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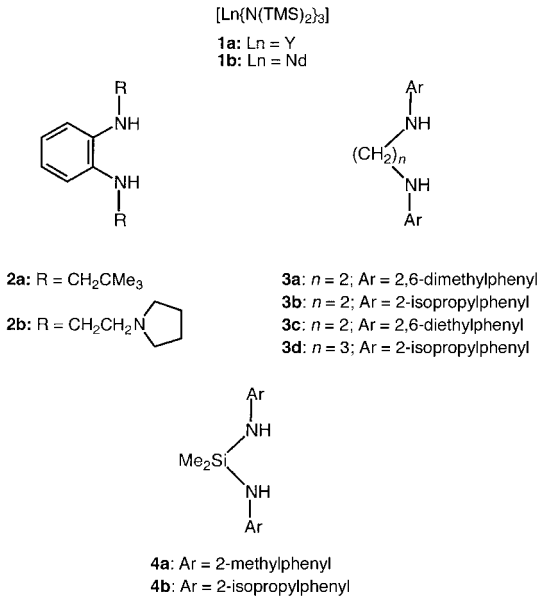
Exceptional Rate Enhancements and Improved Diastereoselectivities through Chelating Diamide Coordination in Intramolecular Alkene Hydroaminations Catalyzed by Yttrium and Neodymium Amido Complexes**

Young Kwan Kim and Tom Livinghouse*

The catalyzed intramolecular hydroamination of carbon–carbon multiple bonds is one of the most important methods for the synthesis of nitrogen heterocycles.[1] Of the variety of metal-based catalysts for this transformation, complexes of the lanthanides appear uniquely well suited for effecting chemoselective alkene hydroaminations under mild reaction conditions.[2,3] The vast majority of the complexes that have found utility for this purpose are comparatively air- and moisture-sensitive metallocene derivatives. We recently disclosed that simple amido derivatives of the Group 3 metals corresponding to the formula $[Ln\{N(TMS)_2\}_3]$ (**1**; Ln = lanthanide, TMS = trimethylsilyl) are competent catalysts for intramolecular alkene hydroamination.[4] Herein we show that catalytic activity can be dramatically increased and cyclization diastereoselectivity improved by coordination of the active metal center to simple chelating diamide ligands (Scheme 1).

As part of our previous study,[4] we noted that the addition of representive amino alkenes to catalytic quantities



Scheme 1. Ligands for lanthanide complexes **1** employed in this study.

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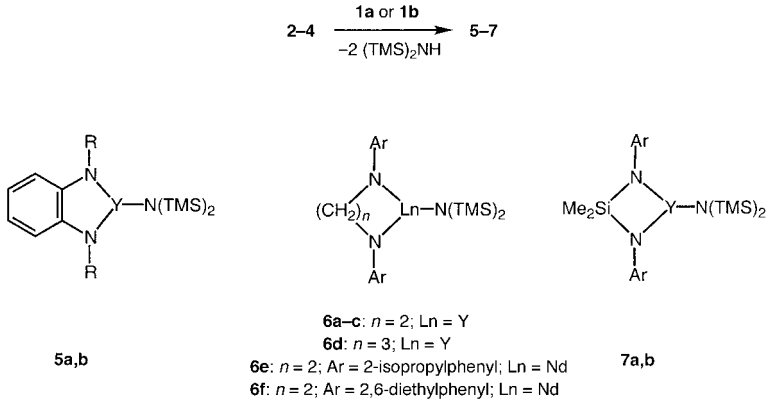
(2.7 mol%) of **1a** or **1b** in C_6D_6 at 24°C resulted in the immediate and apparently quantitative liberation of $(TMS)_2NH$ with concomitant generation of the corresponding and presumably amine-ligated[5] amido complexes. It is well established that the catalytic activity of group 3 metallocenes in alkene hydroamination is quite sensitive to steric perturbations about the metal center.[2a–c] In light of this, we set out to determine the role that sterically hindered chelating diamide ligands might play in altering the reactivity profile of group 3 amido complexes (Scheme 2).

The ligand motifs that were selected for evaluation in this study fell into three categories corresponding to the easily accessible diamines **2**–**4**. The selection of these was based on the consideration that aryl amine moieties would be sufficiently acidic to be irreversibly metallated by bis(trimethylsilyl) amides such as **1a**.[4] This proved to be the case as exposure of **2**–**4** to 1 equiv of **1a** in C_6D_6 or [D_8]toluene led to



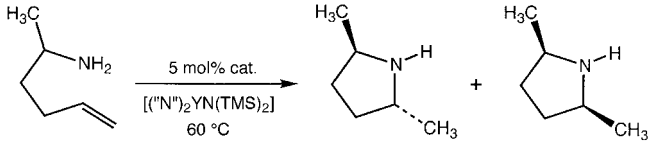
Scheme 2. Formation of the complexes **5**–**7**.

smooth elimination of $(TMS)_2NH$ with simultaneous formation of the yttrium chelates **5**, **6a**–**d**, and **7**.[6,7] The neodymium complexes **6e** and **6f** were obtained from **1b** in an analogous manner.

The catalytic activity of these complexes relative to that of **1a** was first examined in the diastereoselective cyclization of the racemic amino alkene **8**. Whereas the cyclization of **8** to the pyrrolidines **9a** and **9b** in the presence of 5 mol% of **1a** at 60°C was extremely slow, requiring 31 days to reach 95% conversion (**9a**:**9b** = 9:1),[8] cyclization was >95% complete in 15 min at 60°C in the presence of 5 mol% of **6b** (**9a**:**9b** = 19:1). Related catalytic activity enhancements for the chelate complexes **5**–**7** were clearly apparent in an allied series of intramolecular hydroaminations. A compilation of reaction times and diastereoselectivities observed for the cyclization of amino alkene **8** in the presence of the yttrium chelates **5**–**7** appears in Table 1.

Several of the above results are worthy of comment. Five-membered chelates derived from the sterically hindered diamines **3a** and **3b** are clearly superior in activity relative to complex **5a**. The incorporation of secondary ligating domains, as in complex **5b**, results in decreased conversion rates but improved diastereoselectivities compared to those of chelate structures such as **5a** that possess simple alkyl

Table 1. Catalyzed cyclizations of 2-aminohex-5-ene (**8**).



8 **9a** **9b**

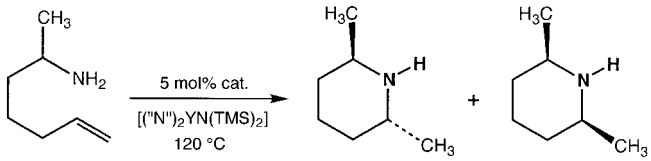
Complex	$t_{React.}$[a]	d.r. (**9a**:**9b**)	Conv. [%][b]
1a	744 h	9:1	>95
5a	51 h	11:1	>95
5b	84 h	19:1	>95
6a	70 min	19:1	>95
6b	15 min	19:1	>95
6d	42 h	11:1	>95
7a	11 h	19:1	>95
7b	2 h	16:1	>95

[a] All reactions were conducted at 60°C. [b] Based on ^{1}H NMR integration.

substituents. Opening of the coordination sphere at the yttrium center by the use of diamines **4a**,**b** that form four-membered chelates results in catalysts (e.g., **7a**,**b**) possessing somewhat lower activity. Six-membered chelates (e.g., **6d**) reminiscent of the zirconium complexes reported by McConville and co-workers[9] are comparatively inferior in terms of activity as well as stereoselectivity. Complexes **5a** and **6a**–**c** were next examined for the diastereoselective cyclization of amino alkene **10** to the piperidines **11a** and **11b** (Table 2). Although these reactions were in general slower and less stereoselective than those involving amino alkene **8**, similar trends in catalytic activity were observed, with **6a**–**c** showing the highest activities. The notable activity of complex **6c** as compared to **6a** or **6b** in this transformation further emphasizes the sensitivity of intramolecular alkene hydroamination to steric perturbations within the ligand domain.

1,2-Disubstituted alkenes have been shown to be the least reactive carbon–carbon double bond substrates toward intramolecular hydroamination thus far.[2c] Despite this, amino alkene **12**[10] was efficiently converted into pyrrolidine **13** at 125°C over 12, 11 and 6.5 hours, respectively, in the presence

Table 2. Catalyzed cyclizations of 2-aminohept-6-ene (**10**).



10 **11a** **11b**

Complex	$t_{react.}$[a]	d.r. (**11a**:**11b**)	Conv. [%][b]
5a	10 h	1:4	>95
6a	45 min	1:4	>95
6b	95 min	1:5	>95
6c	<15 min	1:4	>95

[a] All reactions were conducted at 120°C. [b] Based on integration of the ^{1}H NMR spectrum.

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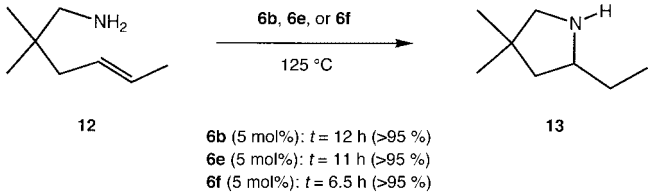
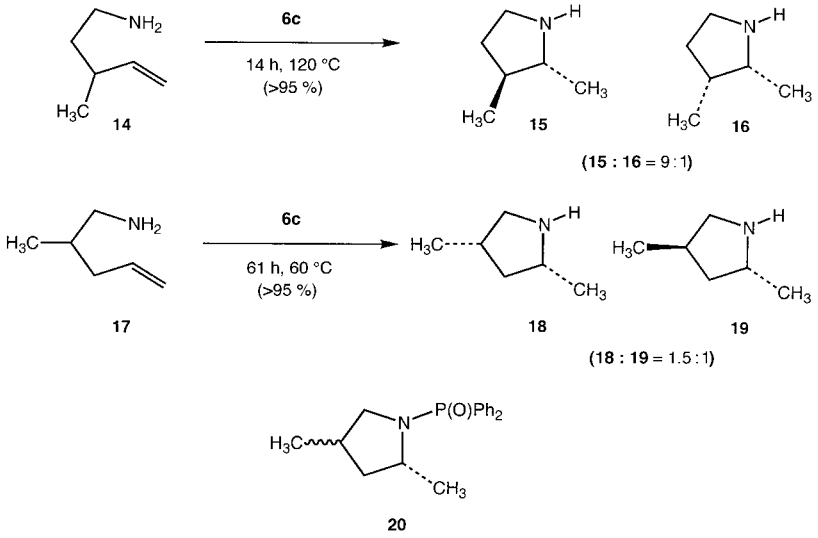


Scheme 3. A 1,2-disubstituted alkene (**12**) as a substrate for the intramolecular hydroamination.

of 5 mol% of **6b**, **6e** or **6f** (Scheme 3). These results are noteworthy as the catalytic activities of these first-generation chelates are comparable, and in the case of **6f**, superior to those of the sensitive and more difficultly accessible metallocene complexes described by Marks and co-workers.[2c]

To estimate the substrate control of diastereoselectivity during the formation of substituted pyrrolidines, the amino alkenes **14**[11] and **17**[11] were subjected to cyclization in the presence of 5 mol% of **6c** (Scheme 4).[12] In the case of **14**, the



Scheme 4. Cyclizations of substituted 1-aminopent-4-enes.

2,3-disubstituted pyrrolidines **15** and **16** were formed in a ratio of 9:1 (> 95% yield by NMR spectroscopy, 81% isolated as the *p*-toluenesulfonamides). As expected, the cyclization of **17** proved less selective, providing the pyrrolidines **18** and **19** with a *cis*/*trans* ratio of 1.5. In this case, the corresponding phosphonamides **20** were secured in 99% yield.[13]

In conclusion, we have demonstrated that modification of the metal center in $[Ln\{N(TMS)_2\}_3]$ (Ln = Y, Nd) is readily achieved by amine elimination in the presence of sterically hindered chelating diamines, in situ, to provide complexes possessing substantially augmented catalytic activities and improved stereoselectivities in intramolecular alkene hydroamination. The utilization of this strategy for the synthesis of chiral Group 3 amido complexes and their use in the asymmetric variation of this reaction in addition to its application to the construction of naturally occurring polyfused ring systems will be the topics of future accounts.

Experimental Section

General procedure for intramolecular alkene hydroaminations: In an argon-filled glove box, $[Ln\{N(TMS)_2\}_3]$ (1.6×10^{-5} mol) and the appropriate diamine (1.6×10^{-5} mol) were introduced into an NMR tube (J. Young) equipped with a teflon screw cap, and then C_6D_6 or $[D_8]$toluene (0.7 mL) was added. The homogeneous reaction mixture was heated to 120°C (C_6D_6) or 150°C ($[D_8]$toluene) to effect ligand exchange until the peak of $[Ln\{N(TMS)_2\}_3]$ had disappeared with concomitant generation of free $(TMS)_2NH$. The appropriate amino alkene (3.2×10^{-4} mol) was added to the resulting complex and the reaction mixture was subsequently heated at 60, 120, or 125°C in an oil bath. ^1H NMR spectroscopy (with a pulse delay of 10 s to avoid signal saturation) was employed to monitor the reactions.

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[7] Metallation of the hindered diamines **3a**,**b** through amine elimination is comparatively slow relative to **2**.

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