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Catalytic synthesis of amines and N-containing heterocycles: Amidate complexes for selective C–N and C–C bond-forming reactions*

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Abstract: The direct, 100 % atom-economic, and selective synthesis of amines is a challenging task that can be achieved, making use of early transition-metal catalysts. Here we report the synthesis and application of group 4 and 5 high-oxidation-state metal amidate complexes in catalytic C–N (hydroamination) and C–C (hydroaminoalkylation) bond-forming reactions to access substituted amines.

Keywords: amidate; asymmetric catalysis; C–C bond formation; C–H activation; C–N bond formation; catalytic amine synthesis; hydroamination; hydroaminoalkylation; tantalum; zirconium.

INTRODUCTION

Catalytic amine synthesis has gained importance due to emerging methods for accessing efficient and selective product formation while avoiding the use of stoichiometric reducing- or N-transfer reagents. Notably, formal addition of an N–H bond across a C–C multiple bond to give C–N and C–H bonds, hydroamination, is of great interest [1]. Metals from across the periodic table have been used to facilitate hydroamination [2–5]. Interestingly, despite enormous effort within the catalysis community, intermolecular alkene hydroamination catalysis remains very rare and often of unfavorably narrow scope [6]. A recently developed complementary alternative to hydroamination for the catalytic synthesis of amines is the catalytic C–C bond-forming reaction, coined "hydroaminoalkylation", resulting from a C–H bond activation on an sp^3-hybridized carbon center α to N [7]. This approach formally parallels C–C bond formation α to hydroxyl groups using group 8 and 9 catalysts (typically Ru, Ir based) making use of their activity in transfer hydrogenation [8].

Both transformations can be realized by using early transition-metal precatalysts and can be used to access value-added N-containing chemicals. In Fig. 1, intramolecular examples of hydroamination and hydroaminoalkylation are depicted in which aminoalkenes are converted to the corresponding cyclized amine products.

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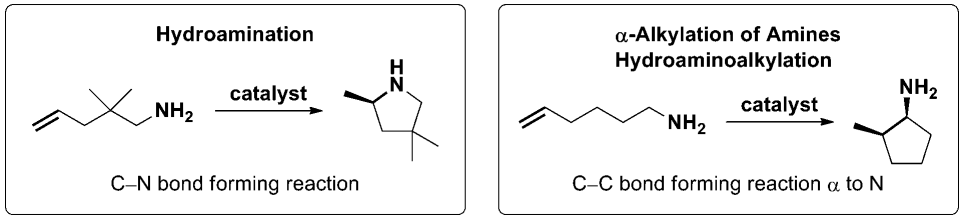


Fig. 1 Examples for hydroamination vs. hydroaminoalkylation for the intramolecular cyclization of aminoalkenes.

Early transition-metal amidate precatalysts, as shown in Fig. 2, can affect a multitude of useful transformations yielding N-containing products and are synthesized by way of a simple protonolysis approach by reacting the corresponding commercially available homoleptic amido complexes with the appropriate amount of organic amide (conveniently prepared from the corresponding acid chlorides and amines on a multigram scale) yielding the target amidate amido complexes under extrusion of amine. Using this straightforward protocol, a multitude of metal complexes can be synthesized with varied steric and electronic properties due to the modular nature of the amide ligands [9].

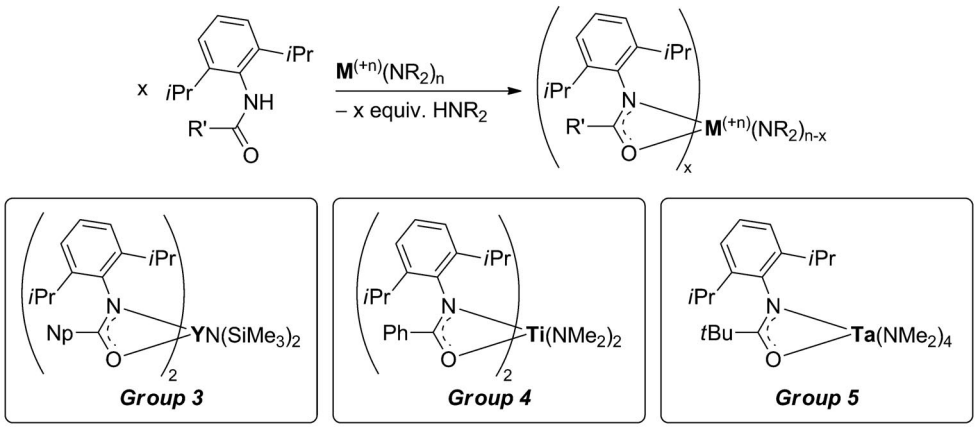


Fig. 2 Overview of catalytically active group 3-, 4-, and 5-based amidate complexes synthesized using protonolysis.

These complexes are competent in the catalytic synthesis of amines such as N-heterocycles (hydroamination of aminoalkenes) [10,11], aldimines (hydroamination of terminal alkynes) [12], ketimines and allylic amines (hydroamination of allenes) [13], α-amino acid derivatives (tandem sequential reaction via hydroamination of alkynes followed by a modified Strecker reaction and hydrolysis of the resultant α-cyanoamine) [14], cycloalkylamines (intramolecular hydroaminoalkylation of aminoalkenes) [15], and secondary amines (intermolecular hydroaminoalkylation of secondary amines with alkenes) [16].

As part of our program exploring new group 4 complexes with a focus on enhanced performance in hydroamination, we identified substituted 2-hydroxypyridines as promising amide analogs. They are synthesized by way of a rearrangement reaction as developed by Overman [17]. This proligand scaffold is of interest for the more electron-withdrawing nature of this amide (based on the lower pK_a of ~15 compared to ~20 of amides) and the diminished steric demand [18]. We were pleased to find that $Zr(NMe_2)_4$ reacts with 6-*tert*-butyl-3-phenyl-2-hydroxypyridine via our previously established protonolysis route to give the corresponding crystalline, monomeric bis(pyridonate) Zr(IV)-complex **1**

(see Fig. 3). Complex **1** was subsequently employed in intramolecular HA of several aminoalkenes as depicted in Fig. 4 and exhibits very promising and unique reactivity [18].

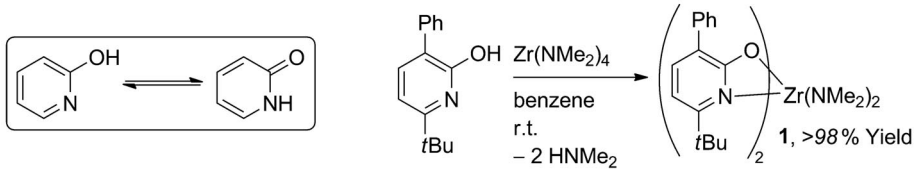


Fig. 3 2-Hydroxypyridines as cyclic amide surrogates and the synthesis of crystalline bis(pyridonate) Zr(IV) bis amido complex **1** by protonolysis.

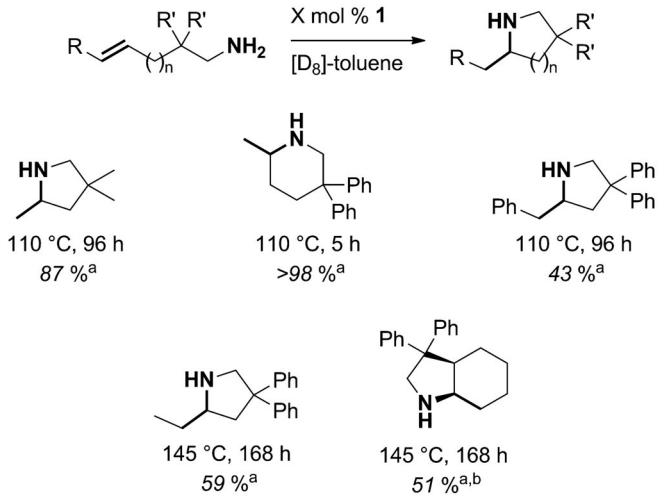


Fig. 4 Hydroamination of terminal and internal aminoalkenes using **1** ([a]Yield determined by NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard; [b]Isolated yield following derivitization with TsCl).

Terminal aminoalkenes are cyclized to give the corresponding substituted pyrrolidines or piperidines. Moreover, challenging 1,2-disubstituted aminoalkenes are converted using higher reaction temperatures and longer reaction times to give the corresponding pyrrolidine heterocycles. Most remarkable, the octahydroindole core can be accessed by using **1** to give the *cis*-fused bicylic product selectively.

In analogy to earlier work on group 4 amidate amido complexes, such reactivity is proposed to occur by a [2 + 2] cycloaddition mechanism involving a reactive terminal Zr-imido intermediate (Fig. 5) [19]. The monomeric Zr-imido is accessed by protonolysis of the corresponding precatalyst, which subsequently undergoes a [2 + 2] cycloaddition with the C–C unsaturation to yield a metallacycle which extrudes the product upon proton transfer with the substrate and regeneration of the key Zr-imido intermediate.

Further support for such a Zr(IV) imido-dependent [2 + 2] cycloaddition mechanism is based on the observation that the analogous N-methylated aminoalkene substrate (to that depicted in Fig. 5) is unreactive under these reaction conditions. In this case, the requisite terminal Zr(IV) imido intermediate cannot be formed, and, thus, product formation does not occur.

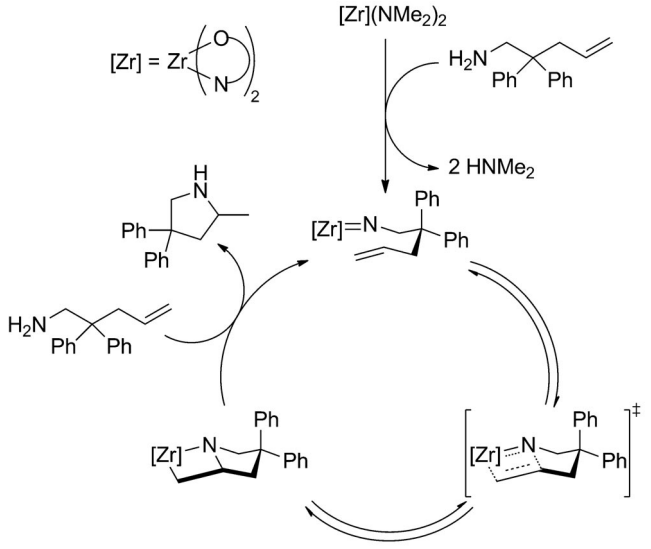


Fig. 5 Proposed mechanism for aminoalkene hydroamination.

To our surprise, we found that substrates that result in sluggish conversion in hydroamination experiments catalyzed by 1, yield a substantial amount of the corresponding α-alkylation by-product (Fig. 6). The formation of 7-membered N-heterocycles by hydroamination is known to be challenging. Here, the cyclohexylamine product is proposed to result from a C–H activation step α to N and a subsequent insertion of the C–C double bond into a reactive Zr–C bond. Such transformations are of particular interest as two adjacent stereocenters, one located α to N, are formed in a single bond-forming process. Furthermore, no N-protecting groups are required in this reaction, and the resultant primary amine can be subjected to further functionalization without protection/deprotection protocols.

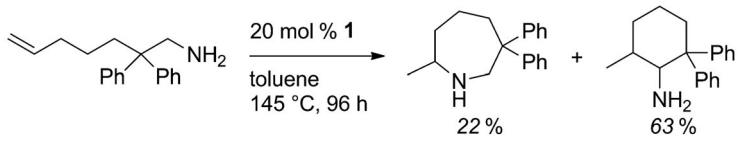


Fig. 6 Hydroamination vs. hydroaminoalkylation using complex **1**.

Such a mechanistic framework involving intermediate metallaaziridines has been proposed for early transition-metal complexes that catalyze the intermolecular α-alkylation of dimethylamine with 1-pentene [20]. Furthermore, Buchwald and co-workers demonstrated that stable, isolable bis(cyclopentadienide) Zr(IV)-aziridine complexes insert a variety of unsaturated reactive molecules, including alkynes and terminal alkenes, into the reactive Zr–C bond to generate 5-membered zirconacycles [21]. This stoichiometric method has been applied in the synthesis of allylic amines from trimethylsilyl-substituted secondary amines and alkynes. Moreover, Barluenga and co-workers have used this approach to access a number of 1,4-diamino-cyclohexanes and other N-containing products from secondary alkene- and alkyneamines via Zr(IV)-aziridine intermediates that were prepared in situ using stoichiometric amounts of *n*-BuLi and $Cp_2Zr(Me)Cl$ [22]. This stoichiometric C–C bond-forming strategy α to N has been elegantly extended by Norton and others to access a broad range of N-containing small molecules [23].

In the case of the competing hydroaminoalkylation reaction shown in Fig. 6, the mechanism depicted in Fig. 7 is proposed, where a monomeric Zr(IV) imido complex serves as a common intermediate in both the hydroamination and hydroaminoalkylation pathways. The monomeric imido intermediate and a corresponding bimetallic bridging imido are proposed to be in a competitive equilibrium, as is known for group 4 imido complexes [24]. We suggest that the bimetallic imido can undergo C–H activation α to N to give a bridging metallaaziridine intermediate that results in product formation via insertion of the olefin moiety into the reactive Zr–C bond.

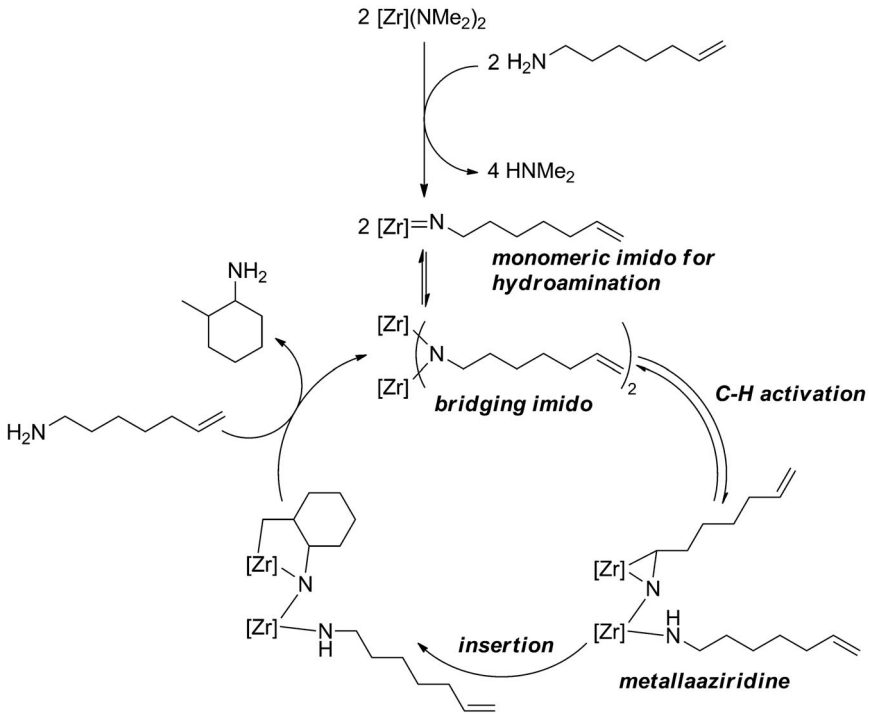
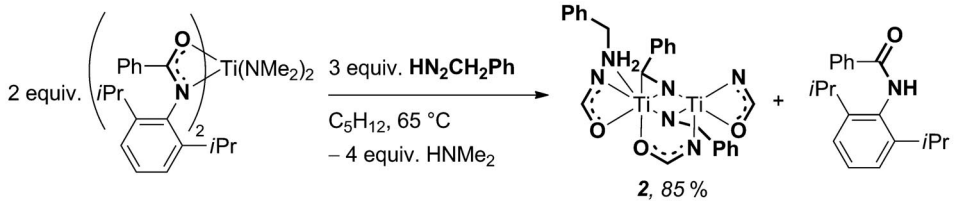


Fig. 7 Proposed mechanism for the Zr-catalyzed intramolecular hydroaminoalkylation of primary aminoalkenes.

In agreement with the proposed occurrence of key imido intermediates, no product formation (either hydroamination or hydroaminoalkylation) is observed for N-methylated substrates when identical reaction conditions are used. Furthermore, varying precatalyst concentration can alter the outcome of the reaction: higher catalyst concentration shifted the product ratio favoring the hydroaminoalkylation product over the hydroamination product, suggesting the preferred formation of the bimetallic intermediate at high metal concentration. Most convincingly, the structural element of a catalytically competent bimetallic bridging imido metallaaziridine could be obtained by reacting a known bis(amidate) bis(amido) Ti(IV) complex with 3 equiv of benzylamine to give **2** and loss of one of the amidate ligands and 4 equiv of dimethylamine (Fig. 8). Interestingly, the shortened C–N bond length of 1.368(4) Å found in the bridging titanaaziridine moiety suggests substantial double bond character, consistent with an η^2-imine complex. This is the first example of a bridging metallaaziridine complex reported to date. It is proposed that the bridging amidate ligand plays an important role in its formation due to the known propensity for this ligand class to yield dinuclear complexes [25].



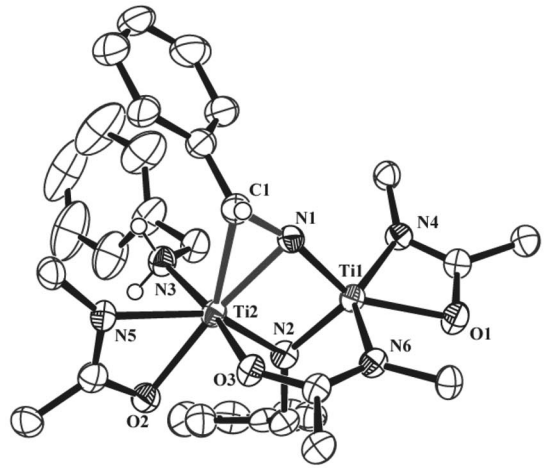


Fig. 8 Synthesis of bimetallic Ti complex **2** with unusual bridging amidate, imido, and titanaaziridine structural elements and an ORTEP representation of its solid-state molecular structure. Selected bond distances (Å) and angles (°): Ti1–N1 1.810(2), Ti2–N1 2.046(2), Ti1–N2 1.843(2), Ti2–N2 1.986(2), Ti2–N3 2.214(2), N1–C1 1.368(4), Ti2–C1 2.219(3), Ti1–N1–Ti2 89.91(9), Ti1–N2–Ti2 90.90(9), N1–Ti1–N2 93.37(10), N1–Ti2–N2 82.46(9).

Unfortunately, **2** displays only limited substrate scope for the hydroaminoalkylation of primary aminoalkenes (Fig. 9) with poor diastereoselectivity.

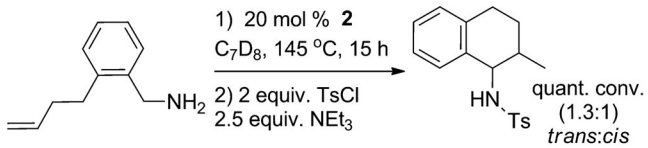


Fig. 9 Hydroaminoalkylation catalyzed by complex **2**.

On the other hand, **1**, with the larger, more sterically accessible Zr metal center, is capable of cyclizing a variety of compounds whose products are depicted in Fig. 10. Moderate *cis*/*trans* ratios are generally observed with the exception of the product derived from the α-phenyl substituted alkeneamine where a high degree of *cis*-selectivity was achieved. Interestingly, this approach is capable of delivering compounds with fully substituted carbon centers α to N, which are challenging to access by other synthetic routes.

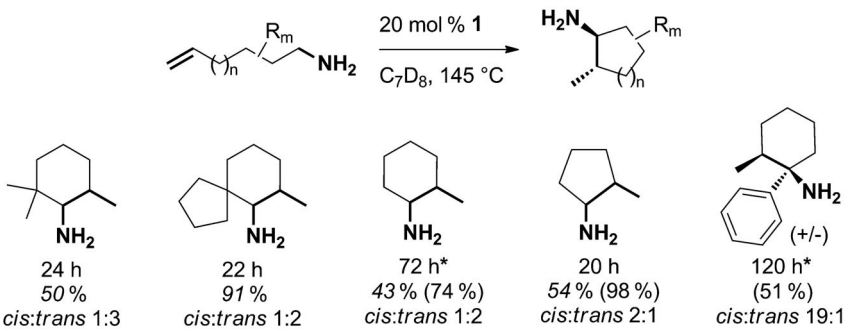


Fig. 10 Hydroaminoalkylation of aminoalkenes. Isolated yields, yields in brackets correspond to NMR yields. *40 mol % catalyst, 155 °C.

A similar mode of reactivity has been previously reported for $Ti(NMe_2)_4$ as a catalyst precursor [26] and is observed for high-oxidation-state group 5 based catalysts as well. Notably, a closely related strategy was recently used to catalytically α-alkylate secondary alkyl amines using Ti-based catalysts or simple homoleptic amido complexes and mixed amido chloro complexes of Ta [27–30]. For all of these transformations, the formation of metallaaziridines as key intermediates prior to the C–C bond-forming step has been suggested. Figure 11 compares the performance of several group 4 and 5 amido complexes, for the hydroaminoalkylation reaction of *N*-methylaniline and 1-octene to give the branched product. The proficiency of $Ta(NMe_2)_5$ for this process shows much promise.

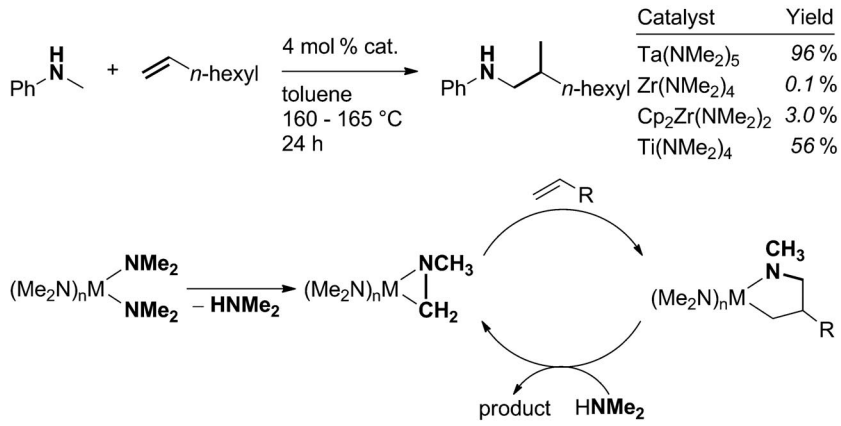


Fig. 11 Intermolecular hydroaminoalkylation using group 4 and 5 amido complexes (top) with a general mechanism for this C–C bond-forming reaction (bottom) [27,29,30].

In group 4 chemistry, we have shown that amidate ligand sets support metallaaziridine species. Considering the desirable transformations promoted by Ta, we sought to prepare the first examples of amidate supported group 5 complexes. We speculated that the same successful protonolysis route could be applied, using the commercially available $Ta(NMe_2)_5$, to efficiently synthesize a family of Ta-amidate amido complexes for application in the hydroaminoalkylation of secondary amines. We were pleased to find this fundamental approach to be viable in the synthesis of a range of mono(amidate) tetrakis(dimethylamido) Ta complexes. In Fig. 12, some ORTEP representations of these highly crystalline materials are depicted.

R^1 = *t*Bu, R^2 = (2,6-diisopropyl)phenyl: **3**
R^1 = Ph, R^2 = (2,6-diisopropyl)phenyl: **4**
R^1 = $Me(F_3C)_2C$, R^2 = (2,6-dimethyl)phenyl: **5**

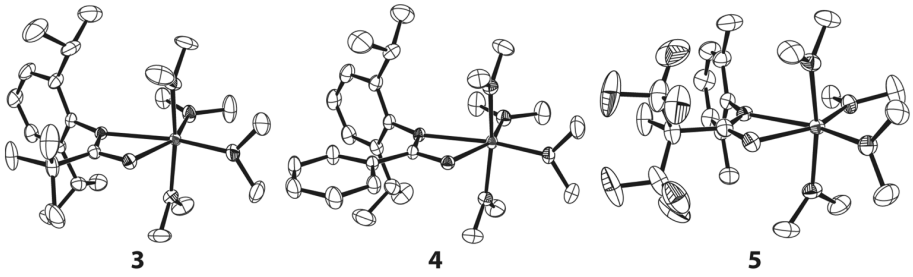
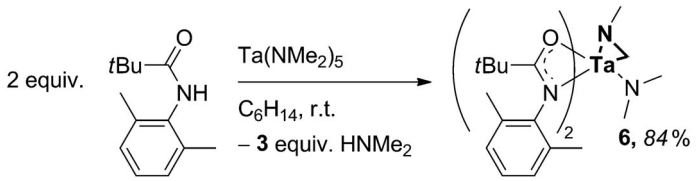


Fig. 12 Synthesis of mono(amidate) Ta complexes and representative compounds.

Due to the success of bis(amidate) complexes of group 4 metals, bis(amidate) Ta(V) complexes were identified as desirable target compounds. Surprisingly, when $Ta(NMe_2)_5$ is combined with 2 equiv of (2,6-dimethylphenyl)pivalamide clean formation of the bis(amidate) amido tantallaaziridine **6** is observed in 84 % yield (Fig. 13).



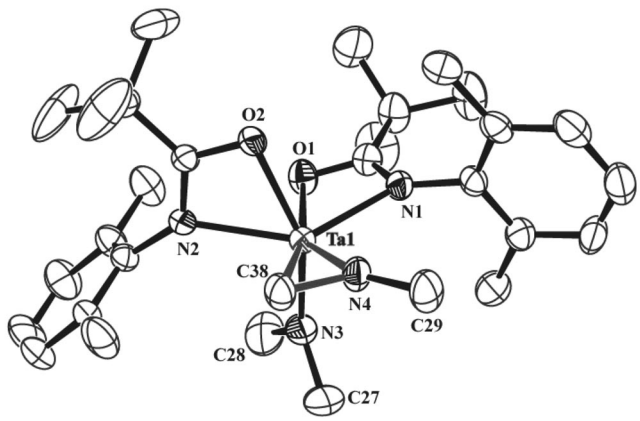


Fig. 13 Synthesis of tantallaaziridine **6** and an ORTEP representation of its solid-state molecular structure. Selected bond distances (Å) and angles (°): Ta1–N1 2.179(4), Ta1–O1 2.214(4), Ta1–N4 1.921(4), Ta1–C38 2.178(5), N4–C38 1.424(6), N4–C29 1.451(7), Ta1–N3 1.970(5), N3–C28 1.459(9), N4–Ta1–C38 40.0(2), C38–N4–Ta1 79.7(3), C29–N4–Ta1 155.8(4).

The C_1 symmetric **6** features diagnostic signals for the diastereotopic protons at δ 2.34 and 2.49 ppm with a geminal coupling constant of $^2J_{H,H}$ = 3.5 Hz. The observed C–N bond length of 1.424(6) Å in the tantallaaziridine structural element in **6** is typical for C–N single bonds supporting the assignment of the formal oxidation state of Ta to remain +5. The spontaneous formation of compound **6** is intriguing since such stable complexes formed by spontaneous, low-temperature β-hydrogen abstraction have been scarcely reported [31]. This highlights the propensity of the amidate spectator ligand to facilitate the formation of highly electrophilic metal centres suitable for the activation of the C–H bond α to N in amido ligands.

Most importantly, complex **6** is found to be a competent catalyst for the hydroaminoalkylation of *N*-methylaniline and 1-octene at 130 °C as shown in Fig. 14. However, prolonged heating is required to drive the reaction to completion.

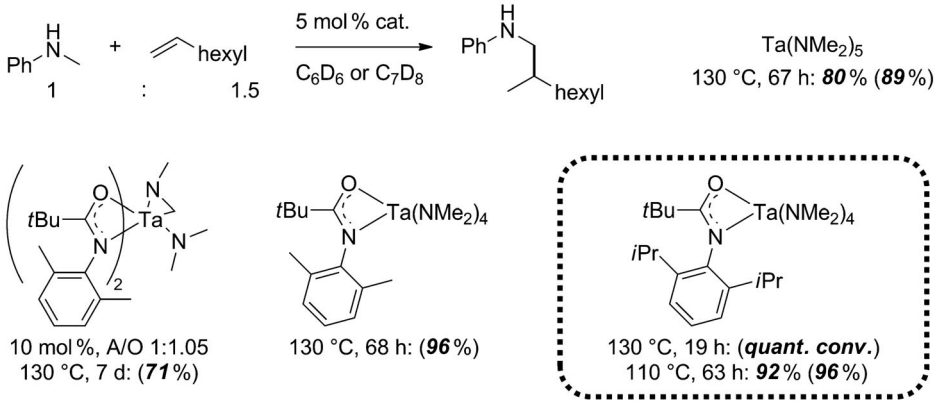


Fig. 14 Precatalyst screening.

In contrast, mono(amidate) tetrakis(dimethylamido) Ta(V) complexes proved to be substantially better catalysts, and importantly (2,6-diisopropylphenyl)pivalamidate tetrakis(dimethylamido) Ta(V) (**3**) cleanly yields the hydroaminoalkylation product at 130 °C in an overnight reaction. This superior reactivity is attributed to enhanced steric bulk to facilitate tantallaaziridine formation, but not so much steric bulk that olefin insertion into the Ta–C bond of the tantallaaziridine is inhibited.

Having identified a promising catalyst for hydroaminoalkylation, several other substrate combinations were successfully explored in this C–C bond-forming reaction. In Fig. 15, the synthesis of functionalized amines catalyzed by mono(amidate) Ta precatalyst **3** are depicted. Apart from activated alkenes such as norbornene, it is possible to subject cyclooctene as an internal olefin to the alkylation of *N*-methylaniline under somewhat harsher conditions. Moreover, employing *tert*-butyldimethylsilane (TBDMS)-protected alcohols and *para*-methoxy-*N*-methylaniline reveals some degree of functional group tolerance, suggesting promise for future application in synthesis.

Having established the fundamental reactivity of Ta(amidate) complexes in the hydroaminoalkylation of several olefin and amine combinations, we were intrigued by the possibility of conducting an asymmetric version of this reaction by using a readily accessible tethered, axially chiral bis(amidate) ligand motif. We speculated, due to the *cis*-orientation of the O-donors in **6**, that enantiopure 2,2'-dicarboxybiphenyl derived bis(amidates) would be a promising starting point for our study. Consequently, starting from the known enantiopure diacid [32], depicted in Fig. 15, several Ta complexes were synthesized. After conversion of the diacid to the corresponding diacidchloride and subsequent reaction with an excess of the aniline derivative, the diamide was isolated and thoroughly dried prior to reaction with $Ta(NMe_2)_5$. Instead of adopting an anticipated tetradentate coordination mode, a bidentate

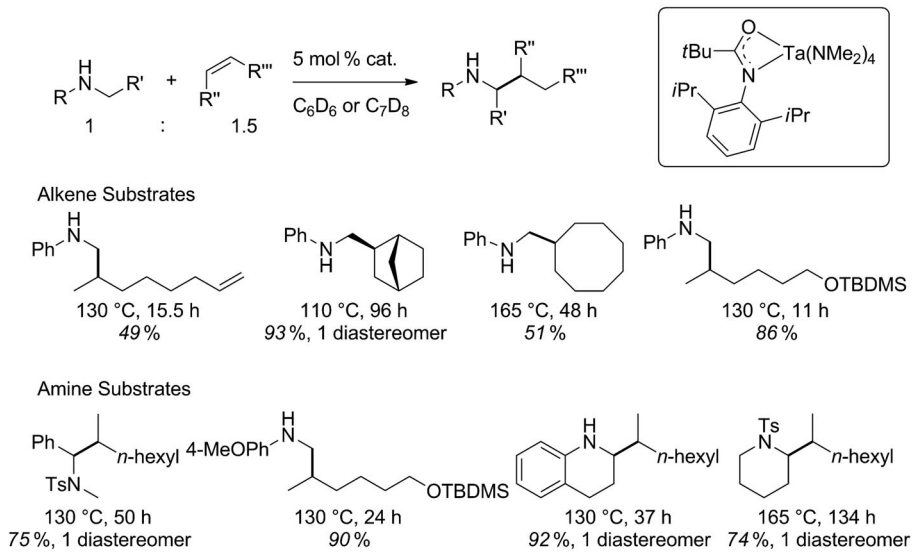


Fig. 15 Scope of (2,6-diisopropylphenyl)pivalamidate tetrakis(dimethylamido) Ta(V) in hydroaminoalkylation.

O,O-coordinated aryliminoalkoxide-like structural motif (R = *i*Pr) with CN bond lengths in the typical range of double bonds (1.277(4) Å and 1.268(4) Å) was observed in the solid state. This results in an overall trigonal bipyramidal coordination geometry about Ta. In solution phase, a species consistent with a C_2 symmetric molecule could be observed by NMR spectroscopy with carbonyl resonances typical for previously characterized oxygen coordinated amidate complexes [33]. This supports a κ*O*, κ*O*' *cisoid* chelating motif of the axially chiral biphenyl bisamidate ligand in the solution phase, as well as the solid state.

This axially chiral Ta(V) complex **7** was found to be a competent catalyst for the asymmetric hydroaminoalkylation reaction, as depicted in Fig. 16. This complex has a somewhat diminished catalytic activity compared to the mono(amidate) congener, which may be attributed to the increased steric bulk of this tethered chelating ligand system.

In these first examples of an enantioselective version of this reaction, norbornene proved to be the olefin of choice for asymmetric hydroaminoalkylation, furnishing to selectivities of up to 61 % ee and exclusive formation of the *exo* diastereomer. *para*-Methoxy as an electron-releasing substituent on the aromatic system allows access to the corresponding enantioenriched primary amine after deprotection under oxidative conditions [34]. These preliminary results showing modest ee's, combined with our intimate understanding of the coordination sphere of the Ta complexes point the way for the development of new catalysts with improved efficiencies and selectivities (Fig. 17).

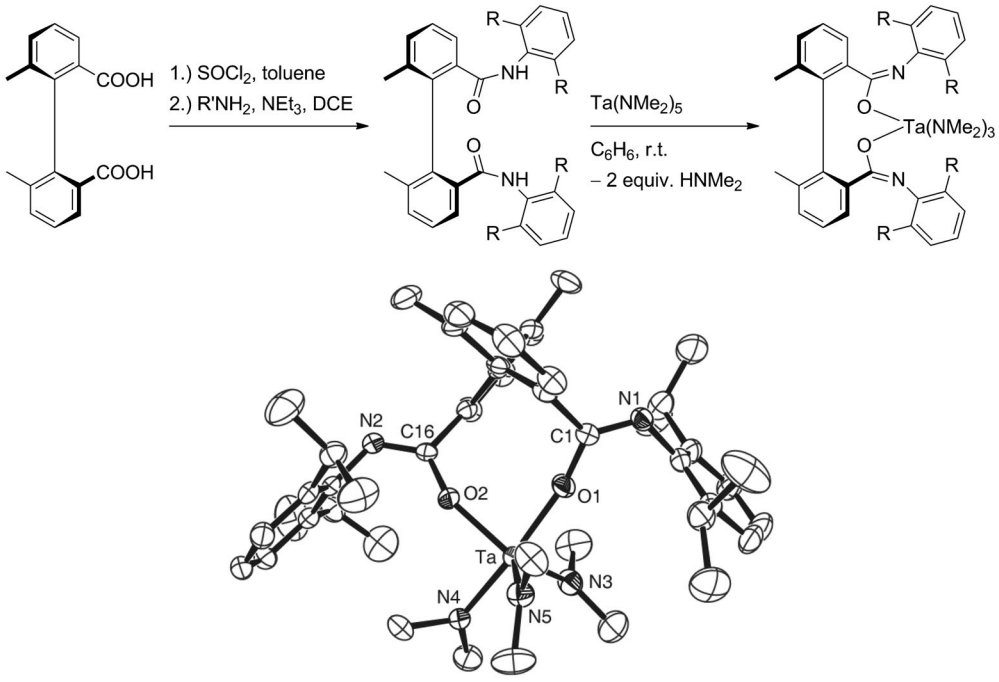


Fig. 16 Synthesis and an ORTEP representation (R = *i*Pr, from a racemic sample) of an axially chiral bis(amidate) Ta(V) complex.

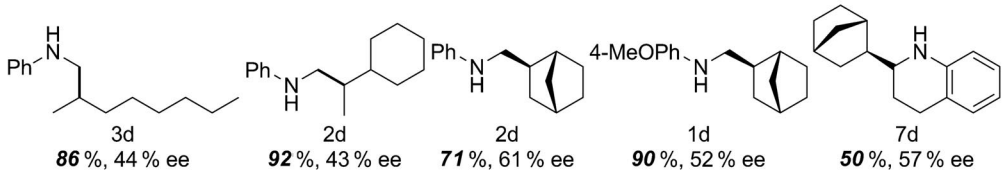


Fig. 17 Asymmetric hydroaminoalkylation utilizing the axially chiral bis(amidate) Ta(V) precatalyst **7**.

CONCLUSIONS

In summary, catalytic hydroamination and hydroaminoalkylation are important and 100 % atom-economic transformations for the catalytic synthesis of amines. These complementary reaction manifolds can be achieved using easily prepared and readily modified amidate complexes of group 4 and 5 metals. The modularity and the convenience of the synthesis of the amide proligands make them an ideal scaffold to explore the reactive nature of these electrophilic metal centers. The results presented here show that they promote unprecedented catalytic reactivity in both hydroamination and hydroaminoalkylation, respectively. Moreover, the first example of asymmetric catalytic secondary amine synthesis via hydroaminoalkylation has been demonstrated. The hydroaminoalkylation reaction provides an alternative synthetic strategy for the synthesis of α-alkylated amines.

SUPPLEMENTARY INFORMATION

Experimental details for the synthesis of new compounds can be found in the supplementary information together with characterization data. Supplementary Information is available online (doi:10.1351/PAC-CON-09-11-27).

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