DOI: 10.1002/ejic.200700036

# Modular *N*,*O*-Chelating Ligands: Group-4 Amidate Complexes for Catalytic Hydroamination

**Alison V. Lee[a] and Laurel L. Schafer*[a]**

**Keywords:** Amidate ligands / Group-4 metal complexes / Hydroamination / Homogeneous catalysis / Asymmetric catalysis

Amidate ligands have been used as a modular ligand set for early transition-metal complexes, and have been found to exhibit high reactivity in the catalytic hydroamination of alkynes, allenes, and alkenes. This microreview focuses on coordination metal complexes containing amidate functionality including their bonding, structure and reactivity trends. The synthesis and characterization of a number of different group-4 metal complexes is presented, and their applications in both hydroamination and organic synthesis are discussed.

## Introduction

Investigations involving cyclopentadienyl (Cp) complexes have been widespread, and their application in many catalytic and stoichiometric synthetic transformations is well established.[1] However, there are several limitations associated with the modification of Cp, leading to extensive research into broadly applicable non-Cp-based ligand sets in which ligand tuning is more easily accomplished.[2,3] Examples of these classes of ligands have included, but are not restricted to, amidinates,[4–8] troponiminates,[9,10] guanidinates,[11–13] sulfonamides,[14,15] nitrogen-based ligands[16–18] and chelating nitrogen and oxygen ligand sets.[19–21] In surveying the literature, it became apparent that while many elaborate ligand classes have been studied, a very simple group of *N*,*O*-chelating molecules, namely deprotonated organic amides (amidates), has been largely overlooked.

Amides are readily synthesized and the starting materials are widely available. Amidate steric and electronic properties are easily varied, resulting in the modular synthesis of a simple, tunable ligand set. An existing limitation of this class of ligands is the variable coordination modes that amidates can adopt when binding to a metal (Figure 1). Poss-

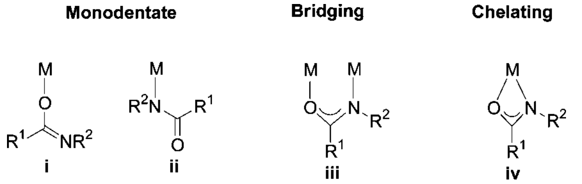


Figure 1. Some of the possible bonding modes of amidate ligands.

---

[a] Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada

*Alison Lee obtained her Bachelor's of Science (Honours) degree from Queen's University, in Kingston, Ontario, Canada in 2002 where she majored in chemistry. She then moved to Vancouver to attend the University of British Columbia and pursue her doctorate degree, with scholarship support from NSERC, under the supervision of Dr. Laurel Schafer. Her research has been focused on both catalyst development for hydroamination, and methodology development for regioselective C–N and C–C bond forming. She plans to finish her degree in the summer of 2007.*

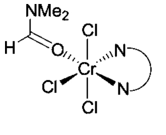
*Laurel Schafer completed her undergraduate and graduate degrees in Canada at the University of Guelph (1993) and University of Victoria (1999), respectively. Upon completion of her doctoral work she joined the laboratories of Prof. T. Don Tilley at the University of California – Berkeley as an NSERC Postdoctoral Fellow. In 2001 she joined the faculty at the University of British Columbia with the support of an NSERC University Faculty Award. In 2004 she received the Boehringer Ingelheim (Canada) Young Investigator Award for Organic Synthesis and more recently in 2007 she was named a Sloan Fellow. Her research program investigating the synthesis, structure and reactivity of early transition metal and lanthanide amidate complexes has resulted in the development of a new family of catalysts for the hydroamination of alkynes, allenes and alkenes.*

ibly it is the numerous potential coordination isomers in resultant complexes that has kept amidates from being fully exploited as auxiliary ligands.

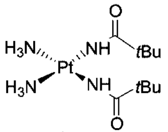
A survey of the literature shows that most characterized examples of amidate metal complexes fall into one of the following four categories: i) monodentate, *O*-bound, ii) mondentate, *N*-bound, iii) bridging and iv) chelating. Examples of several complexes that are used for bioinorganic[22–24] and lanthanide coordination chemistry display these coordination modes,[25,26] however, these are outside the scope of this review, and only a few select examples will be discussed. Also, there are several examples of catalytically relevant complexes with coordinated neutral amides as ligands,[22,27,28] which will be largely excluded from our discussion. In summary, this microreview highlights recent contributions that have used the modular amidate ligand framework to advantage in the facile synthesis of catalytically active complexes. Recent results have shown that with a chelating ligand motif (bonding mode iv) a new family of catalytically active group-4 complexes can be prepared and used for hydroamination. The structure, bonding and reactivity trends observed in this easily synthesized class of compounds will be summarized here.

## Monodentate

There are several examples of amidate ligands coordinating to a metal center in a monomeric fashion through either the oxygen (**i**) or the nitrogen (**ii**). In general, coordination occurs through the more basic oxygen with "hard" metals (**1**),[29] but through the nitrogen to "soft" metals (**2**).[30,31] Most examples are reported as either type **i** or type **ii**, without reference to isomerism between the two. Furthermore, if the amide is in its neutral form, typically the ligand coordinates through the oxygen to the metal center (eg. **1**), (Figure 2).



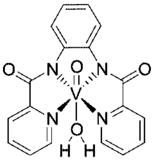
**1**



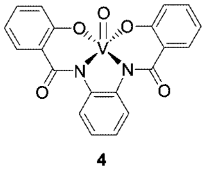
**2**

Figure 2. Examples of complexes that are bound through the amide oxygen, or the amidate nitrogen without further donation from another atom in the same ligand.

Typically, ligands that bind to a metal center solely through the amidate nitrogen have a constrained geometry such that donation through the carbonyl is unfavorable. For example, the diamidate chelating ligands in **3** and **4** in Figure 3 both have other donor atoms in their backbone that restrict the coordination environment. Complexes **3** and **4** were investigated as models for the interaction between metalloenzymes and amides of peptides in biological chemistry23 and in medicinal inorganic chemistry,[32,33] respectively.



**3**



**4**

Figure 3. Examples of constrained bis(amidate) ligands that bind the metal through both the amidate nitrogen, and other atoms in the molecule.

Variations of **4** have been made with $Cu^{II}$, $Ni^{II}$, $Zn^{II}$, $Cr^{III}$, $Fe^{III}$, and $Bi^{III}$ metal centers and were used for catalytic investigations in the selective liquid-phase hydroxylation of phenol.[34,35]

While many examples in coordination chemistry investigations have monodentate binding modes of amidates, few examples of well characterized complexes for catalytic applications have been reported. The few examples included here illustrate the aspects of ligand design which must be considered in preparing well-defined complexes with discrete binding modes for use in further applications.

## Bridging

One of the most common bonding motifs observed with amidates is bonding type **iii** in which the amidate ligand bridges two metal centers. Many of these examples use very simple amidate ligands, to form complexes that have been investigated for their interesting structural features (Figure 4) and stoichiometric reactivity (Figure 5). For example, in 1979 the first Cr (**5**) and Mo complexes containing metal–metal bonds and bridging amidates were reported.[36]

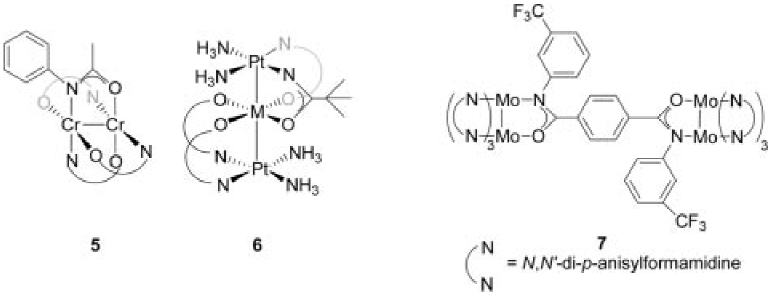
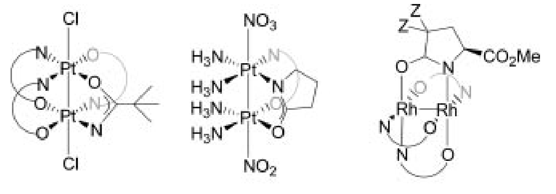


Figure 4. Examples of structurally investigated bridging amidate complexes. Complex **5** showed a very short Cr–Cr bond. Complex **6** is a heterotrimetallic complex in which amidate ligands are bridging two different metal centers, M = Cu, Co, Mn, Cd, In, Ni. Complex **7** is a tetranuclear complex with bridging amidate ligands.



**8** **9** **10**
Z = H, F

Figure 5. Bridging amidates forming lantern-type Pt dimers (**8**) or head-to-head complexes (**9**). Dirhodium(II) carboxamidates (**10**) used in metal carbene transformations.

Another example of type **iii** bonding is seen in complex **6**. These heterotrimetallic complexes contain two platinum atoms and a Cu, Co, Mn, Cd, In, or Ni atom and have been formed with various amidate ligands in which the amidate ligands bridge two metal centers (**6**).[37] Finally, structurally interesting tetranuclear complexes with bridging amidate ligands have been reported with both Mo[38] (**7**) and Re[39] metal centers.

While the aforementioned examples have been used for structural chemistry studies, similar complexes have also been used to probe stoichiometric reactivity and catalysis (Figure 5). For example, bridging amidate complexes involving Pt, as seen in **8** and **9** have been reported,[31,40–42] and their reactivity has been been investigated,[43–45] including their application in catalytic olefin functionalization.[46]

Notably, the group of Doyle and co-workers have made a series of dirhodium(II) carboxamidates of the type shown in complex **10**. These compounds have shown important reactivity in a wide variety of metal carbene transformations[47,48] and as catalysts for enantioselective hetero-Diels–Alder reactions.[49]

## Chelating

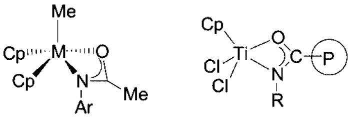
Of particular interest to this review are examples of amidates that chelate through nitrogen and oxygen to a single metal center (bonding type **iv**), which have been more rarely reported in the literature. In one example, simple amidates, such as *N*-*tert*-butylbenzamidate and substituted derivatives have been investigated in conjunction with organoaluminum compounds, such as $AlMe_3$. They have been used for the synthesis of aluminum deketiminates.[27] Furthermore, tris(amidate) aluminum(III) compounds have been synthesized and identified as the catalyst resting state in $Al^{III}$-catalyzed transamidation of carboxamides.[50]

Many of the examples of amidates chelating to metal centers have resulted from organometallic compounds reacting with isocyanates. For example, Nb and Ta complexes of the sort $M(Me)_xCl_y$ readily insert phenyl or methyl isocyanates, resulting in the methyl group adding to the carbon of the newly formed amidate chelate [Equation (1)].[51]

$$M(Me)_3Cl_2 \xrightarrow{RNCO} M(Me)Cl_2(NRC(O)Me)_2 \qquad (1)$$

M = Nb, Ta
R = Ph, Me

Analogous reactions occur with $[Cp_2ZrMe_2]$[52] and $Cp_2TiR$[51] complexes and various isocyanates to give complexes of the type **12** (Figure 6).

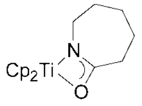


**12** **13**
M = Zr, Ti
P = polymer chain

Figure 6. Amidate complex resulting from reactions with isocyanates.

With respect to polymerization catalysis, complexes like **12** are relevant to more recent examples using $TiCl_3OCH_2CF_3$ and $CpTiCl_2L$ [L = $–OCH_2CF_3$, $–N(CH_3)_2$, $–CH_3$] as catalysts for the living polymerization of isocyanates.[53] It was proposed, based on IR spectroscopic analysis, that the propagating endgroup during chain growth is an amidate-Ti complex, **13** (Figure 6), with a chelating bonding motif.[53]

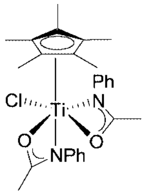
There have only been a few reports of titanium amidate chelates that were not formed as intermediates in organometallic reactions. One example includes the use of caprolactam as a precursor to form the titanium complex **14** (Figure 7), which is postulated to be an intermediate in the ring-opening polymerization of lactams to form polyamides.[54]



**14**

Figure 7. Example of a chelating lactamidate on titanium.

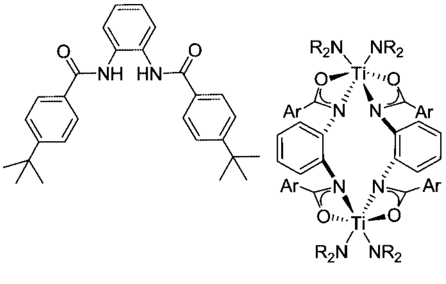
Another example of a sterically congested Cp*–Ti complex was synthesized by Stahl and co-workers, **15** (Figure 8), during investigations of $Ti^{IV}$-catalyzed transamidation.[55]



**15**

Figure 8. Chelating amidate complexes in transamidation investigations.

Finally, an example of a Ti complex with chelating amidates that did not contain any Cp ligands was described in 2001 by the Arnold group.[56] They employed a diamide proligand (Figure 9, left), which reacted cleanly with homoleptic titanium amides to generate a crystalline bimetallic complex **16** which maintained the chelating bonding motif.



**16**

Figure 9. Proligand and resultant bimetallic bis(amidate) complex.

The two reactive $NR_2$ groups on each Ti are oriented in a *cisoid* fashion to one another, and bond lengths indicate delocalization of the amidate double bond. These compounds were screened and showed modest activity for the polymerization of ethylene with methylalumoxane activation.[56]

While a large variety of amidate structures using different metal centers and bonding motifs have been reported in the literature, it is clear that little work has been disclosed using neutral amides as easily synthesized and readily modified precursors to amidate auxiliary ligands. In particular, the variation of electronic and steric effects within the amidate backbone and their impacts on the structural properties of early transition metal complexes had not been investigated, previous to our work in the area. Most importantly, the catalytic potential of these tunable complexes were largely unexplored. The remainder of this microreview will focus on our contributions in the area of amidate-supported group-4 complexes and their applications in hydroamination catalysis.

## Monomeric Chelating Amidate Complexes of Early Transition Metals

### Proligands

Amides are easily synthesized with a variety of steric and electronic properties as the starting materials, acid chlorides and amines, are inexpensive, and commercially available. Once deprotonated, the monoanionic amidate ligand can adopt a conformation to bind the metal in a chelating fashion, in which the anion is delocalized throughout the N,C,O backbone. The hard nature of both the donor atoms in combination with early transition metals suggests that the bonding in these complexes will be largely ionic in character.

The steric nature of both the groups on the carbonyl and on the nitrogen affects the resultant metal complex as the smaller the degree of steric bulk, the greater the possibility of synthesizing dimers and oligomers. Consequently, to minimize this possibility, a certain degree of steric bulk must be maintained in the ligand design.

There are five possible geometric isomers that can result from the formation of monomeric bis(amidate) complexes, as shown in Figure 10. This large number of potential isomers complicates spectral assignments and could be a reason why amidates have been largely overlooked as auxiliary ligands.

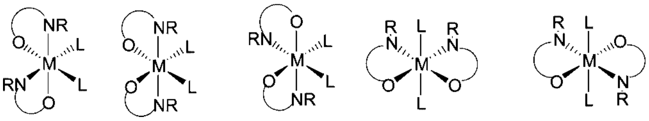
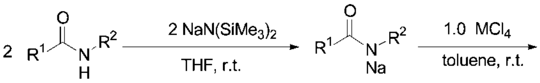


Figure 10. Possible coordination isomers of bis(amidate) complexes; L = chloro, alkyl, amido.

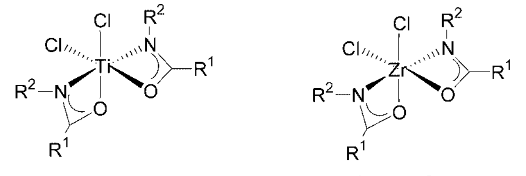
## Coordination Chemistry

### Bis(amidate) Dichloro Complexes

With several proligands in hand, we set out to make bis(amidate)metal dichloride complexes using group-4 metals such as titanium and zirconium. Metal chlorides of titanium and zirconium are inexpensive and readily available, making them attractive starting materials for the preparation of amidate supported organometallic complexes. However, we found salt metathesis with amide proligands to be very base dependent. For example, use of typical bases such as *n*BuLi, NaH, or KH resulted in only insoluble powders, while the Arnold group reported limited success with lithium bis(trimethylsilylamide).[56] However, use of sodium bis(trimethylsilylamide) resulted in a more general route for forming titanium dichlorides with several amidate ligands; see Equation (2) and Figure 11.[57]



$$2\ R^1C(O)N(H)R^2 \xrightarrow[\text{THF, r.t.}]{2\ NaN(SiMe_3)_2} R^1C(O)N(Na)R^2 \xrightarrow[\text{toluene, r.t.}]{1.0\ MCl_4} ML_2Cl_2 \quad (2)$$



**16a**: $R^1$ = Ph, $R^2$ = 2,6-di*i*Pr-$C_6H_3$
**16b**: $R^1$ = *t*Bu, $R^2$ = 2,6-diMe-$C_6H_3$
**16c**: $R^1$ = $C_6F_5$, $R^2$ = 2,6-di*i*Pr-$C_6H_3$
**16d**: $R^1$ = Ph, $R^2$ = 2,6-di*i*Pr-$C_6H_3$
**16e**: $R^1$ = *t*Bu, $R^2$ = adamantyl

Figure 11. Bis(amidate)titanium and -zirconium dichlorides formed through salt metathesis with $NaN(SiMe_3)_2$.

The sodium amidate salts, though isolated as crude materials, are used immediately without any further purification.

Many of these complexes have been crystallographically characterized[57] and an example (**16a**) is shown in Figure 12.

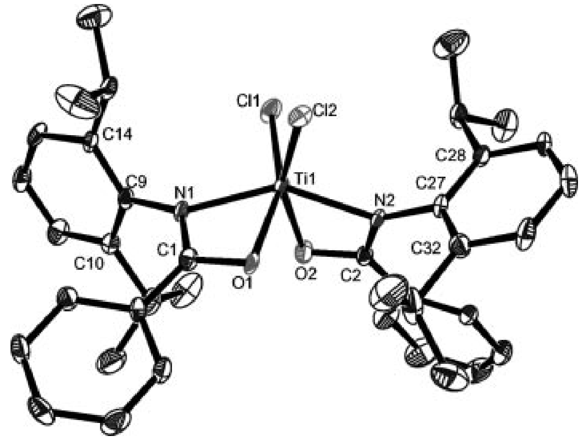
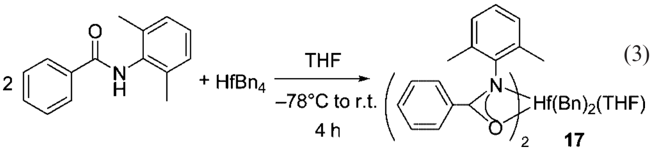


Figure 12. ORTEP plot of bis(amidate)titanium dichloride complex **16a**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Ti–O(1) 2.025(4), Ti–N(1) 2.087(5), Ti–Cl(1) 2.2479(19), O(1)–C(1) 1.313(7), N(1)–C(1) 1.304(8), Ti–N(1)–C(2) 121.6(2), O(1)–C(1)–N(1) 111.7(6).

Complex **16** is pseudo-octahedral and $C_2$ symmetric. The C–O and the C–N bond lengths in the amidate backbone are nearly identical [1.313(7) Å and 1.304(8) Å, respectively] suggesting significant electron delocalization. The Ti–O bond length [2.025(4) Å] is only slightly shorter then the Ti–N bond length [2.087(5) Å]. The Ti–Cl bond lengths of 2.2479(19) Å are typical.[8] The bulky diisopropyl-substituted aryl substituents of the *N*-groups on the amidate backbone are *trans* to one another.

### Bis(amidate) Bis(alkyl) Complexes

While transition metal dichloride complexes are flexible starting materials for the preparation of many different organometallic complexes, an alternative route into organometallic compounds is to start with a homoleptic alkyl metal complex in a protonolysis reaction. Synthesis of group-4 bis(alkyl) complexes with the amidate ligand is easily achieved using this reaction. For example, a protonolysis reaction between *N*-(2,6-dimethylphenyl)benzamide and $Hf(Bn)_4$ [Equation (3)] led to the fully characterized bis(amidate)-dibenzylhafnium complex **17**.[58]



Complex **17** exhibits pseudo-$C_{2v}$ symmetry in a slightly distorted pentagonal bipyramidal geometry. A THF molecule occupies the final equatorial coordination site, which, while bound in the solid state, is labile in solution phase. This complex is stable to heat and light, though sensitive to moisture, such that exposure of **17** to a small amount of adventious moisture led to the formation of an interesting tetrametallic bridged oxo species, in which the amidates adopted both a chelating and a bridging mode of metal coordination.[58] An analogous protonolysis reaction led to the bis(amidate)-dibenzyl-$Zr^{IV}$ complex **18** (Figure 13).

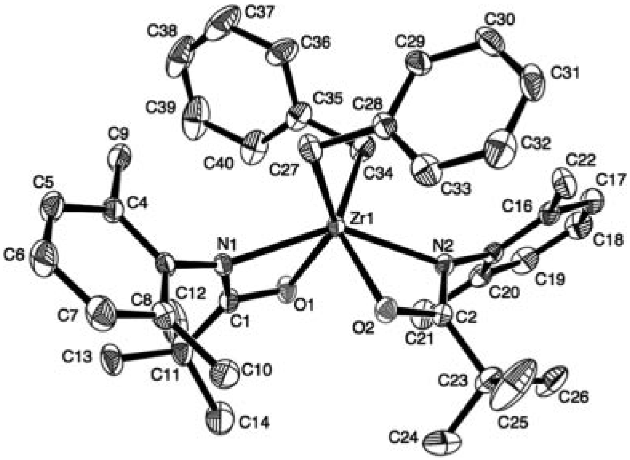
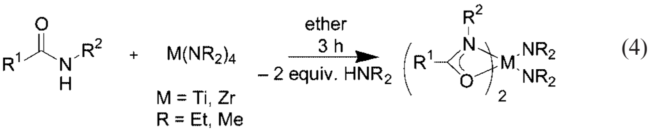


Figure 13. ORTEP plot of bis(amidate)-dibenzyl-zirconium complex (**18**). Selected bond lengths [Å] and angles [°]: Zr–O(1) 2.0988(13), Zr–O(2) 2.1080(13), Zr–N(1) 2.2836(14), Zr–N(2) 2.875(13), Zr–C(27) 2.2440(13), Zr–C(34) 2.2390(19), N(1)–C(1) 1.286(2), C(1)–O(1) 1.307(2), O(2)–Zr–N(2) 58.39(5), C(27)–Zr–C(34) 97.18, N(2)–C(2)–O(2) 112.29(14).

In contrast to the 7-coordinate **17**, **18** is a $C_2$-symmetric, slightly distorted octahedral compound that does not have a bound THF molecule in the solid state.

### Bis(amidate) Bis(amido) Complexes

The most widely synthesized and studied metal complexes in our laboratories are bis(amidate) bis(amido)-titanium and -zirconium complexes. These complexes are both precursors to other organometallic compounds and catalytically active species for synthetic transformations such as hydroamination. Bis(amidate) bis(amido) complexes of titanium and zirconium are easily synthesized in high yields by a protonolysis reaction as shown in Equation (4).



A wide variety of organic amides have been used for making these bis(amidate) bis(amido) complexes.[59] In general, amides containing alkyl groups on both the carbonyl and the nitrogen yield metal complexes that are oily and difficult to purify. A simple switch to a phenyl group on either the nitrogen or the carbonyl yields crystalline metal complexes suitable for X-ray analysis (**19**, Figure 14).

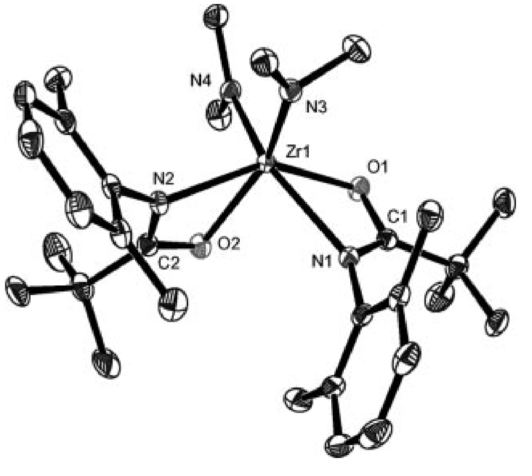
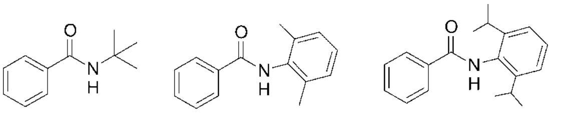


Figure 14. ORTEP plot of bis(amidate) bis(amido)-zirconium complex **19**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Zr–O(1) 2.1524(19), Zr–O(2) 2.201(2), Zr–N(1) 2.403(2), Zr–N(2) 2.3055(19), Zr–N(3) 2.038(3), Zr–N(4) 2.044(2), O(1)–Zr–N(1) 57.25(8), O(1)–C(1)–N(1) 113.8(3).

This $C_2$-symmetric compound **19** exhibits pseudo-octahedral geometry with the dimethylamido ligands oriented in a *cisoid* fashion, which is advantageous for catalytic applications. A switch to proligand *N*-*tert*-butylbenzamide yielded bis(amido) complexes of both titanium and zirconium as different geometric isomers, although the amido ligands remain *cis* to one another. A subsequent investigation kept the phenyl substituent on the carbonyl constant, and varied the steric properties of the nitrogen substituent as shown in Figure 15.[60]



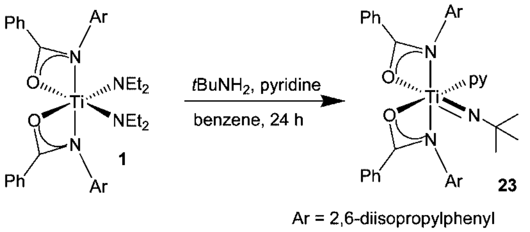
**20** **21** **22**

Figure 15. Proligands with varying degrees of steric bulk on the nitrogen.

Bis(amidate) bis(amido)-titanium complexes were formed using **20**–**22**, and characterized by X-ray crystallography. The steric properties of the proligand affect the geometric isomer observed in the solid state, such that the bulky substituent of **22** ensured that the *N*-substituents are *trans* to each other, in contrast to **20**, where the *N*-substituents are *cis*-oriented. DFT calculations were performed on these complexes in order to better understand the different possible coordination geometries and bonding interactions.[60] The calculations predicted the lowest energy isomers for proligands **20** and **22**, which also matched the structures observed in the solid state. However, in NMR spectroscopic investigations, fluxional behavior is observed suggesting that there is an interconversion between low-energy isomers.

## Bis(amidate) Imido Complexes

As the bis(amidate) bis(amido)-metal complexes proved to be easily accessed with this ligand set, we extended this chemistry further to synthesize bis(amidate) imido complexes. As well as exhibiting interesting coordination chemistry, these complexes are implicated as model systems of mechanistic intermediates (vide infra). The first reported characterized amidate-supported titanium–imido complex **23** was synthesized; see Equation (5).[61]



(5)

This reaction is general to this class of complexes and other terminal imido compounds **24** have been prepared using amidate auxiliary ligands (Figure 16).

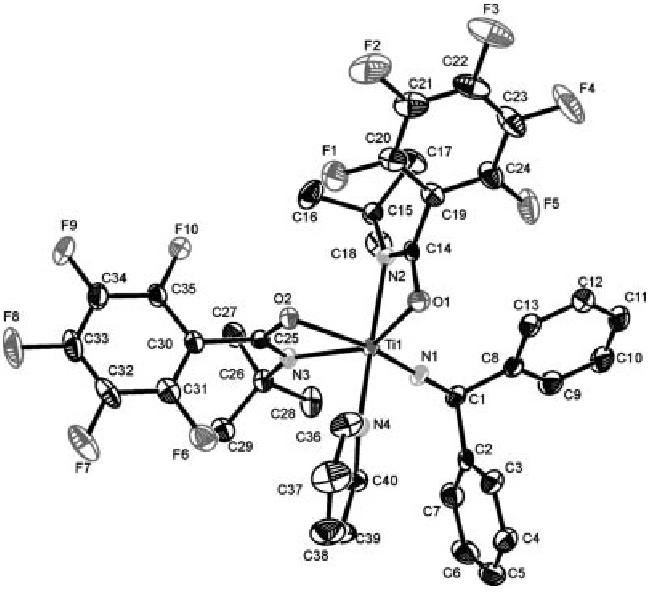
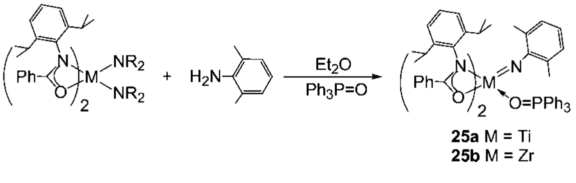


Figure 16. Solid-state molecular structure of bis(amidate) imido-titanium complex **24**. Hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [°]: Ti–N(5) 1.705(3), Ti–O(3) 2.259(2), Ti–O(4) 2.111(2), Ti–N(6) 2.125(3), Ti–N(7) 2.165(3), Ti–N(8) 2.214(3), C(41)–N(5)–Ti 176.3(2), O(3)–C(54)–N(6) 117.9(3).

These group-4 imido complexes can also be trapped with triphenylphosphane oxide as shown in Equation (6).



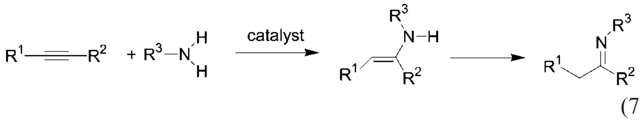
(6)

The solid-state molecular structure of the Zr-imido complex **25b** is of distorted pentagonal-pyramidal geometry where both the amidate and the TPPO ligands are pseudo-equatorial and the imido is in the axial position.[62]

Amidates are a modular ligand set and they have been used in the synthesis of a wide variety of metal complexes. The ease with which both the proligand and the metal complexes are synthesized makes this auxiliary ligand set very desirable for catalytic investigations. As both the steric and the electronic properties of the system can be readily varied, there is enormous potential for tuning of catalytic reactivity.

## Hydroamination Catalysis

One area in which early transition metal bis(amido) complexes have found wide-spread catalytic application is in hydroamination. Hydroamination is the addition of nitrogen and hydrogen across a carbon–carbon multiple bond such as an alkyne (shown), allene or alkene; see Equation (7).

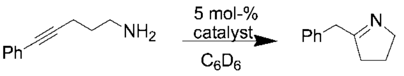


(7)

This leads to the formation of enamines, imines, and amines, which are important building blocks in pharmaceuticals, detergents, and dyes.[63] Furthermore, as many procedures for the synthesis of amines are multi-step and inefficient,[64] catalytic hydroamination has the potential to greatly improve existing methodology. There are no side products in this reaction, thus hydroamination can be used in a tandem reaction sequence, utilizing the imine as an in situ intermediate.[65–68] Following an initial report of titanium catalyzed hydroamination by Rothwell and coworkers,[69] research into hydroamination catalysis has also followed the trend of focusing on Cp-based ligand systems and then moving onto non-Cp-based catalysts. A variety of systems have been developed for hydroamination reactions including work from the groups of Bergman,[15,64,70–73] Livinghouse,[74,75] Odom,[67,76–81] Beller,[65,82–86] Doye,[87–94] ourselves,[59,61,62,95,96] and others.[11,97–105] The low toxicity, low cost, and high availability of group-4 metals make them attractive systems for catalytic applications.[106] To this end, we have established amidate complexes of Ti as tunable catalytic systems for highly reactive and regioselective hydroamination.

### Alkyne Hydroamination

Initial investigations into catalytic hydroamination began using three different proligands: *N*-*tert*-butyl-2-methylpropanamide (**26**), *N*-*tert*-butylbenzamide (**27**), and *N*-*tert*-butylperfluorophenylamide (**28**). Bis(amidate) bis(amido)-titanium and -zirconium complexes were synthesized and the tunable reactivity accessible through modification of the metal and electronic properties of the ligand is shown in Table 1 and Equation (8).



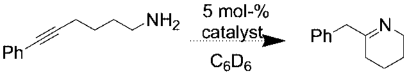
(8)

Table 1. Results for intramolecular hydroamination of alkynes.

| Entry | Proligand | Metal | *T* [°C] | *t* [h] | % Yield[a] |
|---|---|---|---|---|---|
| 1 | **27** | Zr | 60 | 24 | 95 |
| 2 | **28** | Zr | 60 | 7 | 98 |
| 3 | **26** | Ti | 25 | 14 | 99 |
| 4 | **27** | Ti | 25 | 3.5 | 98 |
| 5 | **28** | Ti | 25 | 0.25 | 97 |
| 6 | CpH | Ti | 110 | 4 | 90[b] |
| 7 | $HNMe_2$ | Ti | 25 | 0.5 | quant.[64] |

[a] NMR conversion vs. 1,3,5-trimethoxybenzene. [b] Reported yield for the isolated amine product after reduction of imine.

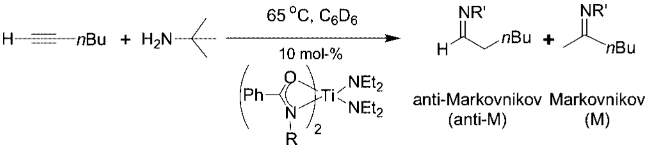
The titanium-based complexes were more active than the corresponding zirconium complexes. It is also apparent that electron-withdrawing substituents enhance the catalytic activity of the complex. Moreover, the most active species (Entry 5) is more active then both the corresponding Cp complex, and $Ti(NMe_2)_4$. As a further comparison to $Ti(NMe_2)_4$, a more challenging intramolecular substrate was attempted; see Equation (9).



(9)

In this case our system went to completion within 3 h at 40 °C whereas use of $Ti(NMe_2)_4$ only went to 30% completion in the same time period.

Encouraged by these initial findings, we set out to screen a number of our bis(amidate) bis(amido)-titanium complexes, particularly to see how steric bulk on the nitrogen would affect the catalytic activity. Furthermore, we wanted to investigate the more challenging intermolecular hydroamination reaction. This transformation can lead to the formation of two regioisomers and thus regioselectivity is also an important concern; see Equation (10) and Table 2.



(10)

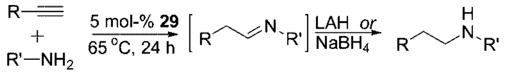
Table 2. Intermolecular hydroamination with tunable bis(amidate) bis(amido)-titanium precatalysts.

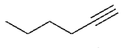
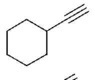
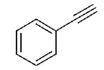
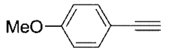
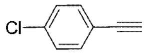
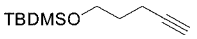
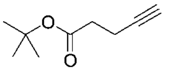
| Entry | R | *t* [h] | % Yield (*anti*-M:M)[a] |
|---|---|---|---|
| 1 | *i*Pr | 24 | no reaction |
| 2 | *t*Bu | 24 | 71 (5:1) |
| 3 | Ph | 24 | 55 (99:1) |
| 4 | 2,6-dimethylphenyl | 10 | 78 (>99:1) |
| 5 | 2,6-diisopropylphenyl | 6 | 82 (>99:1) |

[a] Yields were determined by $^1H$ NMR with an internal standard (1,3,5-trimethoxybenzene). Ratio confirmed by GCMS after hydrolysis.

The complex derived from the proligand with the bulkiest substituent on the nitrogen (Entry 5) was the most effective, giving the highest yield, the lowest reaction time and excellent regioselectivity. Most importantly, this complex **29** affected regioselective hydroamination, in high yield, with a broad range of substrates including the most challenging benzylamine substrate.[65] The wide range of alkynes and functional groups tolerated is illustrated in Table 3.

Table 3. Hydroamination of various terminal alkynes with alkylamines.



| Entry | Alkyne | Amine | % Yield[a] |
|---|---|---|---|
| 1 |  | BnNH$_2$ | 88 |
| 2 |  | *i*PrNH$_2$ | 88 |
| 4 |  | BnNH$_2$ | 87 |
| 5 |  | *i*PrNH$_2$ | 89 |
| 7 |  | BnNH$_2$ | 95 |
| 8 |  | *i*PrNH$_2$ | 82 |
| 9 |  | BnNH$_2$ | 87 |
| 10 |  | *i*PrNH$_2$ | 86 |
| 11 |  | BnNH$_2$ | 83 |
| 12 |  | BnNH$_2$ | 93 |
| 13 |  | BnNH$_2$ | 76 |
| 14 |  | BnNH$_2$ | 80 |

[a] Isolated yield.

In our initial investigations into hydroamination, it was noted that secondary amines did not lead to hydroamination products and only unreacted starting materials were recovered. This suggests that our system mediates alkyne hydroamination via an imido intermediate as elucidated by Bergman and co-workers in the early 90's (Figure 17).[73]

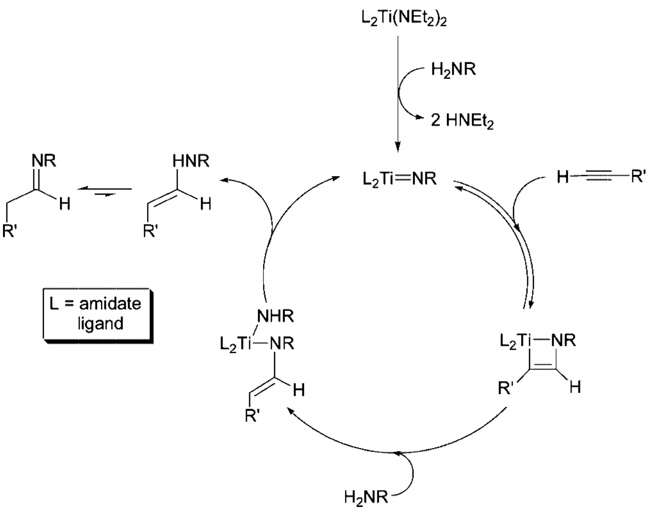


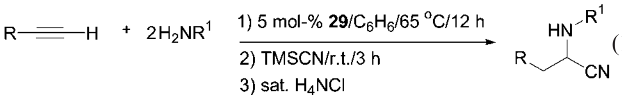
Figure 17. Proposed simplified catalytic cycle for alkyne hydroamination.

The bis(amido) precatalyst reacts with the primary amine to form the requisite titanium–imido complex. Coordination by the alkyne to this electrophilic metal center, followed by cycloaddition leads to the formation of titanaazacyclobutene. Protonation of the Ti–C bond by another equivalent of primary amine gives the enamide-amide complex, which then undergoes α-elimination to give the hydroamination product and regenerate the catalytically active imido species.

We have been successful in synthesizing titanium–imido complexes through reactions of the amido complexes with a stoichiometric amount of primary amine (vide supra). Our system forms the imido species very quickly such that when two hydroamination reactions are carried out side by side, one with the bis(amidate) bis(amido)-titanium precatalyst and the other with the bis(amidate) imido-titanium precatalyst, both show 50% product formation after approximately 50 min.[61] This is in contrast to many literature reports that state that there is a significant induction period required for conversion to the catalytically active imido complex.[70] We propose that the polarization of the M–N bonds and highly electrophilic metal center of the amidate complexes affects both the rate of conversion from the precatalyst to the imido complex, and the subsequent reactivity of this imido species. It is important to note that during all of the aforementioned reactions we have not observed any loss of the amidate ligands.

## Applications in Synthesis

The hydroamination of terminal alkynes with precatalyst **29** leads to the formation of synthetically useful aldimines. These often unstable intermediates are useful in organic chemistry for synthesizing other more complex molecules. For example, catalytic hydroamination has been combined with the Strecker reaction, to give a tandem C–N, C–C bond forming sequence for the synthesis of α-cyano amines; see Equation (11).[66]

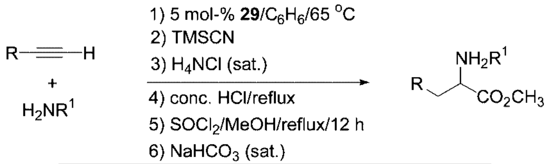


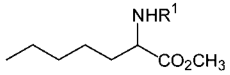
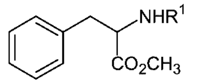
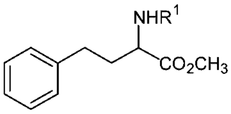
(11)

α-Cyano amines are useful molecules for the synthesis of diamines, amino acids, amino acid derivatives and amino alcohols. This methodology has been applied to the synthesis of a number of amino methyl esters that were synthesized in good overall yields (Table 4).

Precatalyst **29** has also been applied toward the synthesis of a number of biologically important molecules. For example substituted tetrahydroisoquinolines (THIQs), molecules that have promising biological and pharmacological properties, can be synthesized using hydroamination as a key step.[61] Hydroamination can also be used to construct the more complex tricyclic benzo[*a*]quinolizine framework in three tandem reactions (Figure 18).

Table 4. Yields of synthesized α-amino esters.



| α-Amino ester | $R^1$ | % Yield[a] |
|---|---|---|
|  | Bn<br>*i*Pr | 58<br>61 |
|  | Bn<br>*i*Pr | 58<br>54 |
|  | Bn<br>*i*Pr | 58<br>69 |

[a] Isolated yield calculated from terminal alkyne.

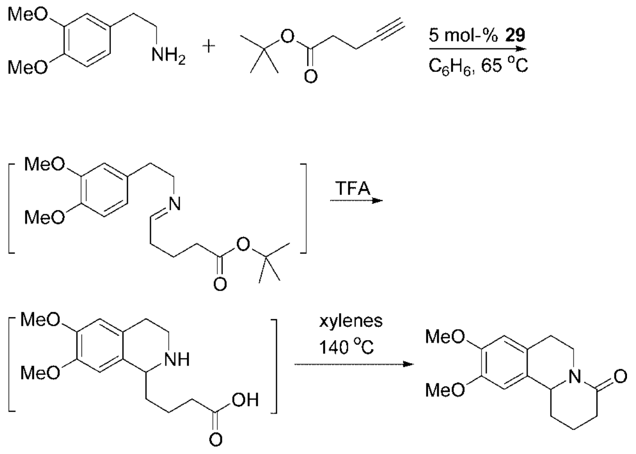


Figure 18. One pot synthesis of tricyclic benzo[*a*]quinolizine framework using hydroamination.

## Allene Hydroamination

The intermolecular hydroamination of allenes is notably more challenging then both the intramolecular hydroamination of allenes and the intermolecular hydroamination of alkynes.[15,64] This reaction can result in the formation of three regioisomers as shown in Figure 19.

While this transformation has received limited attention in the literature, in general it has been found that with early transition metals it is usually regioisomer **30** that is formed (in both the *E* and *Z* isomers).[15,70,73,98,104] With late transition metals, on the other hand, it is regioisomers **31** and **32** that are reported, and the double hydroamination side-product is also observed.[107–111] To begin our investigations into the hydroamination of allenes, we used our most active alkyne hydroamination catalyst, **29**, and investigated the hydroamination of aryl and alkyl allenes with a variety of amines (Table 5).

While these reactions were slower then the corresponding alkyne reactions, the products were formed in 7–24 h at 85–90 °C. In all cases, regioisomer **30** was observed as both the *E* and *Z* isomers. These first examples of intermolecular allene hydroamination with alkylamines require higher temperatures, but are compatible with primary amines of varying steric bulk.[112] The ketimine products isolated here contrast with the aldimine products obtained from terminal al-

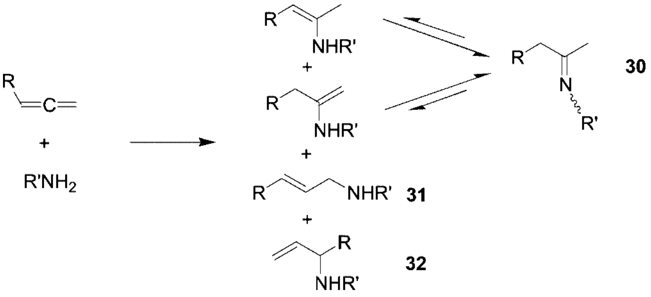
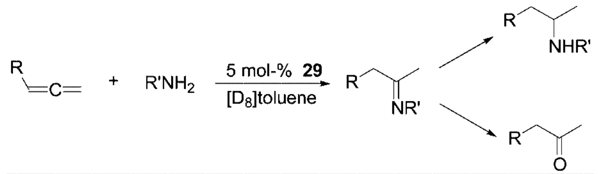
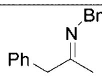
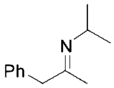
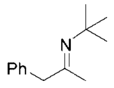
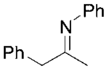
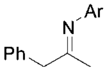
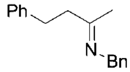
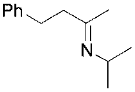
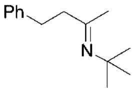
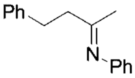
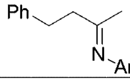


Figure 19. Possible regioisomers resulting from intermolecular allene hydroamination.

Table 5. Intermolecular hydroamination of alkyl- and arylallenes with arylamines (Ar = 2,6-dimethylaniline.).



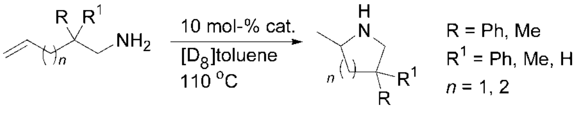
| Entry | R | $R^1$ | Product | Temp. (°C) | % Yield |
|---|---|---|---|---|---|
| 1 | Ph | Bn |  | 120 | 75[a] |
| 2 | Ph | *i*Pr |  | 120 | 65[a] |
| 3 | Ph | *t*Bu |  | 120 | 60[a] |
| 4 | Ph | Ph |  | 90 | 76[b] |
| 5 | Ph | Ar |  | 90 | 64[b] |
| 6 | Bn | Bn |  | 120 | 85[a] |
| 7 | Bn | *i*Pr |  | 120 | 91[a] |
| 8 | Bn | *t*Bu |  | 120 | 71[a] |
| 9 | Bn | Ph |  | 85 | 83[b] |
| 10 | Bn | Ar |  | 85 | 93[b] |

[a] Isolated yield of corresponding ketone product. [b] Isolated yield of the corresponding secondary amine.

kyne hydroamination. Interestingly, the allene substrates used here were prepared from terminal alkyne substrates.[111] Therefore, by judicious selection of the hydroamination substrate either the ketimine or the aldimine products can be selectively obtained with precatalyst **29**.

### Alkene Hydroamination

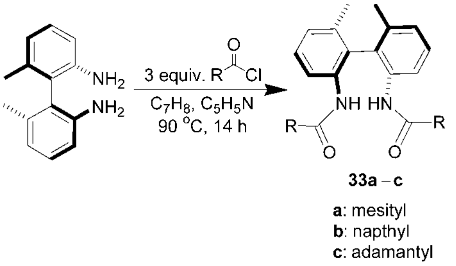
Alkene hydroamination is more challenging then both alkyne and allene hydroamination, and thus initial investigations have focused on the intramolecular hydroamination of aminoalkenes. In general, examples of group-4 metal complexes for alkene hydroamination are much less numerous than alkyne hydroamination. There have been a few reports of cationic group-4 complexes that can catalyze the hydroamination of secondary aminoalkenes.[113,114] These reactions are thought to proceed through a σ-bond insertion mechanism, analogous to the established mechanism for the isovalent lanthanide catalysts.[115,116] Furthermore, these cationic group-4 complexes are unable to catalyze the cyclization of primary aminoalkenes, an observation that was attributed to the formation of catalytically inactive imido complexes. Very recently there have been a few reported examples of neutral group-4 metal complexes for the hydroamination of primary aminoalkenes.[117,118] In light of these results, we wanted to investigate our bis(amidate) bis(amido) complexes for this reaction.[62] Intramolecular reactions can be carried out as shown in Equation (12).



(12)

Both the Ti complex **29** and the Zr analogue can catalyze this reaction, although the Zr complex is the more active. In order to probe the application of Zr-imido complexes for alkene hydroamination, we tested the bis(amidate) imido-metal complexes **25a**,**b** for this desirable hydroamination reaction. Again, both were active in this cyclization, and the Zr complex **25b** was more active then the Ti analogue **25a**. These are the first examples of isolable group-4 imido complexes for the hydroamination of alkenes. Kinetic experiments revealed that the reaction is first-order in catalyst, and first order in substrate. It was also shown that there was no appreciable difference in the half-lives for the bis(amido) and imido precatalysts, implying that both precatalysts share a common catalytically active species. Most importantly, there was no observed activity when these catalysts were used with secondary aminoalkenes. This further supports the imido complex as being the catalytically active species. Preliminary substrate scope investigations showed that both substituted pyrrolidine and piperidine complexes could be formed with this system.[62]

Catalytic asymmetric alkene hydroamination is an extremely attractive goal as it leads to the generation of enantioenriched α-chiral amines. To date, there is no general catalyst that can perform this reaction. Most breakthroughs in this area have been with rare-earth metal catalysts.[119–127] There have also been some chiral late-transition metals that have been investigated for enantioselective intermolecular hydroamination with activated alkene and alkyne substrates.[128–134] The cationic group-4 complexes that were mentioned in the preceding section are capable of asymmetric hydroamination of secondary aminoalkenes, albeit with modest enantioselectivities.[114] Very recently, Bergman and co-workers reported a number of neutral bis(amido)zirconium precatalysts for the asymmetric hydroamination of aminoalkenes which displayed *ee* values of up to 80%.[135] Our efforts in this area include the synthesis of tethered bis(amidate) ligands using 2,2′-diamino-6,6′-dimethylbiphenyl as the diamine backbone to control both the coordination isomerism and the chirality. Three different bis(amides) **33a–c** were synthesized with mesityl, naphthyl, and adamantyl substituents on the carbonyl; see Equation (13).



(13)

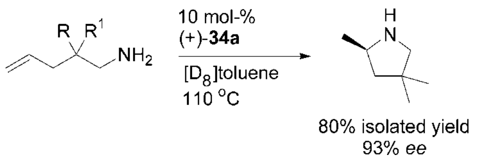
After synthesis of the proligands, neutral κ$^4$-tethered bis(amidate) bis(amido)-zirconium complexes were made to give precatalysts **34a–c** which were screened for catalytic activity in the test reaction shown below (Table 6).

Table 6. Screening for asymmetric hydroamination with precatalysts **34a–c**.

| Entry | Precatalyst | mol-% | *t* [h] | % Conversion[a] | % *ee*[b] |
|---|---|---|---|---|---|
| 1 | (+)-**34a** | 10 | 1.25 | >98 (93)[c] | 74 (*R*)[d] |
| 2 | (+)-**34b** | 10 | 18 | >98 | 31 |
| 3 | (+)-**34c** | 10 | 3 | >98 | 39 |
| 4 | (–)-**34a** | 10 | 1.25 | >98 (93)[c] | 72 (*S*)[d] |
| 5 | (+)-**34a** | 5 | 2.5 | >98 | 74 |

[a] Measured by $^1$H NMR spectroscopy. [b] Enantiomeric excess based on $^1$H NMR spectroscopy of the product following derivatization with (+)-(*S*)-α-methoxy-α-trifluoromethylphenylacetyl chloride. [c] Isolated yield. [d] Absolute stereochemistry assigned based on $^{19}$F NMR of the (+)-(*S*)-α-methoxy-α-trifluoromethylphenylacetyl chloride derivative.

The zirconium complex **34a** gave the highest *ee* values (74%) for this reaction. Comparable *ee* values could be obtained with the other enantiomer of the proligand (72%). When this optimized catalyst is used with the commonly tested dimethyl-substituted substrate [Equation (14)], a remarkable enantioselectivity of 93% was observed.[96] This complex was then fully characterized, and a solid-state molecular structure of the $HNMe_2$ adduct is shown in Figure 20.



(14)

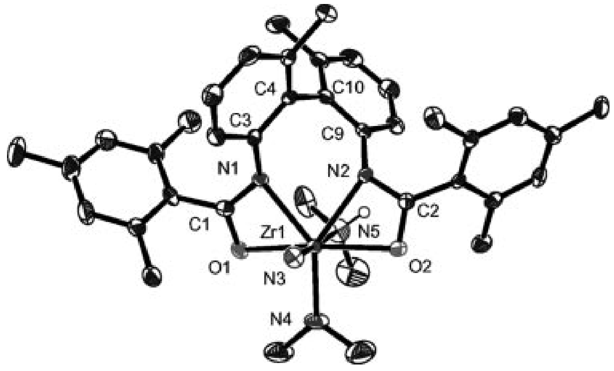


Figure 20. The ORTEP plot of (+)-**34a** (-$CH_3$ substituents omitted from the N4 dimethylamido ligand for clarity).

This is a seven-coordinate monomeric complex with distorted pentagonal-bipyramidal geometry.[96]

Investigations into the mechanism of this reaction are ongoing. As we understand more about how this reaction progresses, we can modify our ligand set to optimize reactivity and enantioselectivity. Ultimately, the goal is to design a precatalyst that would be capable of performing intermolecular alkene hydroamination leading to the general synthesis of enantioenriched α-chiral amines.

## Conclusions

As has been shown in this review, amidates are an excellent class of modular ligands for the synthesis of a wide variety of metal complexes, including catalytically active Group-4 compounds. Most importantly, the bis(amidate) bis(amido) and imido complexes have shown excellent catalytic reactivity for the hydroamination of alkynes, allenes, and alkenes. The ease of synthesis of the proligands has led to the facile tuning of catalytic reactivity and ready evaluation of structure–activity relationships. These catalytic systems show promise for the development of new catalysts that can be used for the synthesis of complex molecules with enantiomerically enriched α-chiral amines.

---

[1] R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965.
[2] R. Kempe, *Angew. Chem. Int. Ed.* **2000**, *39*, 468.
[3] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **1999**, *38*, 428.
[4] P. J. Stewart, A. J. Blake, P. Mountford, *Organometallics* **1998**, *17*, 3271.
[5] J. R. Hagadorn, J. Arnold, *J. Am. Chem. Soc.* **1996**, *118*, 893.
[6] J. R. Hagadorn, J. Arnold, *Inorg. Chem.* **1997**, *36*, 2928.
[7] J. R. Hagadorn, J. Arnold, *Organometallics* **1998**, *17*, 1355.
[8] A. Littke, N. Sleiman, C. Bensimon, D. S. Richeson, *Organometallics* **1998**, *17*, 446.
[9] M. R. Burgstein, H. Berberich, P. W. Roesky, *Organometallics* **1998**, *17*, 1452.
[10] H. V. R. Dias, W. Jin, Z. Wang, *Inorg. Chem.* **1996**, *35*, 6074.
[11] T. Ong, G. P. A. Yap, D. S. Richeson, *Organometallics* **2002**, *21*, 2839.
[12] M. P. Coles, P. B. Hitchcock, *Organometallics* **2003**, *22*, 5201.
[13] P. Bazinet, D. Wood, G. P. A. Yap, D. S. Richeson, *Inorg. Chem.* **2003**, *42*, 6225.
[14] S. Pritchett, P. Gantzel, P. J. Walsh, *Organometallics* **1999**, *18*, 823.
[15] L. Ackermann, R. G. Bergman, R. N. Loy, *J. Am. Chem. Soc.* **2003**, *125*, 11956.
[16] L. H. Gade, *Chem. Commun.* **2000**, 173.
[17] F. Basuli, B. C. Bailey, J. C. Huffman, D. J. Mindiola, *Chem. Commun.* **2003**, 1554.
[18] F. Basuli, J. Tomaszweski, J. C. Huffman, D. J. Mindiola, *J. Am. Chem. Soc.* **2003**, *125*, 10170.
[19] R. Baumann, W. M. Davis, R. R. Schrock, *J. Am. Chem. Soc.* **1997**, *119*, 3830.
[20] R. Duchateau, T. Tuinstra, E. A. C. Brussee, A. Meetsma, P. T. van Duijnen, J. H. Teuben, *Organometallics* **1997**, *16*, 3511.
[21] L. Liang, R. R. Schrock, W. M. Davis, *Organometallics* **2000**, *19*, 2526.
[22] H. Maumela, R. D. Hancock, L. Carlton, J. H. Reibenspies, K. P. Wainwright, *J. Am. Chem. Soc.* **1995**, *117*, 6698.
[23] A. T. Vlahos, E. I. Tolis, C. P. Raptopoulou, A. Tsohos, M. P. Sigalas, A. Terzis, T. A. Kabanos, *Inorg. Chem.* **2000**, *39*, 2977.
[24] H. J. Kruger, G. Peng, R. H. Holm, *Inorg. Chem.* **1991**, *30*, 734.
[25] H. F. Brito, O. L. Malta, M. C. F. C. Felinto, E. E. S. Teotonio, J. F. S. Menezes, C. F. B. Silva, C. S. Tomiyama, C. A. A. Carvalho, *J. Alloys Compd.* **2002**, *344*, 293.
[26] X. Zhou, L. Zhang, M. Zhu, R. Cai, L. Weng, *Organometallics* **2001**, *20*, 5700.
[27] Y. Huang, B. Huang, B. Ko, C. Lin, *J. Chem. Soc., Dalton Trans.* **2001**, 1359.
[28] A. Honda, K. M. Waltz, P. J. Carroll, P. J. Walsh, *Chirality* **2003**, *15*, 615.
[29] J. A. Broomhead, J. Evans, W. D. Grumley, M. Sterns, *J. Chem. Soc., Dalton Trans.* **1977**, 173.
[30] D. P. Fairlie, P. M. Angus, M. D. Fenn, W. G. Jackson, *Inorg. Chem.* **1991**, *30*, 1564.
[31] W. Chen, K. Matsumoto, *Inorg. Chim. Acta* **2003**, *342*, 88.
[32] A. D. Keramidas, A. B. Papaioannou, A. Vlahos, T. A. Kabanos, G. Bonas, A. Makriyannis, C. P. Raptopoulou, A. Terzis, *Inorg. Chem.* **1996**, *35*, 357.
[33] A. S. Borovik, T. M. Dewey, K. N. Raymond, *Inorg. Chem.* **1993**, *32*, 413.
[34] M. R. Maurya, S. J. J. Titinchi, S. Chand, *Catal. Lett.* **2003**, *89*, 219.
[35] M. R. Maurya, S. J. J. Titinchi, S. Chand, *J. Mol. Catal. A* **2004**, *214*, 257.
[36] A. Bino, F. A. Cotton, W. Kaim, *Inorg. Chem.* **1979**, *18*, 3030.
[37] W. Chen, F. Liu, T. Nishioka, K. Matsumoto, *Eur. J. Inorg. Chem.* **2003**, 4234.
[38] F. A. Cotton, L. M. Daniels, J. P. Donahue, C. Y. Liu, C. A. Murillo, *Inorg. Chem.* **2002**, *41*, 1354.
[39] K. J. Nelson, R. W. McGaff, D. R. Powell, *Inorg. Chim. Acta* **2000**, *304*, 130.
[40] T. N. Fedotova, G. N. Kuznetsova, K. L. Minacheva, I. B. Baranovskii, *Russ. J. Inorg. Chem.* **1997**, *42*, 1838.
[41] A. Dolmella, F. P. Intini, C. Pacifico, G. Padovano, G. Natile, *Polyhedron* **2002**, *21*, 275.
[42] T. Abe, H. Moriyama, K. Matsumoto, *Inorg. Chem.* **1991**, *30*, 4198.

[43] K. Matsumoto, J. Matsunami, K. Mizuno, H. Uemura, *J. Am. Chem. Soc.* **1996**, *118*, 8959.
[44] Y. Lin, S. Takeda, K. Matsumoto, *Organometallics* **1999**, *18*, 4897.
[45] Y. Lin, H. Misawa, J. Yamada, K. Matsumoto, *J. Am. Chem. Soc.* **2001**, *123*, 569.
[46] K. Matsumoto, Y. Nagai, J. Matsunami, K. Mizuno, T. Abe, R. Somazawa, J. Kinoshita, H. Shimura, *J. Am. Chem. Soc.* **1998**, *120*, 2900.
[47] D. J. Timmons, M. P. Doyle, *J. Organomet. Chem.* **2001**, *617–618*, 98.
[48] M. P. Doyle, S. B. Davies, W. Hu, *Org. Lett.* **2000**, *2*, 1145.
[49] M. P. Doyle, I. M. Phillips, W. Hu, *J. Am. Chem. Soc.* **2001**, *123*, 5366.
[50] J. M. Hoerter, K. M. Otte, S. H. Gellman, S. S. Stahl, *J. Am. Chem. Soc.* **2006**, *128*, 5177.
[51] P. Braunstein, D. Nobel, *Chem. Rev.* **1989**, *89*, 1927.
[52] S. Gambarotta, S. Strologo, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1985**, *24*, 654.
[53] T. E. Patten, B. M. Novak, *J. Am. Chem. Soc.* **1996**, *118*, 1906.
[54] P. Arndt, C. Lefeber, R. Kempe, A. Tillack, U. Rosenthal, *Chem. Ber.* **1996**, *129*, 1281.
[55] D. A. Kissounko, I. A. Guzei, S. H. Gellman, S. S. Stahl, *Organometallics* **2005**, *24*, 5208.
[56] G. R. Giesbrecht, A. Shafir, J. Arnold, *Inorg. Chem.* **2001**, *40*, 6069.
[57] Manuscript in preparation.
[58] R. K. Thomson, B. O. Patrick, L. L. Schafer, *Can. J. Chem.* **2005**, *83*, 1037.
[59] C. Li, R. K. Thomson, B. Gillon, B. O. Patrick, L. L. Schafer, *Chem. Commun.* **2003**, 2462.
[60] R. K. Thomson, F. E. Zahariev, Z. Zhang, B. O. Patrick, Y. A. Wang, L. L. Schafer, *Inorg. Chem.* **2005**, *44*, 8680.
[61] Z. Zhang, D. C. Leitch, M. Lu, B. O. Patrick, L. L. Schafer, *Chem. Eur. J.* **2007**, *13*, 2012.
[62] K. T. Thomson, J. A. Bexrud, L. L. Schafer, *Organometallics* **2006**, *25*, 4069.
[63] P. W. Roesky, T. E. Muller, *Angew. Chem. Int. Ed.* **2003**, *42*, 2708.
[64] L. Ackermann, R. G. Bergman, *Org. Lett.* **2002**, *4*, 1475.
[65] A. Tillack, I. G. Castro, C. G. Hartung, M. Beller, *Angew. Chem. Int. Ed.* **2002**, *41*, 2541.
[66] A. V. Lee, L. L. Schafer, *Synlett* **2006**, 2973.
[67] C. Cao, Y. Shi, A. L. Odom, *Org. Lett.* **2002**, *4*, 2853.
[68] L. Ackermann, L. T. Kaspar, C. J. Gschrei, *Chem. Commun.* **2004**, 2824.
[69] J. E. Hill, R. D. Profilet, P. E. Fanwick, I. P. Rothwell, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 664.
[70] J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 2923.
[71] L. L. Anderson, J. Arnold, R. G. Bergman, *J. Am. Chem. Soc.* **2005**, *127*, 14542.
[72] A. M. Baranger, P. J. Walsh, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 2753.
[73] P. J. Walsh, A. M. Baranger, R. G. Bergman, *J. Am. Chem. Soc.* **1992**, *114*, 1708.
[74] P. L. McGrane, M. Jensen, T. Livinghouse, *J. Am. Chem. Soc.* **1992**, *114*, 5459.
[75] D. FairFax: , M. Stein, T. Livinghouse, M. Jensen, *Organometallics* **1997**, *16*, 1523.
[76] Y. Li, Y. Shi, A. L. Odom, *J. Am. Chem. Soc.* **2004**, *126*, 1794.
[77] B. Ramanathan, A. J. Keith, D. Armstrong, A. L. Odom, *Org. Lett.* **2004**, *6*, 2957.
[78] C. Cao, J. T. Ciszewski, A. L. Odom, *Organometallics* **2001**, *20*, 5011.
[79] A. L. Odom, *Dalton Trans.* **2005**, 225.
[80] C. Cao, Y. Li, Y. Shi, A. L. Odom, *Chem. Commun.* **2004**, 2002.
[81] Y. Shi, C. Hall, J. T. Ciszewski, C. Cao, A. L. Odom, *Chem. Commun.* **2003**, 586.
[82] A. Tillack, V. Khedkar, M. Beller, *Tetrahedron Lett.* **2004**, *45*, 8875.
[83] V. Khedkar, A. Tillack, M. Beller, *Org. Lett.* **2003**, *5*, 4767.
[84] I. G. Castro, A. Tillack, C. G. Hartung, M. Beller, *Tetrahedron Lett.* **2003**, *44*, 3217.
[85] A. Tillack, H. Jiao, I. G. Castro, C. G. Hartung, M. Beller, *Chem. Eur. J.* **2004**, *10*, 2409.
[86] F. Pohlki, I. Bytschkov, H. Siebeneicher, A. Heutling, W. A. Konig, S. Doye, *Eur. J. Org. Chem.* **2004**, 1967.
[87] K. Marcsekova, B. Wegener, S. Doye, *Eur. J. Org. Chem.* **2005**, 4843.
[88] A. Heutling, F. Pohlki, S. Doye, *Chem. Eur. J.* **2004**, *10*, 3059.
[89] F. Pohlki, A. Heutling, I. Bytschkov, T. Hotopp, S. Doye, *Synlett* **2002**, *5*, 799.
[90] F. Pohlki, S. Doye, *Angew. Chem. Int. Ed.* **2001**, *40*, 2305.
[91] E. Haak, H. Siebeneicher, S. Doye, *Org. Lett.* **2000**, *2*, 1935.
[92] E. Haak, I. Bytschkov, S. Doye, *Angew. Chem. Int. Ed.* **1999**, *38*, 3389.
[93] I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2001**, 4411.
[94] I. Bytschkov, S. Doye, *Tetrahedron Lett.* **2002**, *43*, 3715.
[95] Z. Zhang, L. L. Schafer, *Org. Lett.* **2003**, *5*, 4733.
[96] M. C. Wood, D. C. Leitch, C. S. Yeung, J. A. Kozak, L. L. Schafer, *Angew. Chem. Int. Ed.* **2007**, *46*, 354.
[97] C. Lorber, R. Choukroun, L. Vendier, *Organometallics* **2004**, *23*, 1845.
[98] J. M. Hoover, J. R. Petersen, J. H. Pikul, A. R. Johnson, *Organometallics* **2004**, *23*, 4614.
[99] L. Ackermann, L. T. Kaspar, C. J. Gschrei, *Org. Lett.* **2004**, *6*, 2515.
[100] L. Ackermann, *Organometallics* **2003**, *22*, 4367.
[101] M. A. Esteruelas, A. M. Lopez, A. C. Mateo, E. Onate, *Organometallics* **2006**, *25*, 1448.
[102] E. Smolensky, M. Kapon, M. S. Eisen, *Organometallics* **2005**, *24*, 5495.
[103] H. Wang, H. Chan, Z. Xie, *Organometallics* **2005**, *24*, 3772.
[104] J. R. Petersen, J. M. Hoover, W. S. Kassel, A. L. Rheingold, A. R. Johnson, *Inorg. Chim. Acta* **2005**, *358*, 687.
[105] B. D. Ward, A. Maisse-Francois, P. Mountford, L. H. Gade, *Chem. Commun.* **2004**, *6*, 704.
[106] I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2003**, 935.
[107] D. Lathbury, T. Gallagher, *J. Chem. Soc., Chem. Commun.* **1986**, 114.
[108] S. Arseniyadis, J. Sartoretti, *Tetrahedron Lett.* **1985**, *26*, 729.
[109] L. Besson, J. Gore, B. Cazes, *Tetrahedron Lett.* **1995**, *36*, 3857.
[110] M. Al-Masum, M. Meguro, Y. Yamamoto, *Tetrahedron Lett.* **1997**, *38*, 6071.
[111] M. Meguro, Y. Yamamoto, *Tetrahedron Lett.* **1998**, *39*, 5421.
[112] R. O. Ayinla, L. L. Schafer, *Inorg. Chim. Acta* **2006**, 3097.
[113] D. V. Gribkov, K. C. Hultzsch, *Angew. Chem. Int. Ed.* **2004**, *43*, 5442.
[114] P. D. Knight, I. Munslow, P. N. O'Shaughnessy, P. Scott, *Chem. Commun.* **2004**, 894.
[115] S. Hong, T. J. Mark, *Acc. Chem. Res.* **2004**, *37*, 673.
[116] M. R. Gagne, T. J. Mark, *J. Am. Chem. Soc.* **1989**, *111*, 4108.
[117] J. A. Bexrud, J. D. Beard, D. C. Leitch, L. L. Schafer, *Org. Lett.* **2005**, *7*, 1959.
[118] H. Kim, P. H. Lee, T. Livinghouse, *Chem. Commun.* **2005**, 5205.
[119] N. Meyer, A. Zulys, P. W. Roesky, *Organometallics* **2006**, *25*, 4179.
[120] D. V. Gribkov, K. C. Hultzsch, F. Hampel, *J. Am. Chem. Soc.* **2006**, *128*, 3748.
[121] D. Riegert, J. Collin, A. Meddour, E. Schulz, A. Trifonov, *J. Org. Chem.* **2006**, *71*, 2514.
[122] K. C. Hultzsch, D. V. Gribkov, F. Hampel, *J. Organomet. Chem.* **2005**, *690*, 4441.
[123] J. Y. Kim, T. Livinghouse, *Org. Lett.* **2005**, *7*, 1737.
[124] J. Collin, J. Daran, O. Jacquet, E. Schulz, A. Trifonov, *Chem. Eur. J.* **2005**, *11*, 3455.

[125] S. Hong, S. Tian, M. V. Metz, T. J. Mark, *J. Am. Chem. Soc.* **2003**, *125*, 14768.
[126] P. N. O'Shaughnessy, P. D. Knight, C. Morton, K. M. Gillespie, P. Scott, *Chem. Commun.* **2003**, 1770.
[127] P. N. O'Shaughnessy, P. Scott, *Tetrahedron: Asymmetry* **2003**, *14*, 1979.
[128] K. K. Hii, *Pure Appl. Chem.* **2006**, *78*, 341.
[129] N. T. Patil, L. M. Lutete, H. Wu, N. K. Pahadi, I. D. Gridnev, Y. Yamamoto, *J. Org. Chem.* **2006**, *71*, 4270.
[130] L. M. Lutete, I. Kadota, Y. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 1622.
[131] S. Gischig, A. Togni, *Eur. J. Inorg. Chem.* **2005**, 4745.
[132] L. Fadini, A. Togni, *Chem. Commun.* **2003**, 30.
[133] O. Loeber, M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 4366.
[134] R. Dorta, P. Egli, F. Zurcher, A. Togni, *J. Am. Chem. Soc.* **1997**, *119*, 10857.
[135] D. A. Watson, M. Chiu, R. G. Bergman, *Organometallics* **2006**, *25*, 4731

Received: January 11, 2007