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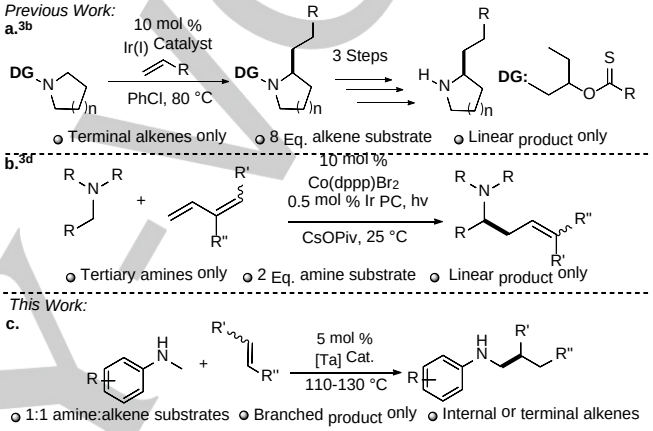
Catalytic and Atom Economic Csp3 – Csp3 Bond Formation α-to Nitrogen. Alkyl Tantalum Ureates for Hydroaminoalkylation

Rebecca C. DiPucchio,[‡] Sorin-Claudiu Roşca,[‡] and Laurel. L. Schafer*

Abstract: Atom-economic and regioselective Csp^3-Csp^3 bond formation has been achieved by rapid C-H alkylation of unprotected secondary arylamines with unactivated alkenes. The combination of $Ta(CH_2SiMe_3)_3Cl_2$, and a ureate *N,O*-chelating ligand salt gives an in situ prepared catalytic system that can realize high yields of β-alkylated aniline derivatives using either terminal or internal alkene substrates. These new catalyst systems realize C-H alkylation in as little as one hour and for the first time a 1:1 stoichiometry of alkene and amine substrates results in high yielding syntheses of isolated amine products by simple filtration and concentration.

The catalytic functionalization of alkenes with amines represents a sustainable and efficient method for generating small molecules relevant to the pharmaceutical, agrochemical and fine chemical industries. Catalytic alkene functionalization is attractive as valuable building blocks can be prepared with 100% atom efficiency from commercially available starting materials.[1] Furthermore, the direct C–H alkylation of amines by hydroaminoalkylation,[2] allows for the synthesis of α (Scheme 1, a & b)[2f,3] and/or β-alkylated amines (Scheme 1, c).[2a-e] Notably, early transition metal catalysts, like tantalum, require no added protecting/directing groups or photoredox catalysts/co-catalysts.[2c] Thus, early transition metal hydroaminoalkylation complements late transition metal variants and provides an alternative disconnection to C-H cross-coupling protocols for the synthesis of Csp^3-Csp^3 bonds α[3, 4] to amines. However, limitations due to modest activity decomposition remain.

Early transition metal complexes using Sc,[5] Ti,[6] Zr,[7], and Ta [8] have been under development for intermolecular hydroaminoalkylation catalysis since the early 1980's.[9] Recent advances have expanded reactivity to include tertiary[5] or secondary amines and terminal alkene[6,7,8] or diene[6i,l] or internal alkenes [8l] to give α and/or β-alkylated products. Our group has shown that *N,O*-chelated Ta amido complexes offer a tunable framework for developing enhanced catalysis with improved substrate scope.[2c] However, the reactive amido ligands result in complicating equilibria and byproduct formation that reduces TOFs (<4/h) and complicates product isolation.[8o,p] Alternatively we have shown that the organometallic precursor, $TaMe_3Cl_2$,[8k] when combined with the electron withdrawing, *N,O*-chelating phosphoramidate ligand, can yield room temperature reactivity.[8h] Unfortunately, such Ta methyl complexes readily decompose resulting in low TONs (<20). Finally, all these systems require excess alkene substrate and isolation of products by column chromatography.



Scheme 1. Hydroaminoalkylation for catalytic Csp^3-Csp^3 bond formation α-to nitrogen using late transition metals catalysts with directing groups (**a**) and photocatalysts (PC; **b**) *or* early transition metals catalysts (**c**).

Ureate ligands are an electron withdrawing *N,O*-chelating ligand that has been used to generate early transition metal hydrofunctionalization catalysts. [10] For example, a zirconium ureate complex, with its very electrophilic metal center, has remarkable C-N bond forming reactivity in hydroamination.[10,11] To date, ureate *N,O*-chelating ligands have not been explored for hydroaminoalkylation. Furthermore, known Ta organometallic reagents that are less susceptible to decomposition than $TaMe_3Cl_2$, such as $Ta(CH_2SiMe_3)_3Cl_2$ [12] and $Ta(CH_2CMe_3)_3Cl_2$,[13] have not been evaluated in hydroaminoalkylation. Here, we show that *in situ* prepared catalyst systems assembled from tunable ureate salts and Ta alkyl reagents can realize improved TOFs (up to 17/h) and TONs (up to 100) in hydroaminoalkylation. The easily varied ureate auxiliary ligand can be modified to optimize reactivity. Finally, this catalyst system requires only a 1:1 stoichiometry of amine:alkene reagents to give uniquely the β-alkylated amine product that can be isolated using a simple filtration protocol.

First, known Ta organometallic reagents[8k,12,13] and established Ta amido reagents[8a,b] were screened for reactivity using a standard benchmark reaction between *N*-methylaniline and 1-octene (Table 1). $Ta(CH_2SiMe_3)_3Cl_2$ provides promising TOFs within the first hour of reaction. In contrast $Ta(CH_2CMe_3)_3Cl_2$ showed no reaction within 1 h, but over 24 h, 21% conversion was observed. The previously explored $TaMe_3Cl_2$ showed good reactivity within the first hour, but this promising reactivity degraded within 5 h. Importantly, $[Ta(NMe_2)_3Cl_2]_2$,[14] showed no reaction at this lower temperature

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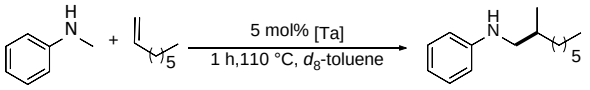
and time. Thus, $Ta(CH_2SiMe_3)_3Cl_2$ was chosen for further catalytic experiments.

Table 1. Screening of tantalum based precursors



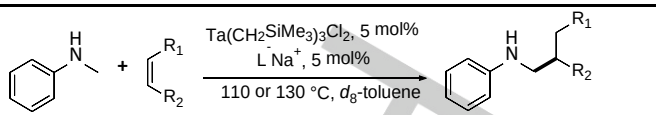
$Ta(CH_2SiMe_3)_3Cl_2$	$Ta(CH_2CMe_3)_3Cl_2$	$TaMe_3Cl_2$	$[Ta(NMe_2)_3Cl_2]_2$
TOF 8/h	1 h, n.r[b]	TOF 6/h	1 h, n.r.[b]

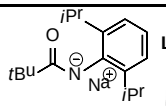
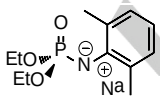
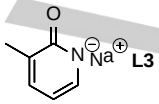
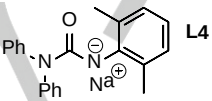
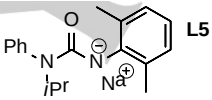
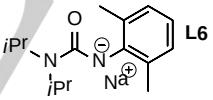
[a] Reaction conditions: amine (0.5 mmol), 1-octene (0.5 mmol), Ta precursor (0.025 mmol), d_8-toluene (0.5 g). TOF determined by ^{1}H NMR spectroscopy. [b] n.r.: no reaction.

Next, ligand effects on hydroaminoalkylation reactivity were investigated using precatalysts generated *in situ* (Table 2).[15] Note that the present state-of-the-art reaction conditions use an isolated Ta precatalyst at 145 °C.[8l] This *in situ* catalyst preparation protocol featured ligands previously used as isolated precatalysts; amidate (**L1**),[8c] phosphoramidate (**L2**),[8h] and pyridonate (**L3**).[8l] For the first time, a variety of ureate (**L4–6**) ligand salts were also explored.

Catalytic screening of *in situ* prepared complexes with amidate **L1** and phosphoramidate **L2** resulted in no conversion, regardless of the alkene substrate. In contrast, using the less sterically encumbered pyridonate ligand salt **L3** proved to be more successful, as 31% and 33% conversions were observed for both terminal and internal alkenes. Next ureate salts **L4**–**6** were tested. These ligands were expected to generate a more electrophilic metal center to give improved reactivity. Gratifyingly, the *in situ* catalyst system with **L4** was excellent, affording 83% conversion in only 1 h for the reaction between 1-octene and *N*-methylaniline; a TOF of more than 16/h. However, when the more challenging cyclohexene substrate was evaluated, only a modest 19% conversion was observed after 20 h. Remarkably, the mixed aryl/alkyl substituted ureate ligand **L5**, resulted in a reversed trend; this system realized higher conversion of the internal alkene substrate (20 h, 83%) but was less effective for the terminal alkene substrate (1 h, 12%). These results are surprising considering that the only change is one N-Ph group of **L4** to an N-^{i}Pr moiety in **L5**. With this empirical observation in hand, we thought to exchange the remaining Ph group of **L5** with an ^{i}Pr group (**L6**). Unfortunately, this change in ligand design did not improve the catalytic system, as only poor conversions were obtained for both alkenes. We propose that the known hemilability of *N,O*-chelating ligands,[16] coupled with the variable coordination modes of ureate ligands would result in a flexible coordination environment about the reactive metal center, thereby promoting reactivity.

Table 2. Study of ligand effects on hydroaminoalkylation[a]



Ligand salt		
 **L1**	1 h, n.r.[b]	20 h, n.r.
 **L2**	1 h, n.r.	20 h, n.r.
 **L3**	1 h, 31%	20 h, 33%
 **L4**	1 h, 83%	20 h, 19%
 **L5**	1 h, 12%	20 h, 83%
 **L6**	1 h, 5%	20 h, 6%

[a] Reaction conditions: amine (0.5 mmol), alkene (0.5 mmol), $Ta(CH_2SiMe_3)_3Cl_2$ (0.025 mmol), ligand salt (0.025 mmol), d_8-toluene (0.5 g). Conversion determined by ^{1}H NMR spectroscopy. All reactions with 1-octene were performed at 110 °C, while those with cyclohexene were performed at 130 °C. [b] n.r. = no reactivity

Next we sought to explore the amine substrate scope of catalysts prepared with **L4** for terminal alkenes (1-octene) and **L5** for internal alkenes (cyclooctene; Table 3). Reaction times were adapted to favor full conversion of substrate and facilitate product isolation *i.e.* 2 h for 1-octene and 6 h for cyclooctene. The desired products were isolated by filtration in >95% purity,[17] and typically column chromatography could be avoided (eg. Entry 1). Furthermore, only 1 mol% of catalyst gave complete conversion (TON = 100), as measured over 30 h by ^{1}H NMR spectroscopy. In Entry 2, cyclooctene was fully converted within 6 h, offering an excellent isolated yield of product (83%). Consistent with previous work, *para*-substituted *N*-methylaniline derivatives (Entries 3-12) are well tolerated, including the *para*-methoxyphenyl substituent

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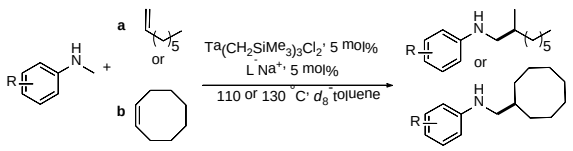
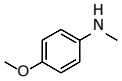
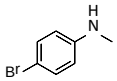
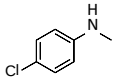
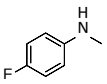
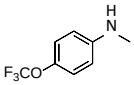
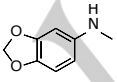
(Entries 3 & 4) can be oxidatively cleaved to access primary amine products. [18] Halide substituents on the aromatic ring (Entries 5 - 10) are completely compatible with this d^0 metal that does not engage in oxidative addition/reductive elimination chemistry. Such aryl halides can then be used in further cross-coupling reactions.[8k] These Lewis acidic tantalum catalysts are compatible with the pharmaceutically relevant trifluoromethoxy groups (Entries 11 & 12) and catechol (Entry 13). As shown, the aniline derivatives are all compatible with both **L4** and **L5**. However, more challenging dialkyl substituted amines do not react.

Table 3. Substrate scope in amine[a]



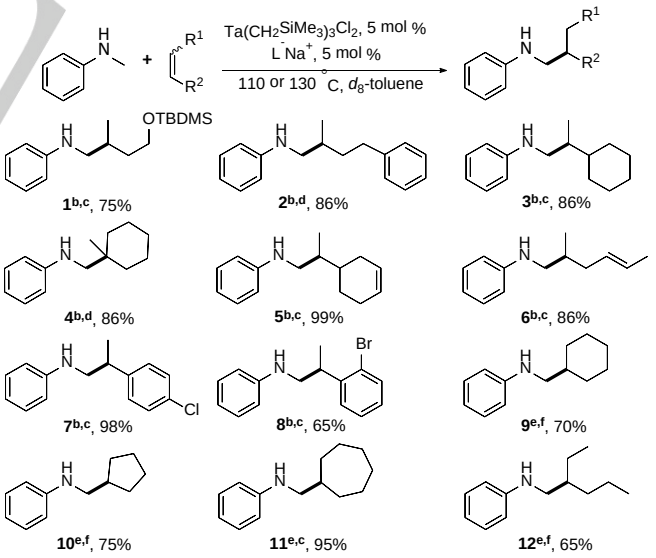
Entry	Amine	Alkene	Isolated Yield (%)
1		a	88
2		b	83
3		a	77
4		b	70
5		a	86
6		b	95
7		a	90
8		b	93
9		a	85
10		b	88
11		a	92
12		b	85
13		a	85

[a] Reaction conditions: amine (0.5 mmol), alkene (0.5 mmol), $Ta(CH_2SiMe_3)_3Cl_2$ (0.025 mmol), ligand salt (0.025 mmol), d_8-toluene (0.5 g). **L4** was used for all terminal alkene substrates at 110 °C over 2 h and **L5** was used for internal alkene substrates at 130 °C over 6 h.

We next switched our attention to exploring the alkene substrate scope with the aforementioned systems; using **L4** for terminal alkenes and **L5** for internal alkenes (Chart 1). [19] Gratifyingly, alkenes containing silyl protected alcohols are good substrates, giving product in 75% yield in only 2 h (**1**). Such aminosilylether products are valuable precursors to β-alkylated heterocycles.[8j,q] Compounds **2** and **3** show that aryl or alkyl groups can be incorporated into the alkene substrates. A *gem*-disubstituted alkene can be used to install a β-quaternary center in high yield (**4**). Products **5** and **6**, prepared from dienes, illustrate the outstanding chemoselectivity of the *in situ* catalyst system with **L4**; only the terminal alkene undergoes hydroaminoalkylation, leaving the internal alkene available for further functionalization. However, when **L5** is used, a mixture of products results from unselective hydroaminoalkylation. Halide substituted styrene derivatives are also compatible with this d^0 metal system (**7**), including an example with the halide in the sterically hindered *ortho*–position (**8**). This result contrasts with the observation that sterically demanding 2-methylstyrene does not react under these conditions. Notably, **8** is a known intermediate *en route* to the β-methylated indoline product obtained after subsequent Buchwald-Hartwig coupling.[8k]

Having obtained such promising results with terminal alkenes, we next investigated the substrate scope with more challenging internal alkenes. Tables 2, 3 and **9** - **11**, show that cyclic alkenes are all viable substrates for hydroaminoalkylation. Due to ring-strain, cycloheptene is the most reactive cyclic alkene, requiring only 2 h to reach full conversion. Linear internal alkenes have reduced reactivity. The reaction with c*is*-3-hexene (**12**) takes 20 h to reach 77% conversion (65% isolated yield). For comparison, the only other reported catalyst for the hydroaminoalkylation of internal alkenes requires 44 h at 145 °C to obtain 69% yield of **12**.[8l] The stereochemistry of the internal alkene affects reactivity, as *trans*-3-hexene results in only 15% conversion.

Chart 1. Substrate scope in alkene[a]



[a] Reaction conditions: amine (0.5 mmol), alkene (0.5 mmol), $Ta(CH_2SiMe_3)_3Cl_2$ (0.025 mmol), ligand salt (0.025 mmol), d_8-toluene (0.5 g). [b] Reaction was run using ligand **L4** at 110 °C. [c] 2 h reaction time. [d] 3 h reaction time. [e] Reaction was run using ligand L5 at 130 °C. [f] from *cis*-3-hexene, 20 h reaction time.

In summary, modified ureate auxiliary ligands in combination with $Ta(CH_2SiMe_3)_3Cl_2$ have been shown to deliver superior TOFs and TONs for the atom- and step-economic hydroaminoalkylation

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reaction. By leveraging the variable ureate framework excellent activity with either terminal or challenging internal alkenes has been realized. This approach is operationally simple in that no amine protecting groups, directing groups or additives are required and products can be isolated by filtration. Furthermore, this new family of easily prepared catalysts is the only class that uses a 1:1 combination of alkene and amine substrates. These new systems address acknowledged problems in catalyst activity. On-going work focuses on mechanistic investigations to understand and optimize ligand substituent effects. Future work aims to enhance substrate scope and selectively modify regio- and stereoselectivity in hydroaminoalkylation.

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Keywords: amines • C-H activation • hydroaminoalkylation • tantalum alkyls • ureates

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