3/k^4, explicitly with no substrate dependence. As the data in Table 2 illustrate, the amount of HA product diminishes as the initial concentration of substrate is reduced (Table 2, entries 5, 6 vs 8). Further, HA product **6a** was not observed to interconvert to OA product **4a** upon extended reaction times. Reversibility of the **9** to **7** interconversion might be expected to convert it over time. These observations are consistent with **9** and **11** not being on the active pathway for OA. Thus, the **8** vs **9** partitioning determines the HA/OA ratio. Complex **10** can be the intermediate to form OA and reduced products via several pathways. For instance, it may undergo a ligand exchange (**10** → **13**) or a hydride shift (**10** → **12**).

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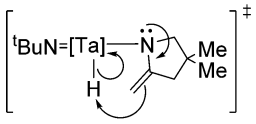
Intermediate **13** may lead to the reduced product through an inter- or intramolecular diimide-like hydrogen transfer.[44]

The computed transition-state free energy for **8** → **10** was 23.3 kcal mol^{-1} (Figure 4), contributing to the plausibility of this pathway. The pathways that remained were **8** → **10** → **12** and **8** → **10** → **13**. While **13** may react with alkene to produce the reduced product, **12** may account for the formation of OA product. Figure 4 demonstrates a proposed pathway of **7** → **8** → **10** → **13**. The computed free energies of activation are reasonable, and the isomerization to the pyrroline product at the end provides a thermodynamic driving force that is exergonic.

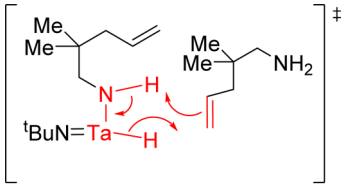
An alternative to β-hydride elimination would be for the N in the imido ligand of **8** to abstract the hydrogen, producing **14** (pictured in Figure S57), a bis(amido)Ta(III) "isomer" of **10**. This pathway would be analogous to the mechanism of hydroaminoalkylation.[45] Structure **14** was computed to be 26.8 kcal mol^{-1} relative to **7** (at 0 kcal mol^{-1}), which is 22.8 kcal mol^{-1} higher in energy than **10**. It is, therefore, higher in energy than the computed transition state **TS-8-10** (see Figure 4). Thus, the pathway involving **10**, with its Ta−H, seems the most plausible pathway at present.

Intermediate **10** is another potential point of bifurcation in the mechanism to produce the two different products. It can undergo exchange with substrate **3a**, yielding directly the enamine isomer **4i** (i = isomer), which isomerizes to pyrroline **4a** and produces intermediate **13**. It could also potentially undergo a "five-center reductive elimination" via a transition state illustrated in **TS-10-12** below, which would produce Ta(III) intermediate **12**. Preliminary computations indicate that the pathways involving Ta(III) are much higher in energy (see Figure S56). Complete details of these computations will be reported separately.



TS-10-12

The transfer of hydrogen to produce the reduced substrate **5** is hypothesized to occur via a transition state much like that for the Noyori bifunctional catalysis in the reduction of polar C═X bonds.[46] It is illustrated in **TS-13-7** below. Preliminary computations using ethylene as a model for the substrate and a *t*-BuNH for the amido ligand are consistent with an accessible transition state for this transformation (see SI, p. S73).



TS-13-7

A reaction manifold intrinsic to the catalytic cycle may produce hydroamination product (**7** → **8** → **9**). In addition, the outer-sphere hydrogenation mechanism of bifunctional catalysis (MH-NHR),[46a,47] which is related to the diimide hydrogenation mechanism,[48] is also a potential pathway for the reduction of oxidative amination product (**4** to produce the hydroamination product **6**). On the basis of the observations herein, intermediate **13** seems to be highly selective for nonpolar C═C bonds over polar C═X bonds. An observation that is the reverse of a typical bifunctional catalyst results.[41,49] A hypothesized outer-sphere hydrogenation transition state in depicted in **TS-13-7**. If this mechanism occurs, this catalytic system appears to be the first that has such high selectivity for C═C bonds. Future experimental and computational work will examine this possibility in detail. It should be noted that recently a report appeared describing selectivity for C═C bonds over C═X bonds for an analogue[50] of the Shvo system.[51] To our knowledge **2** is the first such system (MH-NHR) that is selective for C═C over C═X bonds.

CONCLUSIONS

We have synthesized a CCC-NHC pincer Ta bis(imido) lithium iodide dimer, **2**, which contains N_{imido}−Li bonds consitent with extreme π-loading. It reacts catalytically with aminoalkenes to form a mixture of the corresponding cyclic imine, the reduced substrate (aminoalkane), and cyclic amine. Thus far, when attempting to employ a sacrificial hydrogen acceptor, it was not consumed and did not change the product distribution significantly. A preliminary mechanistic proposal accounts for the HA/OA dependence on the initial substrate concentration via pathway **8** to **10** to **13**. Reactivity has been achieved even with the sterically congested *t*-BuN ligands; thus, use of less sterically demanding substituents is expected to produce even more reactive systems. Further reactivity studies of CCC-NHC pincer Ta bis(imido) complexes, particularly for C−H activation, oxidative amination exclusively by employing a more reactive hydrogen scavenger, a full kinetic and isotopic labeling analysis, and in different oxidation states, are under evaluation and will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. Standard inert atmosphere techniques were used. Complex **1** and lithium *tert*-butyl amide were prepared following previously reported literature procedures.[30f,52] Toluene, CH_2Cl_2, and hexanes were degassed with Ar and passed through two columns of activated alumina.[53] CD_2Cl_2, C_6D_6, and d_8-toluene were purchased from Cambridge Isotopes and passed through a column of activated basic alumina prior to use. No-D NMR experiments were conducted using procedures similar to Hoye's work.[54] ^{1}H and ^{13}C NMR spectra were collected on either a Bruker Avance 300, 500, or 600 MHz NMR at ambient temperatures unless otherwise specified. The ^{1}H NMR spectra were internally referenced from the residual protio-solvent signal: CD_2Cl_2 (δ 5.32), C_6D_6 (δ 7.16), and d_8-toluene (δ 2.09). The ^{13}C NMR spectra were referenced internally using the signal from the deuterated solvent: CD_2Cl_2 (δ 53.84).

Procedures: Preparation of (1,3-Bis(3′-butylimidazol-1-yl-2-idene)-2-phenylene)bis(*tert*-butylimido) tantalum(V) Lithium Iodide Bridged Dimer (2). 1,3-Bis(3′-butylimidazol-1-yl-2-idene)-2-phenylene)(*tert*-butylimido)(dimethylamido)iodotantalum(V) (**1**; 0.200 g, 0.270 mmol) was suspended in toluene (10 mL) in a vial with a Teflon-lined cap, lithium *tert*-butylamide (0.047 g, 0.59 mmol), in toluene (2 mL) was added dropwise. The mixture was heated at 100 °C for 9 h and then cooled to room temperature. The volume was reduced to ∼7 mL. Hexanes (∼15 mL) was then added dropwise precipitating an off-white solid. The mother liquor was decanted from the precipitate. The precipitate was washed with hexanes (3 × 3 mL), and the volatiles removed to yield an off-white solid (0.051 g, 30%). X-ray quality crystals were obtained from layering hexanes onto a reaction solution. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.52 (broad s, 2H, *CH* imidazolyl), 7.30 (t, ^3J = 7.6 Hz, 1H, *CH* arom), 7.15 (broad s, 2H, *CH* imidazolyl), 7.14 (d, ^3J = 7.7 Hz, 2H, *CH* arom), 4.36 (pseudotriplet, ^3J = 8.0 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 1.93 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.56 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.16 (s, 18H,

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HNCMe_3) 1.02 (t, ^3J = 7.4 Hz, 6H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (300 MHz, CD_2Cl_2): δ 200.0, 149.2, 129.3, 128.4, 121.9, 116.4, 109.8, 64.2, 52.9, 36.7, 32.9, 20.5, 14.1. Anal. Calcd for **2**, $C_{28}H_{43}ILiN_6Ta$: C, 43.20; H, 5.57; N, 10.80. Found: C, 38.65; H, 5.30; N, 9.42. Calculated for hydrolysis with loss of one *t*-$BuNH_2$ and addition of two −OH's, $C_{24}H_{36}ILiN_5O_2Ta$: C, 38.72; H, 5.28; N, 9.42.

Oxidative Amination: General Procedure for the NMR-Scale Catalytic Oxidative Aminations (Tables 1 and 2). Method A: (1,3-Bis(3′-butylimidazol-1-yl-2-idene)-2-phenylene)bis(*tert*-butylimido)tantalum(V) lithium iodide bridged dimer (**2**, 0.0031 g, 0.0020 mmol), amine (0.041 mmol), and C_7D_8 (1.75 mL) were combined in an NMR tube. The reaction was heated at 120 °C. The yield was determined by ^1H NMR spectroscopy analysis. Method B: (1,3-Bis(3′-butylimidazol-1-yl-2-idene)-2-phenylene)bis(*tert*-butylimido) tantalum(V) lithium iodide bridged dimer (**2**, 0.0043 g, 0.0028 mmol), amine (0.126 mmol), and C_6D_6 (0.6 mL) were combined in an NMR tube. The reaction was heated at 80 °C. The yield was determined by ^1H NMR spectroscopy analysis.

Time-Dependence of the Yields of Oxidative Amination, Reduction, and Hydroamination Products (Table 2, Entries 3, 4, and 5). (1,3-Bis(3′-butylimidazol-1-yl-2-idene)-2-phenylene)bis(*tert*-butylimido)tantalum(V) lithium iodide bridged dimer (**2**, 0.0078 g, 0.0050 mmol, [**2**] = 0.005 M), (2,2-diphenyl-4-pentenyl)amine (0.0500 g, 0.21 mmol, [amine] = 0.21 M), and C_6D_6 (1.0 mL) were combined in an NMR tube. The reaction was heated at 100 °C and monitored by ^1H NMR spectroscopy.

Concentration-Dependence of the Yields of Oxidative Amination, Reduction, and Hydroamination Products (Table 2, Entries 3, 6, 7, and 8). To four screw-capped NMR tubes were added complex **2** (tubes 1 and 2: 0.5 mg, 0.0003 mmol, [**2**] = 0.0005 M; tubes 3 and 4: 5.0 mg, 0.003 mmol, [**2**] = 0.005 M), (2,2-diphenyl-4-pentenyl)amine (tubes 1 and 3: 3.0 mg, 0.0126 mmol, [amine] = 0.021 M; tubes 2 and 4: 30.0 mg, 0.126 mmol, [amine] = 0.21 M), and C_6D_6 (0.6 mL). The reaction was heated at 100 °C and monitored by ^1H NMR spectroscopy.

Additive-Dependence of the Yields of Oxidative Amination, Reduction, and Hydroamination Products (Table 2, Entries 9, 10, and 11). To a screw-capped NMR tube complex were added **2** (0.5 mg, 0.0006 mmol, [**2**] = 0.001 M), (2,2-diphenyl-4-pentenyl)amine (3.0 mg, 0.0126 mmol, [amine] = 0.021 M), additive (0.0378 mmol, [additive] = 0.063 M), and C_6D_6 (0.6 mL). The reaction was heated at 100 °C and monitored by ^1H NMR spectroscopy.

X-ray Crystallography. A suitable crystal was selected and analyzed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2,[55] the structure was solved with the ShelXT[56] structure solution program using direct methods and refined with the ShelXL[57] refinement package using least squares minimization.

Computational Details. In the case of the mechanistic proposal, for computational convenience, the *n*-butyl groups were trimmed to methyl groups. In the case of the fluxional behavior in **2**, the full CCC-NHC ligand was utilized. Geometries were optimized using the Gaussian09[58] implementation of PBEPBE[59] density functional theory.[60] The LANL2DZ basis set and effective core potential,[61a] as modified by Couty and Hall,[62] were utilized for tantalum. The LANL2DZ(d,p) basis set[61b] and effective core potential[61c] were utilized for iodine. The 6-31G(d′) basis sets[63] were utilized for carbon, nitrogen, and oxygen, and the 6-31G basis set[64] was utilized for hydrogen. Each geometry was optimized in the gas phase and determined to be a minimum energy conformation or a transition state using an analytical frequency calculation. Standard statistical mechanics relationships for an ideal gas at 1 atm and 298 K were used to determine thermodynamic corrections.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00216.

NMR spectra, tables giving full crystallographic data of **2**, and further computational details (PDF)
Crystallographic data for **2** (CIF)
Optimized Cartesian coordinates (XYZ)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ewebster@chemistry.msstate.edu.
*E-mail: khollis@chemistry.msstate.edu.

Present Address

⊥T.R.H., Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439, United States.

Author Contributions

#T.R.H., X.Z., and H.K.B. each contributed significant portions to this work.

Notes

The authors declare no competing financial interest.
Crystallographic data are also available from Cambridge Crystallographic Data Centre (CCDC 1480842) for **2**.

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