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# 2-Aminopyridinate Titanium Complexes for the Catalytic Hydroamination of Primary Aminoalkenes

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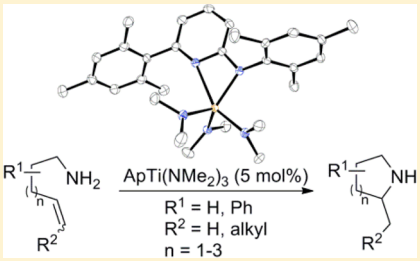
Supporting Information

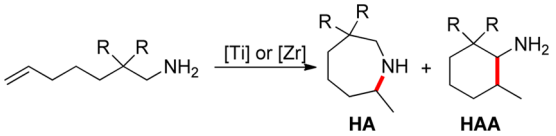
**ABSTRACT:** A series of mono(2-aminopyridinato)tris(dimethylamido) titanium complexes, ApTi($NMe_2$)$_3$ (where Ap = 2-aminopyridinato), have been prepared via protonolysis, and their reactivity for the hydroamination of primary aminoalkenes has been explored. The Ti complex incorporating *N*,6-dimesityl-2-aminopyridinate as the supporting ancillary ligand has been shown to yield a catalyst suitable for room-temperature intramolecular hydroamination reactions to give *gem*-disubstituted five- and six-membered-ring products. The comparison of ApTi($NMe_2$)$_3$ with other group 4 catalysts shows that controlling the steric environment at the metal center is the critical determining factor for hydroamination reactivity. The screening of known challenging primary aminoalkene substrates with the most reactive ApTi($NMe_2$)$_3$ shows good breadth of reactivity for the reaction. This complex is not able to cyclize secondary aminoalkene substrates, suggesting this reaction proceeds via an intermediate imido [2+2] cycloaddition pathway. An Ap-supported Ti imido complex, which also exhibits hydroamination activity, has been prepared and fully characterized from ApTi($NMe_2$)$_3$ and 2,6-dimethylaniline.




## INTRODUCTION

Nitrogen-containing molecules are ubiquitous in biologically active compounds. As such, efficient synthetic routes to access small-molecule amine building blocks are highly desired for agrochemical and pharmaceutical applications. Alkene hydroamination,[1,2] the addition of an N−H bond across a C═C bond, provides an atom-economical route to higher substituted amines via the formation of a new C−N bond. Group 4 metals are particularly attractive for this transformation because of their synthetic applicability, relatively low cost, and low toxicity. After the initial reports of group 4-mediated hydroamination in the early 1990s,[3−5] the first breakthrough in alkene hydroamination was realized about a decade later: cationic Zr and Ti systems[6,7] and neutral complexes such as the commercially available Ti($NMe_2$)$_4$[8] were found to cyclize secondary and primary aminoalkenes, respectively. Significant progress has been made since then,[9−48] but a limitation in Ti- and Zr-catalyzed aminoalkene hydroamination (HA) is that they can undergo $\alpha$-C−H bond functionalization adjacent to the amino group, resulting in a new C−C bond and hydroaminoalkylation side products (Scheme 1).[15,49−56] Ti hydroamination catalysts[8−26] display limited substrate scope, sluggish reactivity, and unwanted byproduct formation during cyclohydroamination of alkenes.[15,50] To date, the most broadly useful group 4 alkene hydroamination catalysts have been reported to use Zr metal centers.[14,18−22,35−38,40,43−46] The smaller ionic radius of Ti and its established utility as a hydroaminoalkylation catalyst may rationalize the paucity of Ti hydroamination catalyst development. Thus, development of a chemoselective catalyst for hydroamination reactivity over hydroaminoalkylation and the development of more selective and active Ti catalyst systems are a challenge within the field.

**Scheme 1. Hydroamination Reactions of Challenging Aminoalkene Substrates with Group 4 Catalysts Can Give Mixtures of Hydroamination (HA) and Hydroaminoalkylation (HAA) Products**




In the pursuit of developing an easily accessed, robust, and effective group 4 hydroamination catalyst, ancillary ligands that incorporate hard donor atoms such as *N*,*O*-chelating (amidate,[42,57] 2-pyridonate,[38] and ureate[35,45,47]) ligands have been shown to be very effective for hydroamination catalysis by our group and others.[18,19,22,31,36] The study of complementary *N*,*N*-chelating (amidinate,[58] guanidinate,[33,59] and 2-aminopyridinate (Ap)[20,60−62]) ligands for group 4 hydroamination catalysis has previously revealed reduced hydroamination reactivity profiles, in comparison with *N*,*O*-chelating motifs. Furthermore, the use of a less sterically demanding Ap Ti complex (*N*-methyl-2-aminopyridinate) has been recently reported by Doye for intermolecular hydroaminoalkylation catalysis.[56] Mixed Zr cyclopentadienyl−guanidinate complexes[33] and both Ti and Zr biphenyl-tethered Ap complexes[20]

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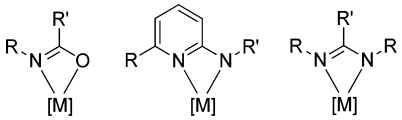
have been tested for unactivated aminoalkene cyclohydroamination, where slow catalysis was observed for both of these Zr systems and no reactivity was observed for the latter Ti system. These *N,N*-chelating ligands remain underexplored and, considering the dramatically different reactivity reported thus far, are an important set of complexes for developing an understanding of hydroamination reactivity trends with group 4 metals.

Considering the asymmetric binding mode and known hemilability of previously reported *N,O*-chelating amidate complexes, the Ap ligands offer similar asymmetry while affording improved opportunities for tailoring the steric bulk about the metal center (Scheme 2).[57,63−67] Furthermore, there

**Scheme 2. Binding Mode of Amidate (Left), Aminopyridinate (Center), and Amidinate (Right) Ligands**[a]



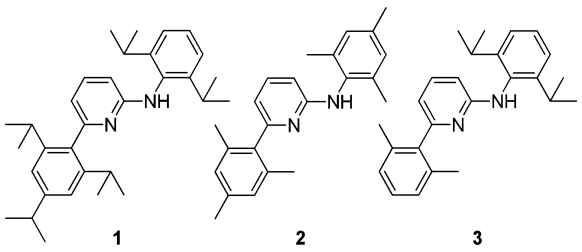

[a][M] = group 4 metal complex; R, R′ = substituent.

is precedent for the preparation of monoligated Ap Ti metal centers,[66,67] while we have been unsuccessful to date in preparing mono(amidate)-ligated group 4 complexes that are resistant to ligand redistribution. Most importantly, there has not been an investigation of such monoligated Ap Ti systems for group 4-catalyzed hydroamination. Titanium Ap complexes[60,61,66−73] have been investigated by several research groups in the past decade, with a focus on olefin polymerization. Two Ti Ap complexes have been examined for hydroamination, both as a bis-ligated systems; however no alkene cyclohydroamination was disclosed.[20,60,61] Currently, there is not an effective or versatile Ti catalyst for alkene cyclohydroamination. Herein, we report the preparation of ApTi($NMe_2$)$_3$ complexes with varying steric bulk, and the finding of a significantly more reactive Ti catalyst with enhanced substrate scope. The observed trends from catalytic investigations reveal the importance of steric tuning to promote enhanced reactivity. We also demonstrate that selective hydroamination over hydroaminoalkylation can be achieved through ligand design.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of ApTi($NMe_2$)$_3$.** The Ap proligands **1**−**3** (Scheme 3) can be synthesized from 2,6-dibromopyridine in two steps according to literature procedures.[74−76] The bulky aryl substituents are installed onto 2,6-dibromopyridine by Ni-catalyzed Kumada coupling

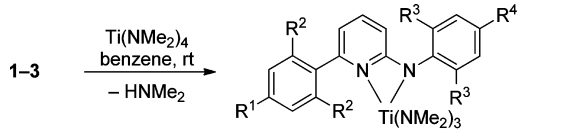
**Scheme 3. Bulky 2-Aminopyridine Proligands**




with aryl Grignard reagents, followed by Pd-catalyzed Buchwald−Hartwig amination with aniline derivatives. The variation of methyl and/or isopropyl substituents on the Ap proligand allows the examination of the influence of the steric environment at the metal center.[77−86]

The direct synthesis of Ti Ap complexes **4**−**6** is easily accomplished using a protonolysis reaction between proligands **1**−**3** and commercially available Ti($NMe_2$)$_4$.[60,61,66−73] The resulting products are isolated in high yields and are easily isolated and purified (Scheme 4). For example, **4** is

**Scheme 4. Synthesis of Mono(2-aminopyridinato)tris(dimethylamido) Titanium Complexes**




$R^1 = R^2 = R^3 = {}^i$Pr, $R^4$ = H; **4** (>98%)
$R^1 = R^2 = R^3 = R^4$ = Me; **5** (95%)
$R^1 = R^4$ = H, $R^2$ = Me, $R^3 = {}^i$Pr; **6** (80%)

quantitatively obtained as an analytically pure, yellow solid after the removal of the reaction solvent under vacuum, without any further purification. In the synthesis of **5** or **6**, trace impurities are present upon completion of the reaction; however purification is easily accomplished by recrystallization from a solution of hexanes at −35 °C to afford yellow crystals of **5** or orange crystals of **6**.

The solid-state molecular structures of **4**−**6** reveal a common $C_1$-symmetric structure with distorted trigonal bipyramidal coordination about the Ti center (Figure 1, Table 1), with N1, N3, and N4 being in the equatorial plane ($\sum$ of the angles in the equatorial plane are 358° (**4**), 355° (**5**), and 354° (**6**)). Taking structure **5** as a representative example, there is a small bite angle [N1−Ti1−N2 58.84(6)°] for the Ap ligand, in agreement with similar, previously reported complexes.[66,67] The binding of this *N,N*-chelating ligand is best described as a monoanionic amido/neutral pyridine bonding motif; the amido N1 at the equatorial site binds to Ti at a much shorter distance [Ti1−N1 2.0548(16) Å] than the pyridine N2 that occupies the axial site [Ti1−N2 2.44478(17) Å]. This Ti1−N2 bond length is unusually long compared to known Ti Ap systems (2.107−2.349 Å),[65] and the presence of three dimethylamido ligands most likely promotes the loose coordination of the pyridine N2 due to the $\pi$-donation and steric bulk of the $NMe_2$ ligands (*vide infra*). The sum of the angles around the dimethylamido N atoms is consistent with trigonal planar $sp^2$-hybridization, and their short bond lengths [1.8929(16)−1.9154(17) Å] confirm the presence of multiple-bond character. The bond lengths and angles of **4** and **6** are also shown in Table 1 for comparison. There are no major discernible differences in Ti−N bond lengths between **4** and **5**. However, the Ti1−N2 bond length of **6** is shorter than both **4** and **5**, which can be attributed to the differing methyl and isopropyl substituents on opposite sides of the Ap ligand. ApTi($NMe_2$)$_3$ complexes are best described as 16 $e^-$ species, with each of the Ap and amido ligands acting as 4 $e^-$ donors to the $Ti^{4+}$ metal center. Most importantly, the different methyl and isopropyl substituents of the ligands vary the steric shielding of the Ti center.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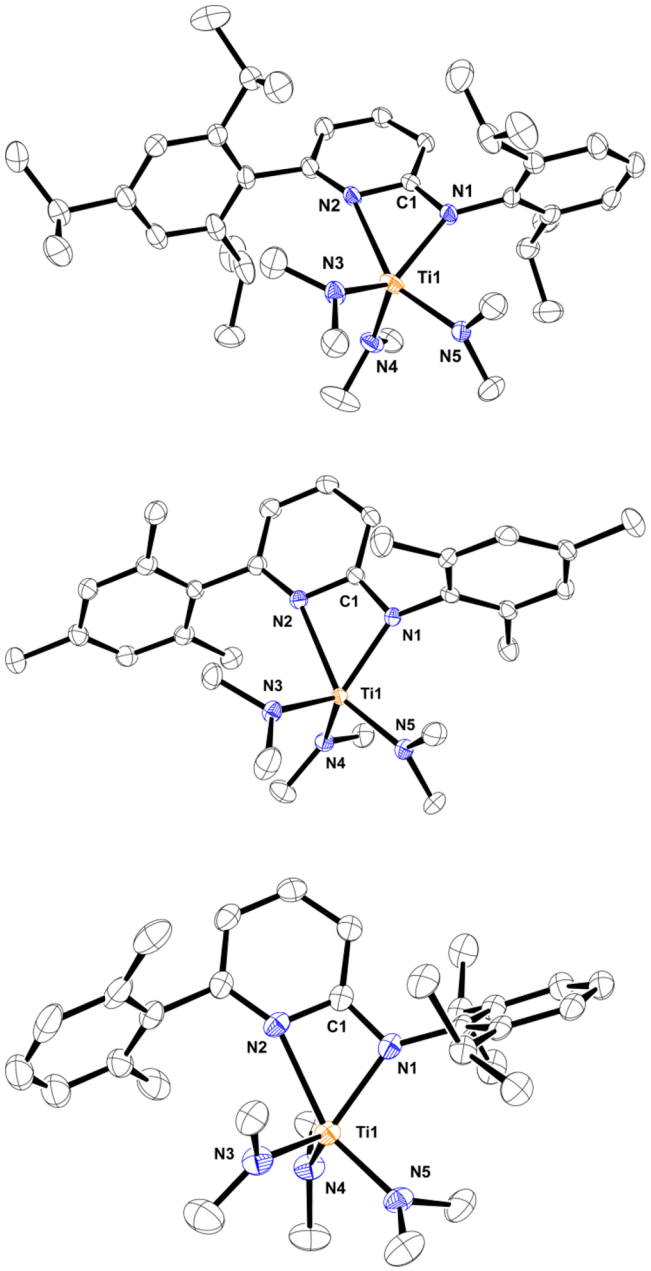



**Figure 1.** ORTEP representation of the solid-state molecular structures of **4** (top), **5** (middle), and **6** (bottom) plotted with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 4–6**

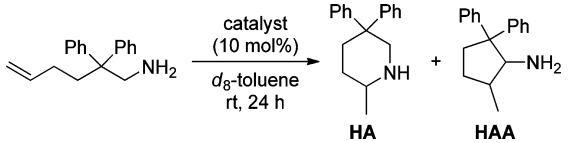
| | 4 | 5 | 6 |
|---|---|---|---|
| Ti1–N1 | 2.0678(17) | 2.0548(16) | 2.081(4) |
| Ti1–N2 | 2.4274(18) | 2.4478(17) | 2.337(4) |
| Ti1–N3 | 1.901(3) | 1.9154(17) | 1.893(4) |
| Ti1–N4 | 1.900(12) | 1.8929(16) | 1.911(4) |
| Ti1–N5 | 1.990(5) | 1.9037(16) | 1.923(4) |
| N1–Ti1–N2 | 59.03(6) | 58.84(6) | 60.50(14) |
| N1–Ti1–N3 | 133.65(12) | 123.09(7) | 131.70(16) |
| N1–Ti1–N4 | 116.4(4) | 122.77(7) | 109.65(16) |
| N3–Ti1–N4 | 107.9(3) | 109.32(7) | 112.88(19) |
| N1–Ti1–N5 | 93.52(13) | 95.10(7) | 98.32(16) |
| N2–Ti1–N5 | 152.40(12) | 153.94(6) | 156.05(16) |

The $^1$H NMR spectra of complexes **4–6** in $C_6D_6$ show a large and broad singlet for the dimethylamido protons in the region $\delta$ 3.04–3.07. The dimethylamido signal integrates to 18 protons relative to the respective proton signals of the bound Ap ligand, consistent with a monoligated complex. The presence of steric congestion surrounding the metal center is evident by the observation of hindered rotation of the aryl rings on the Ap ligand when isopropyl substituents are present. In complex **6**, for example, two doublets ($\delta$ 1.33 and 1.21) are observed for the two isopropyl substituents at $R^3$, whereas one singlet ($\delta$ 2.15) is observed for the two methyl substituents at $R^2$. The comparison of $^{13}$C NMR spectra of **4**, **5**, and **6** shows that these complexes are electronically similar, as the Ap C1 signals are observed at comparable chemical shifts at $\delta$ 170.2, 168.9, and 170.3, respectively. Furthermore, the dimethylamido carbon signals are present at nearly the same chemical shift at ca. $\delta$ 45.9, confirming the electronic similarities between these complexes. These complexes are thermally robust and show no decomposition in $d_8$-toluene when heated at 110 °C for one week or at 145 °C over two days.

In contrast to known bis(Ap)-ligated Ti complexes, attempts to prepare bis-ligated systems with these bulky ligands have not been successful. The bis-ligated analogue of **4** cannot be prepared, even when excess proligand **1** and $Ti(NMe_2)_4$ are heated in noncoordinating solvent at 100 °C for extended reaction times. In a similar experiment, when sterically less bulky proligand **2** and the prepared complex **5** in a 1:1 ratio are heated to 100 °C for one day, the reaction color changes from orange to red. Inspection of the $^1$H NMR spectrum of the reaction indicates the presence of **5** and a slight formation of what may be a bis-ligated analogue of **5**, as determined by the integration of relative peaks. However, this species could not be isolated.

**Catalytic Hydroamination/Cyclization Reactions.** To investigate the catalytic activity of $ApTi(NMe_2)_3$ **4–6**, 2,2-diphenyl-5-hexenyl-1-amine was chosen as the substrate for screening experiments (Table 2). This substrate is a good test substrate, as it is known to give both hydroamination and hydroaminoalkylation products at 105 °C with $Ti(NMe_2)_4$.[15] When the substrate and 10 mol % of **4–6** are left standing at room temperature for 24 h, we were surprised to find room-temperature activity for six-membered-ring hydroamination

**Table 2. Screening of Complexes 4–6 and Group 4 Tetrakis(dimethylamido) Complexes for Intramolecular Hydroamination/Cyclization**




| entry | catalyst | yield (%)[a] (HA:HAA)[b] |
|---|---|---|
| 1 | **4** | 5 (1:0) |
| 2 | **5** | 86 (1:0) |
| 3 | **6** | 20 (1:0) |
| 4 | $Ti(NMe_2)_4$ | 50 (9:1) |
| 5 | $Zr(NMe_2)_4$ | 27 (1:0) |
| 6 | $Hf(NMe_2)_4$ | <2 (1:0) |

[a]Combined NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [b]HA = hydroamination; HAA = hydroaminoalkylation, ratio determined by $^1$H NMR spectroscopy.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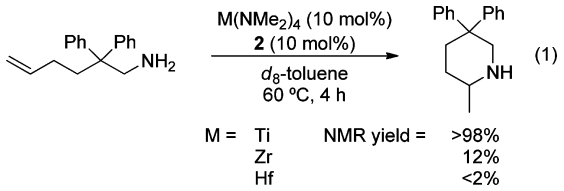
(entries 1–3). Room-temperature activity for alkene hydroamination among group 4 systems is uncommon, as only a few neutral Zr systems have been recently reported for such reactivity.[37,43,45] The activity of the ApTi($NMe_2$)$_3$ system increases with a decreasing amount of steric congestion (**5** > **6** > **4**) present at metal center, where the subtle difference between the methyl and isopropyl substituents in proximity to the metal is crucial. In addition, the commercially available M($NMe_2$)$_4$ (M = Ti, Zr, and Hf) have been tested for comparison, and room-temperature activity is also observed (entries 4–6). Among the group 4 metals of M($NMe_2$)$_4$, Ti is the most active for hydroamination, and the activity decreases down the group (Ti > Zr > Hf). However, the formation of hydroaminoalkylation product is observed when Ti($NMe_2$)$_4$ is utilized (entry 4). In contrast to Ti($NMe_2$)$_4$, there is no observable formation of hydroaminoalkylation product in the reactions catalyzed by **4**–**6**. Moreover, **5** is a much better hydroamination catalyst than Ti($NMe_2$)$_4$ (entry 2), but the activities of **4** and **6** are significantly lower (entries 1 and 3). These results demonstrate that too much steric congestion at the metal center decreases the catalyst's activity. Complex **5** provides a favorable amount of steric accessibility while presumably sufficient steric bulk to inhibit undesired aggregate formation and less reactive bis-ligated complexes via ligand redistribution.

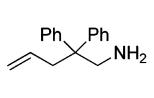
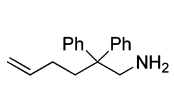
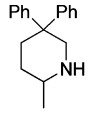
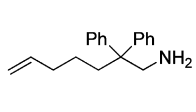
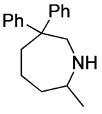
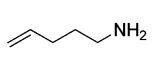
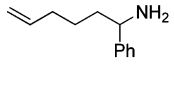
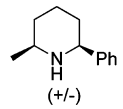
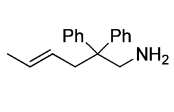
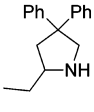
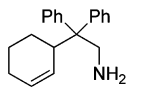
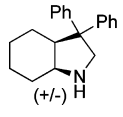
Previous investigations with a variety of bis-ligated systems[10,11,14,18–22] have shown that Zr complexes have improved reactivity over their Ti congeners. Using *in situ* catalyst preparation, we have shown that the cyclohydroamination of 2,2-diphenyl-5-hexenyl-1-amine catalyzed by the prepared complex **5** has the same reactivity as the *in situ* reaction for Ti (eq 1); at 60 °C in 4 h, the reaction goes to




completion by both methods. The *in situ* preparation involves stirring 10 mol % of **2** with an equimolar amount of M($NMe_2$)$_4$ for 5 min in $d_8$-toluene, prior to the addition of substrate. Equation 1 shows that the combination of this ligand with the larger metals, Zr and Hf, is not favorable and the reactivity significantly decreases as one increases the ionic radius. These results are in agreement with the observed trends in the group 4 tetrakis(dimethylamido) complexes in Table 2.

**Hydroamination Substrate Scope of 5.** Encouraged by the room-temperature hydroamination activity, the substrate scope of **5** has been explored using 5 mol % catalyst loading (Table 3). Catalyst **5** has a dramatically improved breadth of reactivity over Ti($NMe_2$)$_4$ and other known Ti systems.[8–26] The hydroamination of five- and six-membered rings is readily feasible in the presence of *gem*-disubstituents on the aminoalkene backbone at room temperature or at 60 °C (entries 1 and 2). More importantly, this Ti complex can effectively cyclize known challenging aminoalkene substrates (entries 3–7). The selective formation of azepane without the formation of $\alpha$-alkylated product is known to be difficult, especially for Ti systems that have been reported to be prone to unwanted hydroaminoalkylation side product formation (*vide supra*).[8,15,50] Here the formation of the seven-membered ring is achieved in

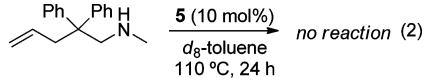
**Table 3. Catalytic Hydroamination of Primary Aminoalkenes by Complex 5**

| entry | substrate | product | condition[a] | yield (%)[b] |
|---|---|---|---|---|
| 1 |  |  | rt 12 h | 93 |
| 2 |  |  | 60 °C 4 h | 94 |
| 3 |  |  | 110 °C 80 h | 89 |
| 4 |  |  | 145 °C[c] 24 h | 74[d] |
| 5 |  |  (+/-) | 110 °C 48 h | 83[e] (18:1)[f] |
| 6 |  |  | 110 °C 48 h | 88 |
| 7 |  |  (+/-) | 130 °C 30 h | 87 (2:1)[f] |

[a]Reaction conditions: substrate (1 mmol), **5** (5 mol %), $d_8$-toluene (1 mL). [b]Isolated yield. [c]10 mol % catalyst. [d]Isolated yield following derivitization with TsCl. [e]Isolated yield of the major isomer. [f]*cis*/*trans* dr.

good yield (entry 3). The Thorpe–Ingold effect[87] is not required, as 4-pentenyl-1-amine is cyclized, but high temperature and increased catalyst loading are needed (entry 4). Catalyst **5** also mediates the formation of $\alpha,\alpha'$-disubstituted piperidines with excellent diastereoselectivity (*cis*/*trans* = 18:1), with the preference of positioning methyl and the phenyl substituent equatorially to minimize the 1,3-diaxial interaction on the chairlike cyclization transition state (entry 5).[88] Among group 4 systems, only a few Zr catalysts have been reported for hydroamination with unactivated internal alkenes,[35,38] and here both the *trans*- and *cis*-aminoalkenes can undergo hydroamination with **5** (entries 6 and 7). The combination of Ti with the increased accessibility of the metal center due to the monoligation of **5** results in reactivity that exceeds anything previously observed for Ti and compares favorably with leading Zr catalyst systems.[14,18–22,35–38,40,43–46]

In an effort to probe the mechanism of hydroamination catalysis it was noted that **5** is unable to promote the cyclization of a secondary aminoalkene substrate at room temperature or higher temperatures (eq 2). When *N*-methyl-2,2-diphenyl-4-




pentenyl-1-amine, in the presence of **5**, is heated at 110 °C for 24 h, there is no formation of the *N*-substituted pyrrolidine product. This result is in stark contrast to that of the primary aminoalkene analogue (Table 3, entry 1) that undergoes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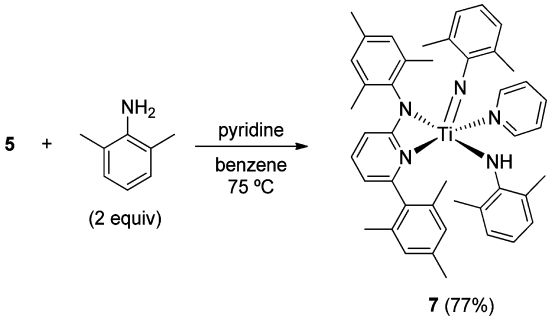
cyclization at room temperature. This is also significantly different from several recently reported Zr catalysts, including $Zr(NMe_2)_4$, that can indeed mediate secondary aminoalkene cyclohydroamination.[14,30,35,43−46] Notably, the Sadow group has shown that with their zwitterionic Zr system secondary aminoalkene cyclohydroamination can only be realized upon the addition of a substoichiometric amount of primary amine.[43] This is proposed to be due to the role of primary amine in the proton-assisted C−N bond formation.[43] However, a similar experiment with 10 mol % of both aminopyridinate precatalyst **5** and *n*-hexylamine with *N*-methyl-2,2-diphenyl-4-pentenyl-1-amine (modified eq 2) shows no reactivity at room temperature nor with heating at 110 °C for 24 h. Since the formation of imido species is inaccessible with a secondary amine substrate, and **5** is catalytically inactive for such substrates even in the presence of a primary amine additive, this observation suggests that intermediate imido species are involved in the C−N bond formation step of the catalytic cycle (i.e., [2+2] cycloaddition), as has been previously reported for Ti hydroamination catalysts.[89,90]

**Synthesis and Characterization of an Imido Complex from 5.** Guanidinate-supported imido complexes have been isolated and crystallographically characterized and have been used as catalytically active complexes, albeit sluggish, for alkyne hydroamination.[59] To investigate whether **5** is able to support such imido species, a stoichiometric reaction of **5** with 2,6-dimethylaniline (2 equiv) has been carried out in the presence of excess pyridine as a trapping agent (Scheme 5). Upon

**Scheme 5. Synthesis of an Imido Complex 7 from 5 and 2,6-Dimethylaniline**




heating the reaction in benzene at 75 °C overnight and after the removal of the reaction solvent under vacuum, the terminal imido complex **7** is obtained. After recrystallization from benzene/pentane, **7** is obtained as an analytically pure, orange crystalline solid in 77% yield. The $^1$H NMR spectrum of **7** in $C_6D_6$ reveals a well-defined monoligated complex that is bound by two 2,6-dimethylaniline (imido and amido) and one pyridine; no dimer formation or equilibria with dimeric species are observed.[45] These characteristics are reminiscent of the known cyclopentadienyl-supported Ti imido complex that is active in allene hydroamination.[91] An X-ray diffraction study of single crystals of **7**, grown from benzene via slow diffusion of pentane, shows a $C_1$-symmetric, distorted square pyramidal structure (Figure 2). The imido Ti=N linkage is confirmed by its short bond length [Ti1−N3 1.7228(13) Å] and the close to linear bond angle [C24−N3−Ti1 175.64(11)°]. The second aniline is bound by an amido linkage [Ti1−N4 1.9777(13) Å], as seen by its longer bond length and its bent nature. In contrast to **5**, the Ap ligand of **7** is rather symmetrically bound

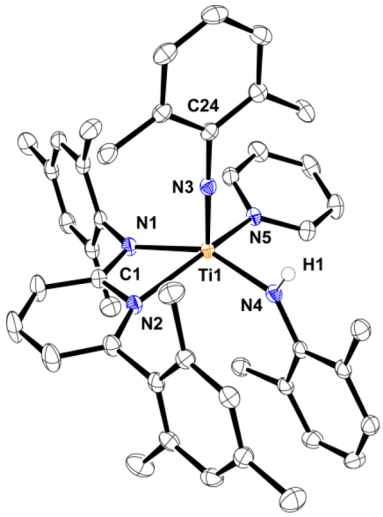
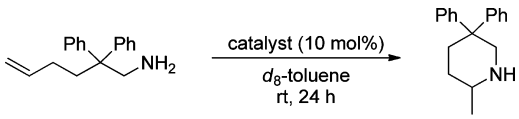



**Figure 2.** ORTEP representation of the solid-state molecular structure of **7** plotted with 50% probability ellipsoids for the non-hydrogen atoms. Selected bond lengths (Å) and angles (deg): Ti1−N1, 2.1524(13); Ti1−N2, 2.1937(13); Ti1−N3, 1.7728(13); Ti1−N4, 1.9777(13); Ti1−N5, 2.2230(13); C24−N3−Ti1, 175.64(11); N1−Ti1−N2, 61.90(5); N1−Ti1−N5, 90.51(5); N2−Ti1−N4, 99.37(5); N3−Ti1−N4, 100.45(6); N4−Ti1−N5, 97.34(5); Ti1−N4−H1, 108.4(14).

to Ti [Ti1−N1, 2.1524(13) Å; Ti1−N2, 2.1937(13) Å], presumably because of the absence of the electronically saturated and sterically demanding dimethylamido ligands.

The isolated imido complex **7** is a competent catalyst for alkene hydroamination, as shown in Table 4. In 24 h at room

**Table 4. Comparison of 5 and 7 for Intramolecular Hydroamination**




| entry | catalyst | yield (%)[a] |
|---|---|---|
| 1 | **5** | 86 |
| 2 | **7** | 57 |
| 3 | **5**[b] | 38 |
| 4 | **5**[c] | 83 |
| 5 | **7**[d] | >98 |

[a]Yield determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b]2,6-Dimethylaniline (0.20 equiv) added. [c]Pyridine (0.20 equiv) added. [d]At 60 °C, 4 h.

temperature, the comparison of **5** and **7** initially shows that **7** is less active than **5** (entries 1 and 2). Upon closer examination however, it is revealed that the presence of 2,6-dimethylaniline dramatically slows the reaction catalyzed by **5** (entry 3), whereas the presence of added pyridine does not inhibit catalysis (entry 4). The slower activity in the presence of 2,6-dimethylaniline can be explained by competitive metal binding of the cyclizable aminoalkene substrate and the noncyclizable 2,6-dimethylaniline.[40] This explanation is confirmed by heating the reaction, to aid in the amido exchange processes, and here the reaction catalyzed by **7** goes to completion in 4 h (entry 5), in agreement with **5** (Table 3, entry 2).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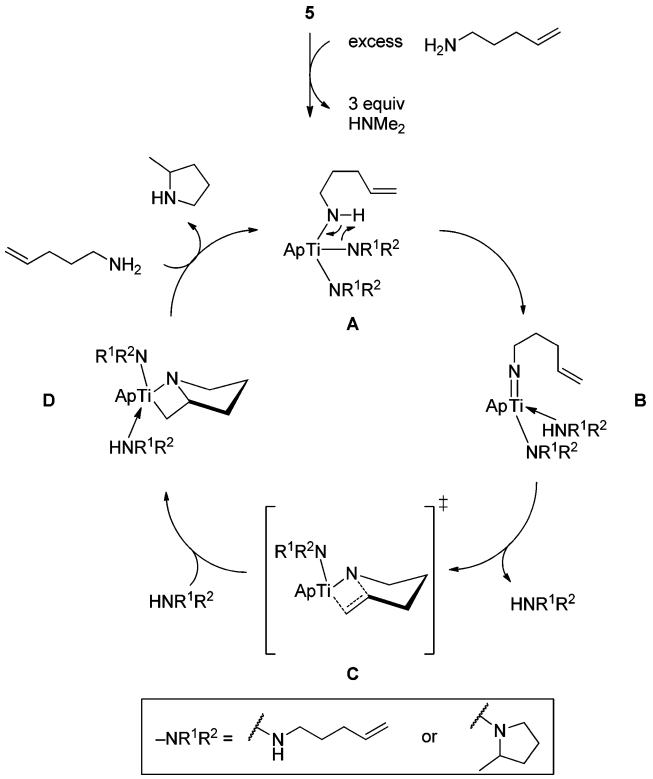
**Proposed Catalytic Cycle.** Three different mechanisms have been postulated for group 4-mediated alkene hydroamination: the imido [2+2] cycloaddition,[10,32,40] the amido σ-bond insertion mechanism,[30] and the closely related proton-assisted C−N bond formation.[43,45,48] Due to the fact that **5** is unreactive with secondary amines and is able to readily access a catalytically active terminal imido species **7**, the hydroamination catalytic cycle of **5** is postulated to proceed via the imido [2+2] cycloaddition pathway, and a plausible mechanism is proposed (Scheme 6). In the presence of excess primary aminoalkene

**Scheme 6. Proposed Mechanism for the Catalytic Cyclohydroamination Using 5**




substrate, dimethylamine is liberated by amido exchange reactions to generate **A**. A five-coordinate imido species **B**, analogous to **7**, is then generated by α-hydrogen elimination. Under catalytic conditions, a neutral amine donor is in place of the pyridine. This neutral donor ligand is then displaced by coordinated alkene, to promote a [2+2] cycloaddition, via a chairlike transition state **C** to yield azametallacyclobutane intermediate **D**. Finally, the protonation of **D** and an amido exchange with the substrate affords the cyclized product, and **A** is regenerated for the next catalytic cycle.

## SUMMARY AND CONCLUSIONS

Ap proligands **1**−**3** with varying amounts of steric bulk have been utilized, and a series of $ApTi(NMe_2)_3$ **4**−**6**, as well as catalytically active titanium Ap-supported imido complex **7**, have been prepared and fully characterized. Investigation of these complexes for alkene cyclohydroamination at room temperature has identified **5**, which employs an Ap ligand of moderate steric bulk (**2**) as a supporting ligand. This complex is a very active Ti alkene hydroamination catalyst and illustrates the catalytic potential of this inexpensive, abundant first-row transition element. The investigations of various ligands show the intense impact of steric bulk for such hydroamination catalysts and points toward the importance of rapidly assembled and easily varied tunable ligand frameworks for the optimization of catalytic activity. However, the *in situ* screening of **2** with Zr and Hf has shown that these larger metals are less reactive than the smaller Ti. These results highlight the importance of controlling steric accessibility at the metal center, through judicious selection of ligand steric bulk and choice of metal. The chemoselectivity between hydroamination over hydroaminoalkylation has been realized, in contrast to other Ti hydroamination catalysts, and the development of more reactive and stereoselective Ti systems is presently under investigation.

## EXPERIMENTAL SECTION

**General Considerations.** All reactions were conducted in oven-dried glassware using standard Schlenk line and glovebox techniques under an atmosphere of dry dinitrogen, unless described otherwise. Benzene, hexanes, and pentane were purified and dried by passage through a column of activated alumina and sparged with dinitrogen. $Ti(NMe_2)_4$ (Sigma-Aldrich), $Zr(NMe_2)_4$ (Strem), and $Hf(NMe_2)_4$ (Strem) were used as received. $d_6$-Benzene and $d_8$-toluene were degassed by three freeze−pump−thaw cycles and dried over activated 4 Å molecular sieves. The Ap proligands **1**−**3** were prepared according to literature procedure[74−76] and sublimed under heat and high vacuum before use. All amine substrates[92] for catalytic reactions were distilled over $CaH_2$ and degassed by three freeze−pump−thaw cycles before use. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker 400 MHz Avance spectrometer at ambient temperature, and chemical shifts are given relative to the corresponding residual *protio*-residual solvent. Mass spectra were recorded on a Kratos MS-50 spectrometer using an electron impact (70 eV) source or a Bruker Esquire LC spectrometer using an electrospray ionization source. Elemental analyses were recorded on a Carlo Erba EA 1108 elemental analyzer. Single-crystal X-ray structure determinations were performed on a Bruker X8 APEX II diffractometer at the Department of Chemistry, University of British Columbia, by Mr. Jacky Yim.

**Synthesis of 4.** *N*-(2,6-Diisopropylphenyl)-6-(2,4,6-triisopropylphenyl)-2-aminopyridine (**1**; 0.274 g, 0.600 mmol) in benzene (∼2 mL) was treated with a solution of $Ti(NMe_2)_4$ (0.135 g, 0.600 mmol) in benzene (∼2 mL), upon which the reaction instantly turned orange. The reaction was stirred overnight at room temperature, during which time the ligand dissolved to give an orange solution. The reaction solvent was removed under vacuum to afford analytically pure **4** as a yellow solid (>98%). Single crystals for X-ray structure determination were obtained by recrystallization from a solution of hexanes at −35 °C. $^1H$ NMR (400 MHz, $C_6D_6$): δ 7.25−7.16 (m, 3H, Ar−*H*), 7.14 (s, 2H, Ar−*H*), 6.87 (dd, 1H, *J* = 8.4, 7.2 Hz, Ap−*H*), 6.26 (d, 1H, *J* = 7.2 Hz, Ap−*H*), 5.60 (d, 1H, *J* = 8.4 Hz, Ap−*H*), 3.55 (septet, 2H, *J* = 6.9 Hz, $-CH(CH_3)_2$), 3.04 (s, 18H, $-N(CH_3)_2$), 2.95 (septet, 2H, *J* = 6.8 Hz, $-CH(CH_3)_2$), 2.84 (septet, 1H, *J* = 6.9 Hz, $-CH(CH_3)_2$), 1.36 (d, 6H, *J* = 6.8 Hz, $-CH(CH_3)_2$), 1.32 (d, 6H, *J* = 6.9 Hz, $-CH(CH_3)_2$), 1.25 (d, 6H, *J* = 6.9 Hz, $-CH(CH_3)_2$), 1.20 (d, 6H, *J* = 6.8 Hz, $-CH(CH_3)_2$), 1.16 (d, 6H, *J* = 6.8 Hz, $-CH(CH_3)_2$). $^{13}C$ NMR (100 MHz, $C_6D_6$): δ 170.2, 158.0, 149.3, 147.1, 145.1, 144.9, 138.9, 136.8, 126.0, 124.3, 120.8, 114.2, 104.6, 45.9, 35.2, 31.0, 28.9, 27.0, 25.5, 24.7, 24.3, 23.3. MS (EI): *m*/*z* = 635 ($M^+$), 591 ($M^+ - NMe_2$), 547 ($M^+ - 2NMe_2$), 503 ($M^+ - 3NMe_2$). Anal. Calcd for $C_{38}H_{61}N_5Ti$: C, 71.79; H, 9.67; N, 11.02. Found: C, 71.96; H, 9.63; N, 10.93.

**Synthesis of 5.** *N*,6-Dimesityl-2-aminopyridine (**2**; 0.661 g, 2.00 mmol) in benzene (∼3 mL) was treated with a solution of $Ti(NMe_2)_4$ (0.448 g, 2.00 mmol) in benzene (∼3 mL), upon which the reaction instantly turned orange. The reaction was stirred at room temperature for 4 h, during which time the ligand dissolved to give an orange solution. The reaction solvent was removed under vacuum, and the resulting compound was recrystallized from a solution of hexanes at −35 °C to give **5** as yellow crystals (0.965 g, 95%). A sample from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these crystals was used for X-ray structure determination. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 6.95 (s, 2H, Ar−*H*), 6.94 (dd, 1H, *J* = 8.4, 7.2 Hz, Ap−*H*), 6.83 (s, 2H, Ar−*H*), 6.08 (d, 1H, *J* = 7.2 Hz, Ap−*H*), 5.62 (d, 1H, *J* = 8.4 Hz, Ap−*H*), 3.07 (s, 18H, −N($CH_3$)$_2$), 2.32 (s, 6H, −$CH_3$), 2.26 (s, 3H, −$CH_3$), 2.18 (s, 6H, −$CH_3$), 2.16 (s, 3H, −$CH_3$). $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ 168.9, 158.0, 144.6, 140.3, 138.2, 137.4, 136.4, 134.0, 133.6, 129.8, 128.5, 112.2, 102.6, 46.0, 21.5, 21.4, 20.8, 19.6. MS (EI): *m*/*z* = 509 ($M^+$), 465 ($M^+$ − $NMe_2$), 421 ($M^+$ − 2$NMe_2$), 377 ($M^+$ − 3$NMe_2$). Anal. Calcd for $C_{29}H_{43}N_5Ti$: C, 68.36; H, 8.51; N, 13.74. Found: C, 68.55; H, 8.50; N, 13.45.

**Synthesis of 6.** *N*-(2,6-Diisopropylphenyl)-6-(2,6-dimethylphenyl)-2-aminopyridine (**3**; 0.179 g, 0.500 mmol) in benzene (∼2 mL) was treated with a solution of Ti($NMe_2$)$_4$ (0.112g, 0.500 mmol) in benzene (∼2 mL), upon which the reaction instantly turned orange. The reaction was stirred overnight at room temperature, during which time the ligand dissolved to give an orange solution. The reaction solvent was removed under vacuum, and the resulting compound was recrystallized from a solution of hexanes at −35 °C to give **6** as orange crystals (0.214 g, 80%). A sample from these crystals was used for X-ray structure determination. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.27−7.16 (m, 3H, Ar−*H*), 7.09 (t, 1H, *J* = 7.5 Hz, Ar−*H*), 6.99 (d, 2H, *J* = 7.5 Hz, Ar−*H*), 6.87 (dd, 1H, *J* = 8.5, 7.1 Hz, Ap−*H*), 5.96 (d, 1H, *J* = 7.1 Hz, Ap−*H*), 5.54 (d, 1H, *J* = 8.5 Hz, Ap−*H*), 3.55 (septet, 2H, *J* = 6.9 Hz, −C*H*($CH_3$)$_2$), 3.05 (s, 18H, −N($CH_3$)$_2$), 2.15 (s, 6H, −$CH_3$), 1.33 (d, 6H, *J* = 6.9 Hz, −CH($CH_3$)$_2$), 1.21 (d, 6H, *J* = 6.9 Hz, −CH($CH_3$)$_2$). $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ 170.3, 157.5, 145.0, 144.7, 140.9, 139.9, 136.5, 127.7, 125.9, 124.3, 111.6, 104.3, 45.9, 28.9, 25.4, 24.2, 20.8. MS (EI): *m*/*z* = 537 ($M^+$), 493 ($M^+$ − $NMe_2$), 449 ($M^+$ − 2$NMe_2$), 405 ($M^+$ − 3$NMe_2$). Anal. Calcd for $C_{31}H_{47}N_5Ti$: C, 69.26; H, 8.81; N, 13.03. Found: C, 69.26; H, 8.76; N, 12.81.

**Synthesis of 7.** To **5** (0.102 g, 0.200 mmol) dissolved in benzene (∼1 mL) were added 2,6-dimethylaniline (0.0485 g, 49.2 μL, 0.400 mmol) and pyridine (0.0633 g, 64.7 μL, 0.800 mmol). The resulting red solution was heated at 75 °C for 18 h, and the reaction solvent was removed under vacuum. The residue was dissolved in benzene (∼1 mL), layered with pentane (∼4 mL), and left at room temperature overnight, during which time crystals formed. The mother liquor was decanted, and volatiles were removed under vacuum to give **7** as an orange crystalline solid (0.107 g, 77%). Single crystals for X-ray structure determination were obtained by slow diffusion of pentane into a solution of **7** in benzene at room temperature. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 9.77 (br s, 1H, −N*H*−); 8.53 (m, 2H, py−$H_{ortho}$), 7.02 (s, 1H, Ar−*H*), 6.99 (d, 2H, *J* = 7.4 Hz, Ar−*H*), 6.94 (d, 2H, *J* = 7.4 Hz, Ar−*H*), 6.91 (dd, 1H, *J* = 8.5, 7.1 Hz, Ap−*H*), 6.86 (s, 1H, Ar−*H*), 6.74 (t, 1H, *J* = 7.4 Hz, Ar−*H*), 6.69 (s, 1H, Ar−*H*), 6.67 (t, 1H, *J* = 7.4 Hz, Ar−*H*), 6.51 (s, 1H, Ar−*H*), 6.48 (m, 1H, py−$H_{para}$), 6.09 (m, 2H, py−$H_{meta}$), 5.94 (d, 1H, *J* = 7.1 Hz, Ap−*H*), 5.75 (d, 1H, *J* = 8.5 Hz, Ap−*H*), 2.74 (s, 3H, −$CH_3$), 2.54 (s, 6H, −$CH_3$), 2.40 (s, 3H, −$CH_3$), 2.29 (s, 3H, −$CH_3$), 2.20 (s, 3H, −$CH_3$), 2.10 (s, 6H, −$CH_3$), 1.84 (s, 3H, −$CH_3$), 1.75 (s, 3H, −$CH_3$). $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ 167.0, 161.2, 158.7, 154.1, 150.8, 144.1, 141.1, 138.6, 137.1, 137.0, 136.9, 136.2, 135.3, 134.6, 133.4, 132.9, 130.6, 129.9, 128.8, 128.3, 128.0, 124.4, 122.7, 120.2, 118.1, 109.9, 104.3, 21.5, 21.4, 21.1, 20.8, 20.7, 20.5, 19.8, 19.6. Anal. Calcd for $C_{44}H_{49}N_5Ti$: C, 75.96; H, 7.10; N, 10.07. Found: C, 76.04; H, 7.37; N, 9.94.

**General Procedure for Monitoring Intramolecular Hydroamination/Cyclization Reactions (eq 2, Tables 2 and 4).** Catalyst (0.0150 mmol, 10 mol %) and 1,3,5-trimethoxybenzene (1.25 M in $d_8$-toluene, 40 μL, 0.0500 mmol) were dissolved in $d_8$-toluene (460 μL) in a small vial. The substrate 2,2-diphenyl-5-hexenyl-1-amine (1.50 M in $d_8$-toluene, 100 μL, 0.150 mmol) was then added and mixed with a Pasteur pipet. The resulting solution was transferred to a J. Young NMR tube and either left at room temperature or heated to 60 °C for the specified time. The reaction progress was monitored by $^1$H NMR spectroscopy.

**General Procedure for Catalytic Hydroamination of Aminoalkenes by Complex 5 (Table 3).** Complex **5** (0.0510 g, 0.0500 mmol) and the aminoalkene (1.00 mmol) were dissolved in $d_8$-toluene (1 mL) by mixing with a Pasteur pipet in a small vial. The resulting solution was transferred to a J. Young NMR tube and heated in an oil bath at the specified temperature. Once >95% conversion was achieved as monitored by $^1$H NMR spectroscopy, the tube was opened and the contents were diluted with diethyl ether. When the mixture clarified upon standing at room temperature, it was filtered through Celite, and the volatiles were removed under reduced pressure. The amines were purified by flash chromatography on silica gel.

## ■ ASSOCIATED CONTENT

### Supporting Information

CIF files of complexes **4**−**7** and NMR spectra of new compounds and hydroamination products. 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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## ■ REFERENCES


(1) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.
(2) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795.
(3) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708.
(4) McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459.
(5) McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *115*, 11485.
(6) Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N.; Scott, P. *Chem. Commun.* **2004**, 894.
(7) Gribkov, D. V.; Hultzsch, K. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5542.
(8) Bexrud, J. A.; Beard, J. D.; Leitch, D. C.; Schafer, L. L. *Org. Lett.* **2005**, *7*, 1959.
(9) Müller, C.; Loos, C.; Schulenberg, N.; Doye, S. *Eur. J. Org. Chem.* **2006**, 2499.
(10) Thomson, R. K.; Bexrud, J. A.; Schafer, L. L. *Organometallics* **2006**, *25*, 4069.
(11) Watson, D. A.; Chiu, M.; Bergman, R. G. *Organometallics* **2006**, *25*, 4731.
(12) Lee, A. V.; Schafer, L. L. *Organometallics* **2006**, *25*, 5249.
(13) Marcsekova, K.; Loos, C.; Rominger, F.; Doye, S. *Synlett* **2007**, 2564.
(14) Majumder, S.; Odom, A. L. *Organometallics* **2008**, *27*, 1174.
(15) Müller, C.; Saak, W.; Doye, S. *Eur. J. Org. Chem.* **2008**, 2731.
(16) Graebe, K.; Pohlki, F.; Doye, S. *Eur. J. Org. Chem.* **2008**, 4815.
(17) Müller, C.; Koch, R.; Doye, S. *Chem.—Eur. J.* **2008**, 10430.
(18) Zi, G.; Liu, X.; Xiang, L.; Song, H. *Organometallics* **2009**, *28*, 1127.
(19) Zi, G.; Zhang, F.; Xiang, L.; Chen, Y.; Fang, W.; Song, H. *Dalton Trans.* **2010**, *39*, 4048.
(20) Zi, G.; Zhang, F.; Liu, X.; Ai, L.; Song, H. *J. Organomet. Chem.* **2010**, *695*, 730.
(21) Xiang, L.; Zhang, F.; Zhang, J.; Song, H.; Zi, G. *Inorg. Chem. Commun.* **2010**, *13*, 666.
(22) Wang, Q.; Song, H.; Zi, G. *J. Organomet. Chem.* **2010**, *695*, 1583.

(23) Janssen, T.; Severin, R.; Diekmann, M.; Friedemann, M.; Haase, D.; Saak, W.; Doye, S.; Beckhaus, R. *Organometallics* **2010**, *29*, 1806.
(24) Ayinla, R. O.; Schafer, L. L. *Dalton Trans.* **2011**, *40*, 7769.
(25) Helgert, T. R.; Hollis, T. K.; Valente, E. J. *Organometallics* **2012**, *31*, 3002.
(26) Jaspers, D.; Saak, W.; Doye, S. *Synlett* **2012**, *23*, 2098.
(27) Kim, H.; Lee, P. H.; Livinghouse, T. *Chem. Commun.* **2005**, 5205.
(28) Kim, H.; Kim, Y. K.; Shim, J. H.; Kim, M.; Han, M.; Livinghouse, T.; Lee, P. H. *Adv. Synth. Catal.* **2006**, *348*, 2609.
(29) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 354.
(30) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149.
(31) Gott, A. L.; Clarke, A. J.; Clarkson, G. J.; Scott, P. *Organometallics* **2007**, *26*, 1729.
(32) Gott, A. L.; Clarke, A. J.; Clarkson, G. J.; Scott, P. *Chem. Commun.* **2008**, 1422.
(33) Gott, A. L.; Clarkson, G. J.; Deeth, R. J.; Hammond, M. L.; Morton, C.; Scott, P. *Dalton Trans.* **2008**, 2983.
(34) Cho, J.; Hollis, K. T.; Helgert, T. R.; Valente, E. J. *Chem. Commun.* **2008**, 5001.
(35) Leitch, D. C.; Payne, P. R.; Dunbar, C. R.; Schafer, L. L. *J. Am. Chem. Soc.* **2009**, *131*, 18246.
(36) Reznichenko, A. L.; Hultzsch, K. C. *Organometallics* **2010**, *29*, 24.
(37) Manna, K.; Ellern, A.; Sadow, A. D. *Chem. Commun.* **2010**, *46*, 339.
(38) Bexrud, J. A.; Schafer, L. L. *Dalton Trans.* **2010**, *39*, 361.
(39) Hu, Y. C.; Liang, C. F.; Tsai, J. H.; Yap, G. P. A.; Chang, Y. T.; Ong, T. G. *Organometallics* **2010**, *29*, 3357.
(40) Allan, L. E. N.; Clarkson, G. J.; Fox, D. J.; Gott, A. L.; Scott, P. *J. Am. Chem. Soc.* **2010**, *132*, 15308.
(41) Antunes, M. A.; Munha, R. F.; Alves, L. G.; Schafer, L. L.; Martins, A. M. *J. Organomet. Chem.* **2011**, *696*, 2.
(42) Ayinla, R. O.; Gibson, T.; Schafer, L. L. *J. Organomet. Chem.* **2011**, *696*, 50.
(43) Manna, K.; Xu, S.; Sadow, A. D. *Angew. Chem., Int. Ed.* **2011**, *50*, 1865.
(44) Mukherjee, A.; Nembenna, S.; Sen, T. K.; Sarish, S. P.; Ghorai, P. K.; Ott, H.; Stalke, D.; Mandal, S. K.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2011**, *50*, 3968.
(45) Leitch, D. C.; Platel, R. H.; Schafer, L. L. *J. Am. Chem. Soc.* **2011**, *133*, 15453.
(46) Wang, X.; Chen, Z.; Sun, X.-L.; Tang, Y.; Xie, Z. *Org. Lett.* **2011**, *13*, 4758.
(47) Payne, P. R.; Bexrud, J. A.; Leitch, D. C.; Schafer, L. L. *Can. J. Chem.* **2011**, *89*, 1222.
(48) Tobisch, S. *Inorg. Chem.* **2012**, *51*, 3786.
(49) Kubiak, R.; Prochnow, I.; Doye, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 1153.
(50) Bexrud, J. A.; Eisenberger, P.; Leitch, D. C.; Payne, P. R.; Schafer, L. L. *J. Am. Chem. Soc.* **2009**, *131*, 2116.
(51) Prochnow, I.; Kubiak, R.; Frey, O. N.; Beckhaus, R.; Doye, S. *ChemCatChem* **2009**, *1*, 162.
(52) Roesky, P. W. *Angew. Chem., Int. Ed.* **2009**, *48*, 4892.
(53) Kubiak, R.; Prochnow, I.; Doye, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 2626.
(54) Prochnow, I.; Zark, P.; Müller, T.; Doye, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 6401.
(55) Ramanathan, B.; Odom, A. L. *J. Am. Chem. Soc.* **2006**, *128*, 9344.
(56) Dörfler, J.; Doye, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 1806.
(57) Lee, A. V.; Schafer, L. L. *Eur. J. Inorg. Chem.* **2007**, 2243.
(58) Weitershaus, K.; Ward, B. D.; Kubiak, R.; Müller, C.; Wadepohl, H.; Doye, S.; Gade, L. H. *Dalton Trans.* **2009**, 4586.
(59) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 2839.
(60) Smolensky, E.; Kapon, M.; Eisen, M. S. *Organometallics* **2005**, *24*, 5495.
(61) Smolensky, E.; Kapon, M.; Eisen, M. S. *Organometallics* **2007**, *26*, 4510.
(62) Bertolasi, V.; Boaretto, R.; Chierotti, M. R.; Gobetto, R.; Sostero, S. *Dalton Trans.* **2007**, 5179.
(63) Kempe, R.; Noss, H.; Irrgang, T. *J. Organomet. Chem.* **2002**, *647*, 12.
(64) Kempe, R. *Eur. J. Inorg. Chem.* **2003**, 791.
(65) Deeken, S.; Motz, G.; Kempe, R. *Z. Anorg. Allg. Chem.* **2007**, *633*, 320.
(66) Noor, A.; Kretschmer, W. P.; Glatz, G.; Kempe, R. *Inorg. Chem.* **2011**, *50*, 4598.
(67) Hafeez, M.; Kretschmer, W. P.; Kempe, R. *Eur. J. Inorg. Chem.* **2011**, 5512.
(68) Talja, M.; Luhtanen, T.; Polamo, M.; Klinga, M.; Pakkanen, T.; Leskela, M. *Inorg. Chim. Acta* **2008**, *361*, 2195.
(69) Shen, H.; Chan, H. S.; Xie, Z. *Organometallics* **2007**, *26*, 2694.
(70) Fandos, R.; Hernandez, C.; Otero, A.; Rodriguez, A.; Ruiz, M. J. *J. Organomet. Chem.* **2005**, *690*, 4828.
(71) Noor, A.; Kempe, R. *Eur. J. Inorg. Chem.* **2008**, 2377.
(72) Smolensky, E.; Kapon, M.; Woollins, J. D.; Eisen, M. S. *Organometallics* **2005**, *24*, 3255.
(73) Westmoreland, I.; Munslow, I. J.; O'Shaughnessy, P. N.; Scott, P. *Organometallics* **2003**, *22*, 2972.
(74) Scott, N. M.; Schareina, T.; Tok, O.; Kempe, R. *Eur. J. Inorg. Chem.* **2004**, 3297.
(75) Kretschmer, W. P.; Meetsma, A.; Hessen, B.; Scott, N. M.; Qayyum, S.; Kempe, R. *Chem.—Eur. J* **2006**, *12*, 8969.
(76) Schmalz, T.; Burkhardt, J.; Irrgang, T.; Kempe, R. *Z. Kristallogr.—New Cryst. Struct.* **2005**, *220*, 405.
(77) Scott, N. M.; Kempe, R. *Eur. J. Inorg. Chem.* **2005**, 1319.
(78) Guillaume, S. M.; Schappacher, M.; Scott, N. M.; Kempe, R. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3611.
(79) Kretschmer, W. P.; Hessen, B.; Noor, A.; Scott, N. M.; Kempe, R. *J. Organomet. Chem.* **2007**, *692*, 4569.
(80) Noor, A.; Wagner, F. R.; Kempe, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 7246.
(81) Noor, A.; Glatz, G.; Müller, R.; Kaup, M.; Demeshko, S.; Kempe, R. *Nat. Chem.* **2009**, *1*, 322.
(82) Döring, C.; Kretschmer, W. P.; Kempe, R. *Eur. J. Inorg. Chem.* **2010**, 2853.
(83) Kretschmer, W. P.; Bauer, T.; Hessen, B.; Kempe, R. *Dalton Trans.* **2010**, 6847.
(84) Schwarzmaier, C.; Noor, A.; Glatz, G.; Zabel, M.; Timoshkin, A. Y.; Cossairt, B. M.; Cummins, C. C.; Kempe, R.; Scheer, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7283.
(85) Haas, I.; Kretschmer, W. P.; Kempe, R. *Organometallics* **2011**, *30*, 4854.
(86) Noor, A.; Tamne, E. S.; Qayyum, S.; Bauer, T.; Kempe, R. *Chem.—Eur. J.* **2011**, *17*, 6900.
(87) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.
(88) Molander, G. A.; Dowdy, E. D.; Pack, S. K. *J. Org. Chem.* **2001**, *66*, 4344.
(89) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104.
(90) Severin, R.; Doye, S. *Chem. Soc. Rev.* **2007**, *36*, 1407.
(91) Johnson, J. S.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 2923.
(92) See Supporting Information.