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Highly Active and Diastereoselective *N,O*- and *N,N*-Yttrium Complexes for Intramolecular Hydroamination

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Abstract: The intramolecular hydroamination of aminoalkynes and unactivated aminoalkenes catalyzed by yttrium *N,O*- and *N,N*-complexes has been investigated. The *N,N*-yttrium complexes are highly active, catalyzing the conversion of a wide range of terminal aminoalkenes at room temperature, and internal aminoalkenes at elevated temperature, to yield pyrrolidine and piperidine products in high yields. A high diastereoselectivity of up to 23:1 is observed at 0 °C with 1-methyl-4-pentenylamine as substrate.

Keywords: cyclohydroamination; hydroamination; rare earth metals; yttrium

Introduction

The hydroamination reaction (addition of N–H across a carbon-carbon multiple bond) is a very powerful and efficient method for C–N bond formation.[1] In particular, intramolecular hydroamination is a very selective and atom economic reaction to synthesize nitrogen heterocycles, which play an important role in material and life sciences.[2] Pioneering work in the development of catalytic inter- and intramolecular hydroamination reactions was conducted by Marks and co-workers[3] using rare earth elements, while Bergman achieved this transformation using group 4 metals.[4] Further research in the field by Livinghouse,[5] Odom,[6] ourselves[7] and others[8] has focused on non-cyclopentadienyl (non-Cp) ligands in combination with a broad range of metals. Our research group has shown that commercially available Ti(NMe_2)$_4$[9] is an effective precatalyst for the intramolecular hydroamination of unactivated olefins, and we have also disclosed one of the first applications of scandium as a reactive metal with *N,O*- and *N,N*-chelating ligands for alkene hydroamination.[10] In this work we have observed that improved access to the metal coordination sphere improves reactivity. Thus, when the smaller scandium complexes or Ti(NMe_2)$_4$ are used as catalysts for intramolecular hydroamination, reaction temperatures of 65 to 110 °C are typically required.

Indeed the impact of ionic radius upon reactivity in rare earth complexes has been investigated by Marks for a series of related Cp* (C_5Me_5) ligated complexes.[8f,11] These investigations showed that increased ionic radius results in higher turnover frequencies. Furthermore, modification of the ligand environment to include constrained geometry organolanthanide catalysts {CGC, $Me_2Si[\eta^5$-$C_5Me_4)(t$-BuN)]LnN($SiMe_3$)} revealed that less sterically demanding ligand sets also result in improved reactivity.[12] Thus, as non-Cp derived systems have emerged as easily tunable catalyst systems,[1] the variable steric bulk of different ligand sets can be used to advantage to promote desirable reactivity and selectivity trends.

Compared to scandium, yttrium has a larger ionic radius and thus the coordination sphere is more accessible in these systems. Furthermore, by varying the number of auxiliary ligands, the steric accessibility of the coordination sphere can be further tuned. Here we present highly active and diastereoselective *N,O*- and *N,N*-chelated yttrium complexes for the room temperature intramolecular hydroamination of a wide range of terminally substituted aminoalkynes and aminoalkenes.[13] This series of complexes further illustrates the influence of steric effects upon reactivity trends in rare earth cyclohydroamination catalysis.

Results and Discussion

Metal Complexes

Preferred ligand sets for non-Cp rare earth hydroamination precatalyst synthesis include a variety of *N* and/or *O* bound ligands such as amides,[5a,14] aryloxides,[15] guanidinates,[14a] amidates,[16] and β-diketiminate derived systems.[8f,10,17] Very reactive and selective *N,S*-chelating complexes have also been used to advantage for selective hydroamination catalysis.[5c,e] While high reactivities are typically observed for aminoalkyne and aminoalkene intramolecular hydroamination, comparisons of various yttrium complexes provide valuable insight for ligand design.

This investigation focuses on *N,O*-chelating bis(salicylaldiminato) complex **1** and the *N,N*-chelating anilido-imine complexes **2a** and **2b (**Figure 1). The syntheses of these complexes have been previously reported, and their application in hydroamination catalysis is disclosed here.[18,19]

Hydroamination Catalysis

For the initial experiments, 5-phenyl-4-pentynyl-1-amine (**3**) (Table 1) has been employed as the intramolecular hydroamination substrate for catalyst screening purposes. Product formation of the pyrrolidine **4** can be monitored by ^{1}H NMR spectroscopy using an NMR tube loaded with the appropriate catalyst, substrate **3**, and C_6D_6 under an inert atmosphere. The conversion of substrate to product is observed with the appearance of the benzylic singlet at $\delta = 3.55$, indicating product formation as well as the disappearance of the diagnostic triplet at $\delta = 2.45$ ($C{\equiv}CCH_2$), characteristic of the starting material.

As shown in Table 1 all three yttrium complexes catalyze the reaction at room temperature in 25 min with a catalyst loading of 5 mol%. These results are consistent with many other rare earth catalysts.[1] Here, due to the rapid reactivity using aminoalkyne **3**, we cannot differentiate between the bis-ligated and the mono-ligated complexes. This rapid reactivity prompted further investigation of these catalyst systems with the more challenging unactivated aminoalkenes.

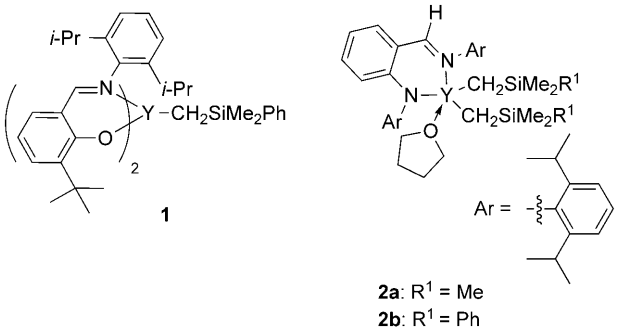
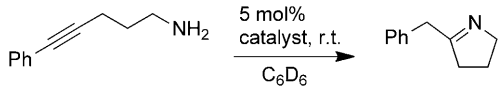


Figure 1. *N,O*- and *N,N*-chelating yttrium complexes for hydroamination catalysis.

Table 1. Intramolecular alkyne hydroamination.

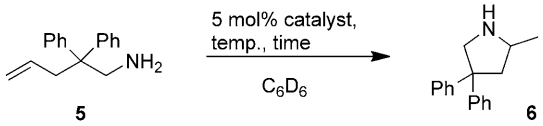


3 4

Entry	Catalyst	Time [min]	Conversion [%][a]
1	**1**	25	>95
2	**2a**	25	>95
3	**2b**	25	>95

[a] Conversions determined by ^{1}H NMR spectroscopy

Table 2. Intramolecular hydroamination of aminoalkene **5**.



5 6

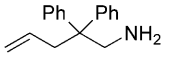
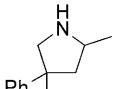
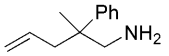
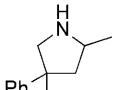
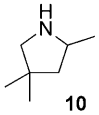
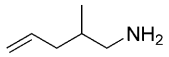
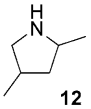
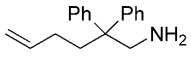
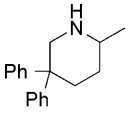
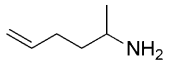
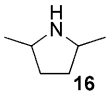
Entry	Catalyst	Temp. [°C]	Time [min]	Yield [%][a]
1	**1**	65	180	>95
2	**2a**	25	40	>95
3	**2b**	25	40	>95

[a] Yield determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

To this end, the hydroamination of 2,2-diphenyl-4-pentenylamine (**5**) (Table 2) catalyzed by **1** and **2**, has been performed. Reaction progress is monitored by the disappearance of the characteristic alkene proton signals at $\delta = 5.03$ and 5.40 ppm, and the appearance of the diagnostic multiplet at $\delta = 3.18$.

As observed with the alkynes, all three yttrium complexes are able to promote the reaction in excellent yields (>95% with 5 mol% catalyst loading). However, disparate reactivity between the yttrium complexes could be observed in the conversion of aminoalkene **5**. While the bis(salicylaldiminato) complex **1** requires a reaction temperature of 65 °C to reach yields greater than 95% within 3 h, the monoligated complexes **2a** and **2b** can promote the reaction at room temperature in 40 min. Temperatures of >50 °C are often reported for yttrium-catalyzed aminoalkene hydroamination,[5e,14c,17,20] however, room temperature hydroamination of disubstituted pyrrolidine has been reported for complexes with geometrically constrained tethered ligand sets, where accessibility to the metal center is enhanced.[13,15,16b,21] Thus, the increased accessibility of the metal center in the monoligated complexes **2a** and **2b** results in higher ac-

Table 3. Scope of reactivity with monoligated complex **2a** as catalyst.

Entry	Catalyst	Aminoalkene	Product	Time	Temperature [°C]	Yield[a] [%]
1	**2a**	 **5**	 **6**	40 min	25	>95
2	**2a**	 **7**	 **8**	40 min	25	>95
3	**2a**	 **9**	 **10**	50 min	25	>93
4	**2a**	 **11**	 **12**	18 h	25	>92
5	**2a**	 **13**	 **14**	24 h	25	>95
6	**2a**	 **15**	 **16**	36 h	25	>95

[a] Yield determined by *p*-xylene as internal standards. All reactions were performed in toluene-d_8 with 5% catalyst **2a**.

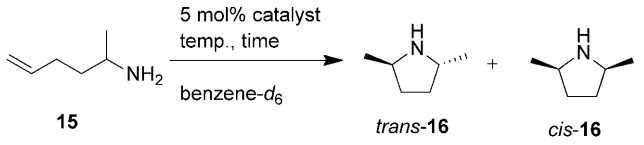
tivity compared to the bisligated complex. As expected, there is no difference between the reactivity of catalysts **2a** and **2b**, consistent with the mechanistic interpretation that these catalysts, upon treatment with excess aminoalkene substrate, undergo protonolysis of the Y–C bonds to yield the catalytically active yttrium amido complexes. Therefore, only complex **2a** has been employed to determine the scope of reactivity with a variety of aminoalkene hydroamination substrates.

As shown in Table 3, all substrate scope reactions have been carried out with 5 mol% catalyst loading at room temperature with excellent yields (>92%). The first three entries in Table 3 indicate that disubstitution at the β-position (diphenyl, methyl/phenyl or dimethyl substitution) promotes reactivity, as reaction times are under one hour. This is consistent with the Thorpe–Ingold effect being significant for this yttrium complex. For example, when there is only one methyl group in the ß-position, thereby significantly reducing the steric bulk, the reaction time increases to 18 h at room temperature (entry 4, Table 3, *dr* not recorded). As shown in entry 5, it is also possible to synthesize substituted piperidines, such as **14**, at room temperature in 24 h in yields greater than 95%. The longer reaction time compared to the pyrrolidine product **6** (40 min) may be due to the seven-membered transition state required for the piperidine substrate. Most importantly, the more hindered α-branched aminoalkene 1-methyl-4-pentenylamine (**15**) can also be converted to the desired product **16** in >95% yield at room temperature with extended reaction times (36 h) (see also Table 4).

Encouraged by the efficient catalysis of the challenging α-branched aminoalkenes, an unactivated internal aminoalkene, 2,2-diphenyl-4-hexenylamine (**17**) (Scheme 1), has been evaluated. Initial experiments with up to 10 mol% catalyst at room temperature provide no conversion, however increasing the reaction temperature to 65 °C results in product formation. Indeed a change of solvent from benzene-d_6 to toluene-d_8, and subsequent heating to 100 °C provides the product in quantitative yield in 3 h with 5 mol% catalyst loading.

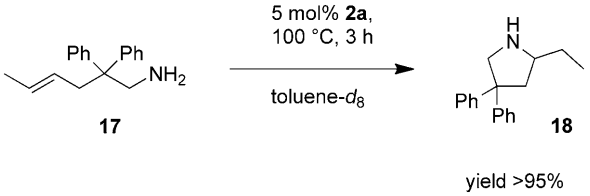
Even with these optimized conditions, secondary α-branched aminoalkenes, such as butyl-(1-methyl-4-

Table 4. Diastereoselectivity of intramolecular alkene hydroamination.



Entry	Catalyst	Temp.	Time [h]	Yield [%][a]	*trans*/*cis*[a]
1	**2a**	25 °C	36	>95	17:1
2	**2b**	25 °C	36	>95	17:1
3	**2b**	65 °C	1.5	>95	11:1
4	**2b**	0 °C	48	>80	23:1[b]

[a] Yield and diastereoselectivity determined by ^{1}H NMR spectroscopy, *p*-xylene is used as an internal standard.
[b] Toluene-d_8 was used as solvent.



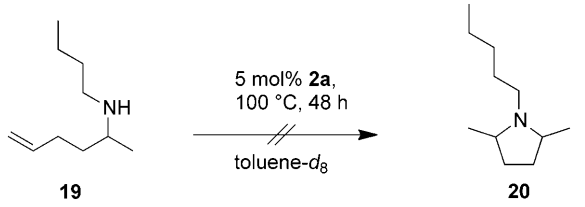
Scheme 1. An internal aminoalkene as substrate for the intramolecular hydroamination with complex **2a**.

pentenyl)amine (**19**) (Scheme 2) are unsuitable substrates and no *N*-substituted pyrrolidine product formation can be observed regardless of catalyst loading and reaction temperature.[22]

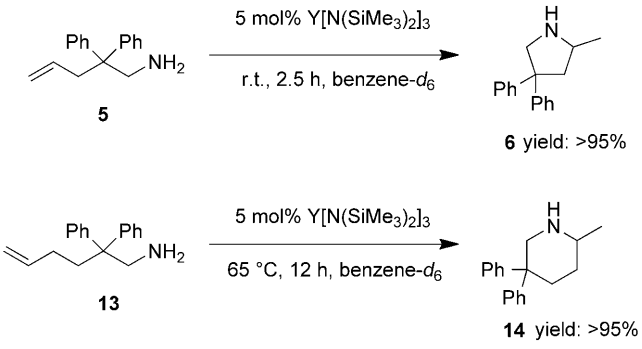
Similarly, catalysis of the intermolecular hydroamination of 1-hexyne and *tert*-butylamine did not prove possible with our preferred yttrium complex. Indeed, intermolecular hydroamination with rare earth complexes is much less common than cyclohydroamination.[23]

With the substrate scope of the yttrium complexes established, further experiments were conducted to determine the stereoselectivity of the reaction. The intramolecular hydroamination of α-branched aminoalkene 1-methyl-4-pentenylamine (**15**) (Table 4) in the presence of 5 mol% of **2a** or **2b** proceeds in quantitative yield and with a 17:1 diastereomeric ratio, of the *trans*-pyrrolidine as the major product. When the temperature is increased to 65 °C with catalyst **2b** in an attempt to reduce the reaction time, yields of >95% were obtained within 90 min, however, the *trans*/*cis* ratio dropped significantly to 11:1. Following this trend, an improved diastereoselectivity of 23:1 was achieved with a reaction temperature of 0 °C. While some high diastereoselectivities have been previously reported for yttrium complexes, these are for dianionic, tethered ligand sets which typically result in the formation of sterically demanding reactive sites.[5a,e,8g,24] Thus the anilido-imine ligand reported here provides desirable stereochemical control and good reactivity with a simple monoanionic ligand framework. Indeed the hydroamination reaction at 0 °C is a testament to the reactive nature of the sterically accessible *N,N*-chelating yttrium anilido-imine complexes. In fact, yields of >90% are obtained by longer reaction times (up to 4 days) without sacrificing diastereoselectivity.

Persuaded by the results with commercially available $Ti(NMe_2)_4$,[9] and the noted impact of the auxiliary ligand on slowing reactivity due to reduced steric accessibility of metal center, we also tried a comparison with the known hydroamination catalyst $Y[N(SiMe_3)_2]_3$, which has no auxiliary ligands.[25] Indeed this complex shows good reactivity with select substrates. Pyrrolidine **6** (Scheme 3) could be synthesized in >95% yield with 5 mol% of this commercially available precatalyst at room temperature in 2.5 h. It is also possible to catalyze the conversion of substrate **13** to the piperidine product **14** with 5 mol% catalyst loading to obtain yields >95%, although here a reaction temperature of 65 °C is required. Notably, the monoligated **2a** can promote this reaction at room temperature. The fact that improved substrate scope and reactivity can be promoted through judicious selection of auxiliary ligands with tunable steric bulk can be seen when comparing entry 4 Table 3 (>90% yield in 18 h at room temperature) with a previous report using $Y[N(SiMe_3)_2]_3$ (>95% yield in 10 days at 90 °C).[25a] Furthermore, only modest diastereoselectivity (*trans:cis*, 7:1)[25a] was reported for the cyclohy-



Scheme 2. Secondary α-branched aminoalkenes are not suitable substrates



Scheme 3. $Y[N(SiMe_3)_2]_3$ as a precatalyst for aminoalkene hydroamination.

droamination of **15** with $Y[N(SiMe_3)_2]_3$ as precatalyst, which further illustrates the dramatic impact this one monoanionic ligand has upon reactivity and selectivity in hydroamination.

Conclusions

We have presented bisligated *N,O*- and monoligated *N,N*-yttrium complexes for intramolecular hydroamination. The monoligated *N,N*-yttrium complexes **2a** and **2b** show the highest reactivity over a wide range of substrates with yields >92% at room temperature. Only the internal aminoalkene required a reaction temperature of up to 100 °C. While steric accessibility promotes reactivity, a well-defined coordination sphere promoted by an auxiliary ligand is preferred, as $Y[N(SiMe_3)_2]_3$ only shows high reactivity with select substrates.[25] The catalysts **2a** and **2b** are sufficiently reactive that reaction temperatures as low as 0 °C can be used, resulting in high diastereoselectivity (up to 23:1). Even with the increased steric accessibility of **2**, the sterically bulky secondary aminoalkene **19** could not undergo cyclohydroamination, even at elevated temperatures. In conclusion, these results illustrate how subtle changes in steric bulk on either the substrate or the rare earth catalyst can dramatically perturb reactivity trends. Furthermore, we have shown that a monosubstituted yttrium complex, with a simple, monoanionic and sterically demanding chelating ligand can provide an excellent balance of desirable reactivity and selectivity trends. On-going efforts address the development of improved catalysts with broad substrate scope, with the aim of realizing intermolecular hydroamination catalysis at modest temperatures.

Experimental Section

General

^1H and ^{13}C NMR spectra were recorded on either a Bruker 300 MHz or 400 MHz Avance spectrometer at ambient temperature. Chemical shifts are given relative to residual solvent. IR samples were prepared as nujol mulls on NaCl disks or KBr pellets and recorded on a BOMEM Michelson Series MB-100 FT-IR spectrophotometer. Mass spectra were recorded on a Kratos MS-50 spectrometer using an electron impact (70 eV) source. HR-MS determinations were performed at the Department of Chemistry, University of British Columbia.

All reactions were carried out using standard Schlenk line and glovebox techniques, under an atmosphere of nitrogen, unless stated otherwise. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under an inert gas atmosphere. Hexanes and toluene were purified by passage through a column of activated alumina and degassed with nitrogen. Benzene-d_6 was degassed and dried over molecular sieves. *p*-Xylene as was distilled from sodium under an atmosphere of argon and stored over molecular sieves.

All aminoalkenes were distilled from CaH_2 under reduced pressure or under an argon atmosphere and stored in the glove box, for details see ref.[10] Aminoalkenes 2,2-diphenyl-4-pentenyl-1-amine (**5**),[26] 2-methyl-2-phenyl-4-pentenyl-1-amine (**7**),[7c] 2,2-diphenyl-5-hexenyl-1-amine (**13**),[27] 1-methylpent-4-enylamine (**15**),[28] 2,2-dimethyl-4-pentenyl-1-amine (**9**) and 2-methyl-4-pentenyl-1-amine (**11**)[29] were prepared as described in the literature. The spectral data for the *cis*- and *trans*-isomers of 2,5-dimethylpyrrolidine (*cis*-**16** and *trans*-**16**)[28] were entirely consistent with those described in the literature. The diastereoselectivity for the cyclization of **15** to *trans*-**16** and *cis*-**7f** was determined based on ^1H NMR integration; *trans*-**16**/*cis*-**16** = 3.14 (septet)/2.93 (m) for NCH peaks.

General Procedure for Intramolecular Aminoalkene Hydroamination Reactions

All reactions were carried out in an N_2-filled glovebox on an NMR-tube scale. The NMR tubes were equipped with a Teflon screw cap. In the NMR tubes the aminoalkene, the internal standard (1,3,5-trimethoxybenzene or *p*-xylene), the complexes and benzene-d_6 or toluene-d_8 were combined. The reactions were either heated in an oil bath to 65 °C, cooled to 0 °C in a cryostat apparatus or allowed to stand at room temperature.

2-Methyl-5,5-diphenyl-piperidine (14): Colourless liquid: ^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 (d, J = 6.4 Hz, 3H, CH_3), 1.17 (m, J = 3.1, 10.9 Hz, 1H, CH*H*-CHCH$_3$), 1.64 (dd, J = 3.1, 13.3 Hz, 1H, C*H*H-CHCH$_3$), 2.10–2.30 (m, 2H, N-*H*, CPh$_2$CH*H*CH$_2$), 2.67 (dq, J = 3.1, 13.6 Hz, 1H, CPh$_2$C*H*HCH$_2$) 2.75–2.90 (m, 1H, C*H*CH$_3$), 3.10 (d, J = 13.7, 1H, C*H*HNH), 3.92 (dd, J = 2.9, 13.6 Hz, 1H, CH*H*NH) 7.05–7.43 (m, 10H, $H_{arom.}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.07 (*C*H$_3$), 32.60 [*C*H$_2$CH(CH$_3$)], 36.71 [*C*H$_2$CH$_2$CH-(CH$_3$)], 46.62 (CH$_2$*C*Ph$_2$CH$_2$), 53.77 (*C*HCH$_3$), 56.88 (*C*H$_2$NH), 127.32, 127.84, 129.59, 129.67, 130.13, 145.86, 149.99 ($C_{arom.}$); EI-MS (50 eV): *m/z* (%) = 252 (2) [M+H$^+$], 251 (7) [M$^+$], 236 (2), 221 (2), 205 (2), 180 (20), 165 (18), 91 (8), 71 (6), 58 (100); HR-EI-MS: *m/z* = 251.1673, calcd.: 251.1674.

2-Ethyl-4,4-diphenyl-pyrrolidine (**18**): Colourless liquid; R_f = 0.24 (CH$_2$Cl$_2$/5% MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.41 Hz, 3H, C*H*$_3$), 1.40–1.67 (m, J = 6.87 Hz, 2H, C*H*$_2$CH$_3$), 2.05 [dd, J = 11.67 Hz, 1H, C*H*HCH(NH)CH$_2$CH$_3$], 2.80 [dd, J = 11.33 Hz, 1H, CH*H*CH(NH)CH$_2$CH$_3$], 2.86–3.05 (bs, 1H, N*H*), 3.06–3.26 [m, 1H, C*H*(NH)CH$_2$CH$_3$], 3.43 (d, J = 9.90 Hz, 1H, C*H*HNH), 3.74 (d, J = 9.36 Hz, 1H, C*H*HNH), 7.03–7.37 (m, 10H, $H_{arom.}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.49 (*C*H$_3$), 29.63 (*C*H$_2$CH$_3$), 44.75 [*C*H$_2$CH(NH)], 56.46 ($C_{quart.}$), 57.08 (*C*H$_2$NH), 59.55 (*C*H), 126.05 ($C_{arom.}$), 126.87 ($C_{arom.}$), 126.95 ($C_{arom.}$), 128.27 ($C_{arom.}$), 128.36 ($C_{arom.}$), 146.49 ($C_{arom., quart.}$), 147.32 ($C_{arom. quart.}$); EI-MS (50 eV): *m/z* (%) = 251 (10) [M$^+$], 223 (26), 222 (100), 178 (65), 165 (67), 115 (61), 91 (51), 71 (98), 70 (89), 56 (90); HR-EI-MS: *m/z* = 251.1673, calcd. 251.1674.

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