New Yttrium Complexes Bearing Diamidoamine Ligands as Efficient and Diastereoselective Catalysts for the Intramolecular Hydroamination of Alkenes and Alkynes

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New diamidoamine yttrium complexes [Y(Mes$_2$N$_2$NMe){N(SiHMe$_2$)$_2$}(THF)] (Mes$_2$N$_2$NMe^{2-} = (2,4,6-Me$_3$C$_6$H$_2$NCH$_2$CH$_2$)$_2$NMe^{2-}), [Y(Ar$_2$N$_2$NMe){N(SiMe$_3$)$_2$}], and [Y(Ar$_2$N$_2$NMe)(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] (Ar$_2$N$_2$NMe^{2-} = (ArNCH$_2$CH$_2$)$_2$NMe^{2-} with Ar = 2,4,6-Me$_3$C$_6$H$_2$, 2,6-Et$_2$C$_6$H$_3$, 2,6-Cl$_2$C$_6$H$_3$) were prepared by transamination or arene elimination reactions starting from the corresponding trisamido or trisaryl yttrium complexes. The structures of [Y(Mes$_2$N$_2$NMe){N(SiHMe$_2$)$_2$}(THF)] and [Y{(2,6-Et$_2$C$_6$H$_3$)$_2$N$_2$NMe}(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] were shown by X-ray crystallography to be trigonal bipyramidal, where the amine donor and coordinated THF molecule in [Y(Mes$_2$N$_2$NMe){N(SiHMe$_2$)$_2$}(THF)] and both amine donors in [Y{(2,6-Et$_2$C$_6$H$_3$)$_2$N$_2$NMe}(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] occupy axial positions. All complexes catalyze intramolecular hydroamination of aminoalkynes and aminoalkenes. Those having bis(trimethylsilyl)amido or (*o*-C$_6$H$_4$CH$_2$NMe$_2$) ligands show significantly higher activity than the complex containing the bis(dimethylsilyl)amido ligand, whose activity is impeded by sluggish initiation and not by THF coordination. While [Y(Mes$_2$N$_2$NMe)(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] decomposes by a first-order rate law with $t_{1/2}$ = 348 ± 8 min at 25 °C, the corresponding 2,6-diethylphenyl- and 2,6-dichlorophenyl-substituted complexes are significantly more thermally stable. The electron-withdrawing effect of the dichlorophenyl substituents increases the stability of the catalyst toward protonolysis, as exemplified by a superior activity in the cyclization of pent-4-enylamine and 5-phenylpent-4-ynylamine. Ring-closing of 1-methylpent-4-enylamine proceeds with high *trans* selectivity and good activity (*trans*:*cis* = 22:1 and TOF = 7.8 h^{-1} at 25 °C for [Y(Mes$_2$N$_2$NMe)(*o*-C$_6$H$_4$CH$_2$NMe$_2$)]). Bicyclization of 2-allyl-2-methylpent-4-enylamine was achieved at 60 °C, giving a mixture of *endo*,*exo*- and *exo*,*exo*-2,4,6-dimethyl-1-aza-bicyclo[2.2.1]heptane.

Introduction

The catalytic addition of amines to alkenes and alkynes, the so-called hydroamination reaction, is a highly atom efficient reaction of potentially great preparative value for the synthesis of basic and fine chemicals, pharmaceuticals, and other industrially relevant building blocks.[1] Catalyst development has significantly intensified in recent years, and many catalyst systems based on early[2,3] or late[4] transition metals have been reported. Despite this, catalytic activity is often restricted to more activated substrates.

The application of organometallic rare earth metal catalysts in organic[5] and polymer[6] synthesis has significantly advanced over the last two decades with catalyst development depending heavily on cyclopentadienyl ligands.[7] Catalyst systems based on rare earth metals have proven to be among the most active in hydroamination reactions, catalyzing the addition of amines to nonactivated double bonds.[1b,c,8,9] Reports

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using cyclopentadienyl-free catalyst systems have emerged only recently.[9,10] These so-called post-metallocene catalyst systems[11] can be expected to show deviating reactivity and selectivity from their metallocene counterparts and therefore expand the spectrum of catalysts available. Non-cyclopentadienyl systems could gain significant importance, especially with respect to enantioselective hydroamination.[1i,9e,f,h−k] This is because the application of chiral lanthanocene complexes is hampered by their facile epimerization under the catalytic conditions.[8f,q] As part of our ongoing interest in developing new, chiral, cyclopentadienyl-free rare earth metal based hydroamination catalysts[9f,k] we chose the diamidoamine ligand set as a promising achiral model system to probe steric and electronic requirements of such non-cyclopentadienyl hydroamination catalyst systems. Group 4 metal complexes of diamido and diamido/donor ligands[12,13] have attracted considerable interest as living α-olefin polymerization catalysts.[11] Similar complexes of rare earth metals have evolved recently,[14] often with potential applications in polymer chemistry. We hoped that the amine donor in tridentate diamidoamine complexes would give the catalyst a more rigid structure and thereby ease stereocontrol over the hydroamination/cyclization process. Indeed, an important finding recently reported by Anwander and co-workers showed that diamidoamine scandium complexes containing a pyridine donor functionality exhibit good activity for the polymerization of MMA, whereas diamido complexes lacking this additional donor were found to be catalytically inactive.[14k]

During the course of our investigations, Livinghouse reported the highly stereospecific hydroamination/cyclization of 1-methylpent-4-enylamine using a catalyst system prepared in situ by extensive heating of [Y{N(SiMe$_3$)$_2$}$_3$] with a *N*,*N*′-diarylethane-1,2-diamine.[9d,15] Herein we report our results utilizing well-defined diamidoamine yttrium complexes as efficient and diastereoselective hydroamination catalysts.

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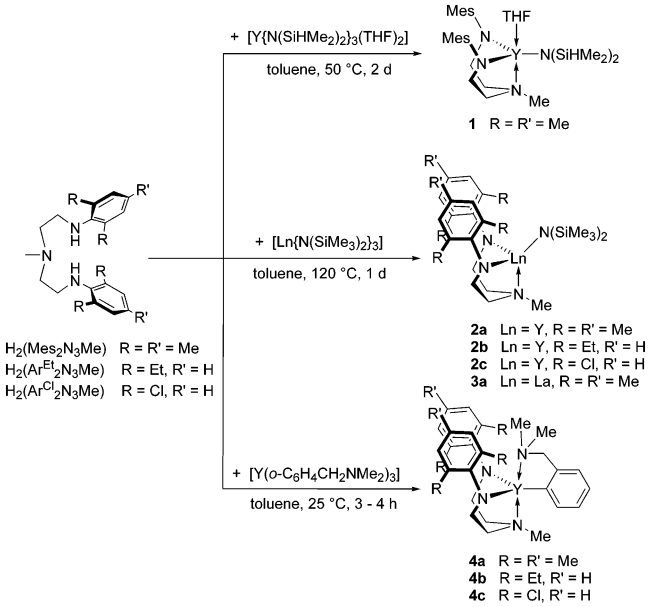
(15) These catalysts have only been prepared in situ directly prior to the catalytic reaction. Analytical data of the resulting species have been limited to a crystal structure of a pentacoordinate bis(thiophosphinic amidate) complex,[9g] but no spectroscopic data were disclosed.

Scheme 1



Results

The yttrium trisamido complex $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$[16] reacts cleanly with (2,4,6-$Me_3C_6H_2NHCH_2CH_2)_2NMe$ ($H_2(Mes_2N_2NMe)$)[12] in toluene at 50 °C over a two-day period providing the diamidoamine complex **1** in 77% yield after crystallization from hexanes at −30 °C (Scheme 1). A single-crystal X-ray diffraction analysis of **1** confirmed that one molecule of THF is retained and its monomeric structure (vide infra). NMR-scale reactions revealed that the formation of **1** proceeded very cleanly, and only signals corresponding to **1** could be observed. The corresponding THF-free trisamido complex $[Y\{N(SiMe_3)_2\}_3]$[17] gave one major product, complex **2a** (in ca. 90% as judged by integration of the ^{1}H NMR spectrum), when the reaction with $H_2(Mes_2N_2NMe)$ was performed at 120 °C in toluene. Reactions performed at 60 °C or lower temperatures resulted in the formation of a mixture of products, with a minimum of three different sets of signals for the diamidoamine ligand. Heating of this mixture of products to 120 °C did not transform these byproducts to the desired complex **2a**, and therefore they are not intermediates in the formation of **2a**. Reaction of $H_2(Mes_2N_2NMe)$ with $[La\{N(SiMe_3)_2\}_3]$ proceeded less cleanly even at high temperature, and the analogous complex **3a** could not be isolated in pure form to date.

Starting from the readily available trisaryl complex $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$[18] the synthesis of the THF-free aryl complex **4a** in toluene at room temperature was achieved in 59% yield after crystallization from pentane at −30 °C (Scheme 1). However, the synthesis of complex **4a** was complicated by its instability at room temperature, giving rise to a decomposition pathway that was calculated to be by a first-order rate law[12c,d,19]

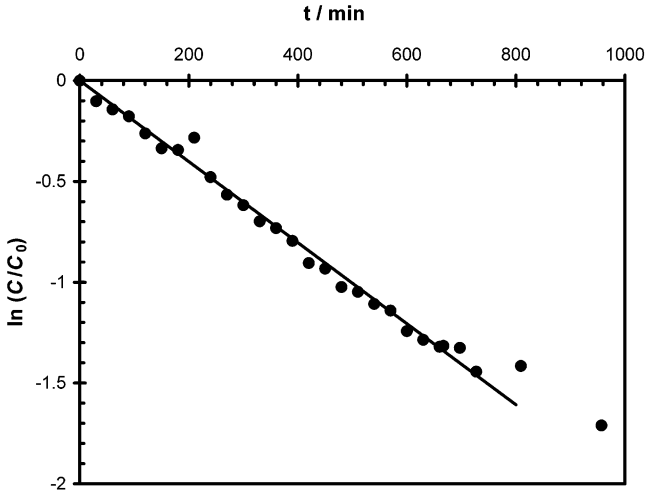


Figure 1. First-order rate plot for the thermolysis of **4a** in C_6D_6 at 25 °C. The line through the data points represents the least-squares fit for all data.

where $k = (3.32 \pm 0.06) \times 10^{-5}$ s^{-1} ($t_{1/2} = 348 \pm 8$ min) in C_6D_6 at 25 °C (Figure 1). The formation of *N*,*N*-dimethylbenzylamine was also observed in parallel to this reaction. The ultimate fate of the (Mes_2N_2NMe) moiety is not known with certainty. ^{1}H and ^{13}C{^{1}H} NMR spectra of the resulting deep red solution show numerous different species. More than 20 methylene carbon signals in the range 47−60 ppm (apparently from ligand backbone ethylene groups and potentially from benzylic groups attached to yttrium[20]) and more than 10 mesityl methyl groups were observed in the ^{13}C DEPT spectrum. The sterically more encumbered complex $[Y(Ar^{Et}{}_2N_2NMe)(o\text{-}C_6H_4CH_2NMe_2)]$ (**4b**) ($Ar^{Et}{}_2N_2NMe^{2-}$ = (2,6-$Et_2C_6H_3NCH_2CH_2)_2NMe^{2-}$) is significantly more stable ($t_{1/2} \approx 2.5$ days at 25 °C), while $[Y(Ar^{Cl}{}_2N_2NMe)(o\text{-}C_6H_4CH_2NMe_2)]$ (**4c**), prepared in 91% yield from the corresponding 2,6-dichlorophenyl-substituted ligand $H_2(Ar^{Cl}{}_2N_2NMe)$ ($Ar^{Cl}{}_2N_2NMe^{2-}$ = (2,6-$Cl_2C_6H_3NCH_2CH_2)_2NMe^{2-}$),[12c] shows no sign of decomposition in C_6D_6 solution after 4 days at 25 °C and 1 h at 70 °C. The amido complexes **1** and **2a**−**c** are thermally robust and can be heated above 100 °C in toluene-d_8 solution without degradation. Consequently, it was not surprising to find that complex **4a** is stable during catalytic hydroamination reactions (vide infra) since the *ortho*-(dimethylaminomethyl)phenyl ligand is substituted for an amido ligand during the initiation step of the catalytic reaction.

Additional signs of steric hindrance, in complex **4b**, are the broad signals corresponding to the ethyl group protons in the ^{1}H NMR spectrum at room temperature, indicative of slow rotation about the nitrogen aryl bond. Variable-temperature ^{1}H NMR spectra of **4b** revealed decoalescence of these signals at 10 °C, while decoalescence of the mesityl *ortho*-methyl groups and mesityl aromatic protons in **4a** was observed at −60 °C. The 2,6-dichlorophenyl-substituted complex **4c** was found to

(16) Anwander, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1998**, 847.

(17) (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021. (b) Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233.

(18) The trisaryl complex $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ has rarely been used for complex synthesis, despite its convenient large-scale synthesis, see: Booij, M.; Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *364*, 79.

(19) For other examples of decomposition reactions with first-order rate dependence see: (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (b) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (c) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026.

(20) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228.

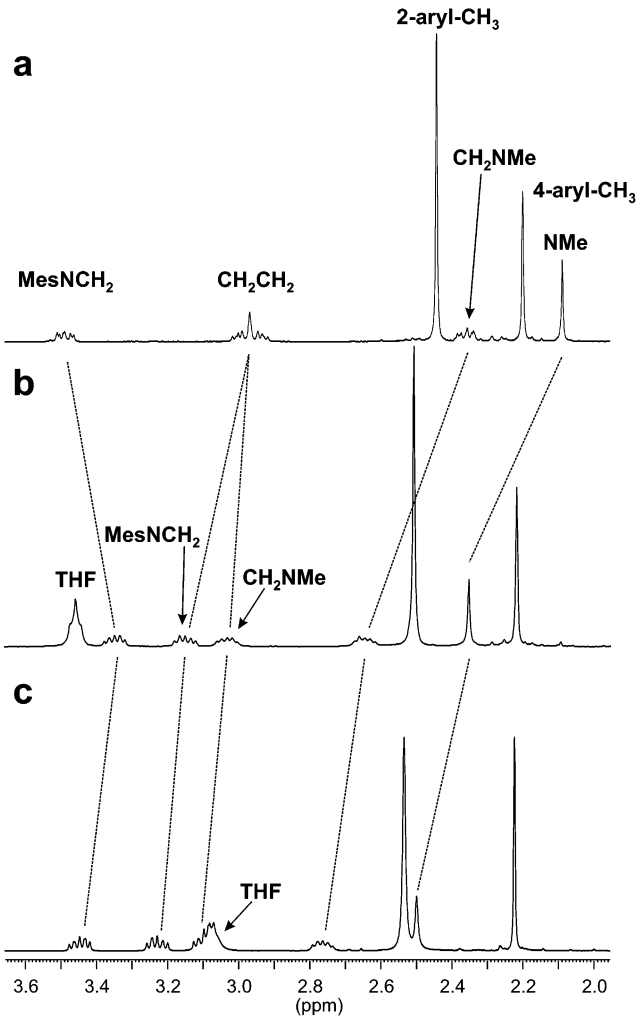


Figure 2. Comparison of the ^{1}H NMR spectra of complex **2a** before (a) and after (b) addition of 1.2 equiv of THF with that of complex **1** (c). Only the part relevant for the diamidoamine ligand framework is shown.

be the least hindered complex, where decoalescence of the aromatic signals became visible only at −90 °C.

Complex **2a** does readily coordinate THF, as exemplified by significant changes in the spectroscopic features after addition of 1.2 equiv of THF (Figure 2). The pattern of the signals for the ligand framework in **2a**·THF resembles those of the pentacoordinate complex **1**. Three protons of the ethylene ligand backbone experience a downfield shift in the range 0.06−0.29 ppm relative to the signals in **2a**. The fourth proton, attached to the anilido methylene carbon atom, is shifted to higher field by 0.14 ppm, possibly due to interaction of this proton with the ring current of the anilido aromatic ring when the coordination geometry around yttrium is shifted from tetracoordinate to pentacoordinate. The amino methyl group is shifted downfield from 2.09 ppm in **2a** to 2.35 ppm in **2a**·THF, which is closer to the 2.50 ppm observed in **1**. The pentacoordinate complex **4a** on the other hand shows no interaction with THF, as confirmed by NMR spectroscopy.

Molecular Structure of [Y(Mes$_2$N$_2$NMe){N(SiHMe$_2$)$_2$}(THF)] (1) and [Y(Ar^{Et}$_2$N$_2$NMe)(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] (4b). Single-crystal X-ray diffraction analyses of both complex **1** (Figure 3) and complex **4b** (Figure 4) confirmed their monomeric structure in the solid state

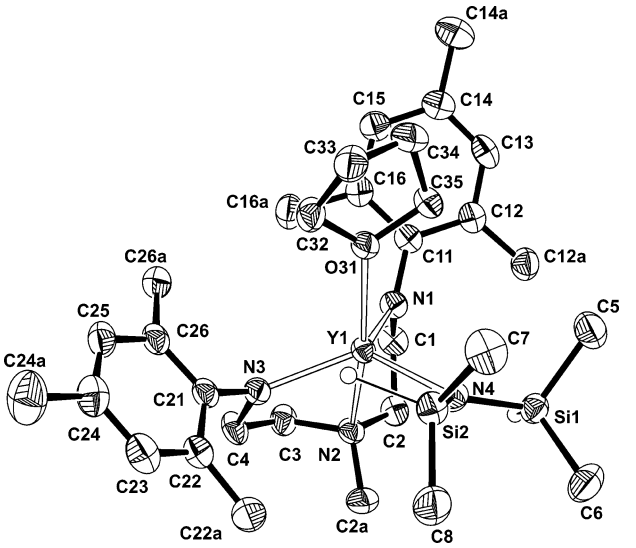


Figure 3. ORTEP diagram of the molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms except for those bonded to silicon have been omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y1−N1 2.240(3), Y1−N2 2.480(3), Y1−N3 2.245(3), Y1−N4 2.263(3), Y1−O31 2.348(2), Y1···Si2 3.195(1), Y1···Si1 3.560(1), N1−Y1−N2 71.08(10), N1−Y1−N3 117.55(10), N1−Y1−N4 111.98(10), N2−Y1−N3 72.94(10), N2−Y1−N4 99.80(9), N3−Y1−N4 123.23(10), N1−Y1−O31 94.70(10), N2−Y1−O31 162.75-(8), N3−Y1−O31 106.96(9), N4−Y1−O31 94.53(9), Si1−N4−Si2 125.32(16), Y1−N4−Si1 127.31(15), Y1−N4−Si2 106.63(13).

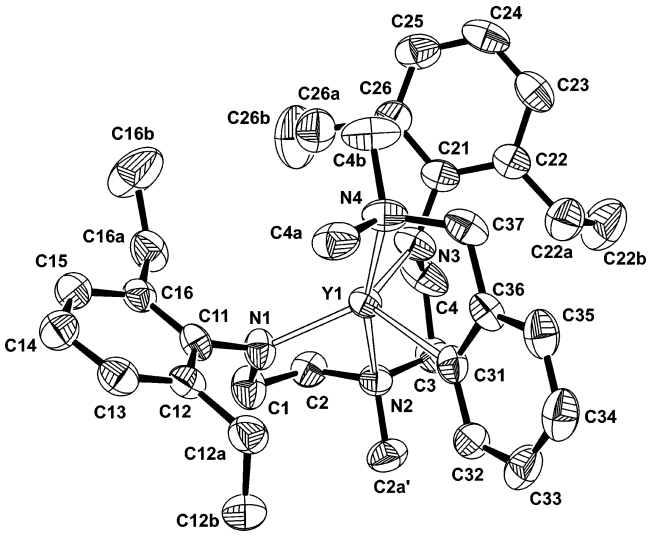


Figure 4. ORTEP diagram of the molecular structure of **4b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the disordered carbon atoms C2a, C2′, and C3′ have been omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y1−N1 2.172(4), Y1−N2 2.466(3), Y1−N3 2.219(4), Y1−N4 2.527-(3), Y1−C31 2.461(4), N1−Y1−N2 73.67(12), N1−Y1−N3 119.51(14), N1−Y1−N4 118.34(13), N2−Y1−N3 71.96(12), N2−Y1−N4 167.48(13), N3−Y1−N4 102.71(12), N1−Y1−C31 118.38(14), N2−Y1−C31 99.98(12), N3−Y1−C31 115.50(14), N4−Y1−C31 71.70(12), C31−C36−C37−N4 40.5(5).

and revealed a distorted trigonal bipyramidal geometry. In complex **1**, the amine donor and coordinated THF molecule are occupying axial positions and the amido

ligands are in equatorial positions. In complex **4b** both amine donors occupy axial positions and the chelating amido ligands and the aryl ligand reside in equatorial positions. The diamidoamine ligand adopts a "*fac*" coordination mode, as indicated by the angle between the N1−Y1−N2 and N2−Y1−N3 planes of 128° for **1** and 129.4° for **4b**, similar to the cationic zirconium alkyl complex $[(Mes_2N_2NMe)Zr(Me)(OEt_2)][B(C_6F_5)_4]$.[12b] While the yttrium-amido (2.240(3)−2.263(3) Å) and yttrium−THF (2.348(2) Å) bond lengths in **1** are unexceptional,[21] the yttrium−amine bond (2.480(3) Å) is relatively short.[22] The dimethylsilylamido ligand in complex **1** displays a monoagostic β-SiH interaction[23] with a short Y1···Si2 distance (3.195(1) Å) and a small Y1−N4−Si2 angle (106.63(13)°), while the Si1−N4−Si2 angle (125.32-(16)°) remains typical. Additionally, the N3−Y1−N4 angle (123.23(10)°) is significantly widened compared to the N1−Y1−N4 angle (111.98(10)°). The bonds of yttrium to the tridentate diamidoamine ligand in **4b** (Y−N(amido) = 2.172(4), 2.219(4) Å; Y−N(donor) = 2.466(3) Å) are shorter than the corresponding bonds in **1**, suggesting a more electrophilic character of yttrium in complex **4b**. The bond of yttrium to the bidentate aryl ligand in **4b** (Y1−N4 = 2.527(3) Å, Y1−C31 = 2.461(4) Å) is in the expected range observed for similar *ortho*-(dimethylaminomethyl)phenyl complexes.[22a,d,24] Within the five-membered metallacyclic ring, consisting of Y1, C31, C36, C37, and N4, the yttrium atom and three carbon atoms are coplanar, while the nitrogen atom resides 0.83 Å out of the plane. The torsion angle that involves the nitrogen atom and the three carbon atoms of the ring (40.5(5)°) is the second largest observed so far, only surpassed by a torsion angle of −45.6(7)° observed in $[Cp^*Y(o\text{-}C_6H_4CH_2NMe_2)_2]$.[22a]

Hydroamination/Cyclization Catalysis. Complexes **1**−**4** are active catalysts in the hydroamination/cyclization of various aminoalkenes and aminoalkynes (Table 1−3). Complexes **2**−**4** generally show significantly higher catalytic activities than complex **1**, which requires higher reaction temperatures. The initiation step for complexes **2**−**4** is fast, showing only formation of free hexamethyldisilazane or *N*,*N*-dimethylbenzylamine, while reaction mixtures of complex **1** show only partial liberation of tetramethyldisilazane. For example, in a catalytic cyclization of **5** (0.71 mmol mL^{-1}) using **1** (0.022 mmol mL^{-1}) in C_6D_6 at 60 °C only 12% of free tetramethyldisilazane was observed and the majority of complex **1** remained intact. No significant change in this ratio was observed during the course of the reaction. NMR spectroscopic analysis of the catalytic reaction

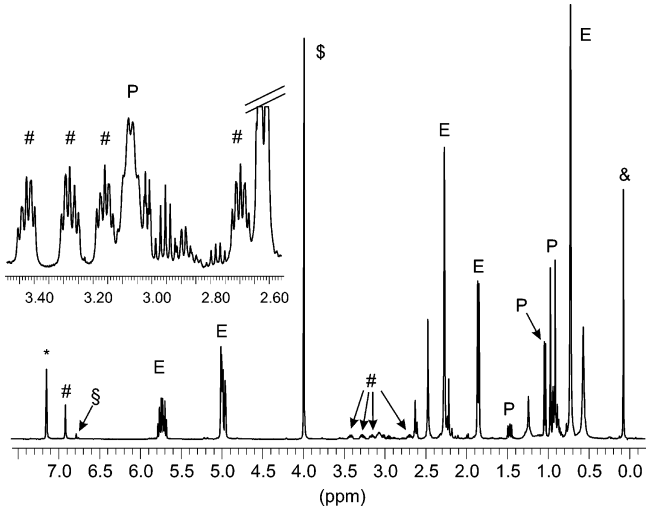


Figure 5. ^{1}H NMR spectrum of the catalytic hydroamination/cyclization of **5** (0.72 M) using 4.6 mol % **4a** (0.033 M) in C_6D_6 (*) at 25 °C. The inset shows the region of the ethylene ligand backbone of the catalyst. (E = starting aminoalkene (**5**), P = product (**6**), # = catalyst, § = free diamidoamine ligand, & = free $HN(SiMe_3)_2$, $ = ferrocene internal standard.)

mixture shows that for most catalysts and most substrates the diamidoamine ligand is coordinated to the metal, with some exceptions (vide infra). Observation of diastereomeric ethylene protons of the ligand backbone, during the catalytic reaction, indicates that the amine donor of the tridentate ligand remains coordinated to the metal center at least on the NMR time scale (Figure 5). Fast dissociation and recoordination should render both protons on each methylene group equal.[25]

Catalytic activity and diastereoselectivity of complexes **2** and **4** with the same diamidoamine ligand compare well, suggesting identical catalytically active species. The electron-withdrawing effect of the 2,6-dichlorophenyl substituents in complexes **2c** and **4c** slightly diminishes the catalytic activity for 2,2-dimethylpent-4-enylamine (**5**) and 2-allyl-2-methylpent-4-enylamine (**13**) in comparison to the mesityl- and 2,6-diethylphenyl-substituted complexes **2a**,**b** and **4a**,**b** (Table 1, entries 3, 5−7, 10, and 11; Table 3, entries 1−4 respectively).

When a thermally decomposed sample of complex **4a** was employed in the catalytic hydroamination of aminoalkene **5**, a diminished catalytic activity of just 5.6 h^{-1} was observed. Although in this case the initial reaction with the substrate seemed to "regenerate" the catalyst[8p,26] providing the same catalytically active species (as judged by ^{1}H NMR spectroscopy), a significant amount of free protonated diamidoamine ligand (25%) was also observed.

Complex **4c** shows better activity in the ring-closing of pent-4-enylamine (**7**) and 5-phenylpent-4-ynylamine

(21) Typical range for Y−NR_2 = 2.18−2.33 Å and Y−O(THF) = 2.32−2.49 Å, see ref 20.

(22) The typical range for Y−NR_3 is 2.49−2.74 Å, see for example: (a) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H. *Organometallics* **1989**, *8*, 2454. (b) Schumann, H.; Erbstein, F.; Weimann, R.; Demtschuk, J. *J. Organomet. Chem.* **1997**, *536*−*537*, 541. (c) Roussel, P.; Alcock, N. W.; Scott, P. *Chem. Commun.* **1998**, 801. (d) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 485. (e) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197. (f) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, 637. See also ref 14h.

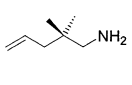
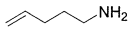
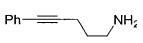
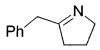
(23) For discussions on similar β-SiH interactions in other rare earth metal complexes of this amido ligand see: (a) Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A. Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080. (b) Hieringer, W.; Eppinger, J.; Anwander, R.; Herrmann, W. A. *J. Am. Chem. Soc.* **2000**, *122*, 11983. (c) Kimpel, M. G.; Görlitzer, H. W.; Tafipolsky, M.; Spiegler, M.; Scherer, W.; Anwander, R. *J. Organomet. Chem.* **2002**, *647*, 236.

(24) Rausch, M. D.; Foust, D. F.; Rogers, R. D.; Atwood, J. L. *J. Organomet. Chem.* **1984**, *265*, 241.

(25) Reaction of **4c** with stoichiometric amounts or excess *n*-propylamine yields a species that we currently believe to be $[Y(Ar^{Cl}{}_2N_2\text{-}NMe)(NH\text{-}nPr)]_n$. Low-temperature NMR at −30 °C shows a highly nonsymmetrical ligand coordination with both aromatic rings, all eight ethylene protons, and the four carbon atoms of the ligand backbone being inequivalent. Hultzsch, K. C. Unpublished results.

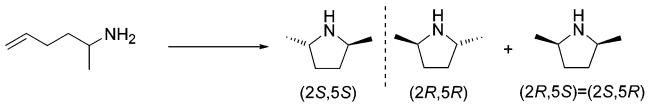
(26) (a) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701. (b) Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3246.

Table 1. Catalytic Hydroamination/Cyclization of Aminoalkenes and an Aminoalkyne[a]

entry	substrate	product	cat.	[cat.]/[s] (mol %)	*T* (°C)	time (h)	conv. (%)	TOF (h^{-1})
1			**1**	4	40	13	41	1.3
2			**1**	4	60	2.5	98.5	20
3			**2a**	3	25	3.5	96	8.4
4			**2a** + 1.2 equiv THF	3	25	3	94	8.4
5			**2b**	3	25	4	98	8.9
6			**2c**	2	25	41	92	1.2
7			**4a**	3	25	3.65	95	10
8			**4a** + 1.1 equiv THF	5	25	2.6	95	6.6
9	**5**	**6**	**4a** + 5 equiv THF	5	25	4	96	5.5
10			**4b**	3	25	5	97	7.6
11			**4c**	3	25	25	96	1.2
12			[Y(*o*-$C_6H_4CH_2NMe_2)_3$]	3	25	13	89	2.6
13			[Y{$N(SiMe_3)_2$}$_3$]	3	25	3	89	11.6
14			[Y{$N(SiHMe_2)_2$}$_3$$(THF)_2$]	3	50	9	34.5	1.2
15			**4a**	3	90	30	4	
16			**4c**	3	60	60	97	
17	**7**	**8**	[Y{$N(SiMe_3)_2$}$_3$]	3	80	216	6	
18			[La{$N(SiMe_3)_2$}$_3$]	3	80	168	80	
19			**1**	3	60	20	97	2.2
20			**4a**	3	60	7.5	70	
21			**4b**	3.5	60	12.5	83	
22	**9**	**10**	**4c**	3	25	12.5	75	
23			**4c**	3	60	0.25	93	
24			[Y{$N(SiMe_3)_2$}$_3$]	3	60	23	91	1.3

[a] Reaction conditions: C_6D_6, Ar atm.

Table 2. Catalytic Hydroamination/Cyclization of 1-Methylpent-4-enylamine (11)[a]



11 *trans*-**12** *cis*-**12**

entry	cat.	[cat.]/[s] (mol %)	*T* (°C)	time (h)	conv (%)	TOF (h^{-1})	dr[b] (*trans*:*cis*)
1	**2a**	3	25	5.3	83	5.2	22:1
2	**2b**	3	25	4.4	91	6.2	19:1
3	**2c**	1.6	25	7.9	92	9.1	14:1
4	**4a**	3	25	5	98	7.8	22:1
5	**4a**	3	60	0.1	97	> 300	9:1
6	**4b**	3	25	8	89	4.3	23:1
7	**4c**	3	25	6	91	6.8	13.5:1
8	[Y(*o*-$C_6H_4CH_2NMe_2)_3$]	6	90	87	88		5.2:1
9	[La{$N(SiMe_3)_2$}$_3$]	3	90	13	>99		4:1

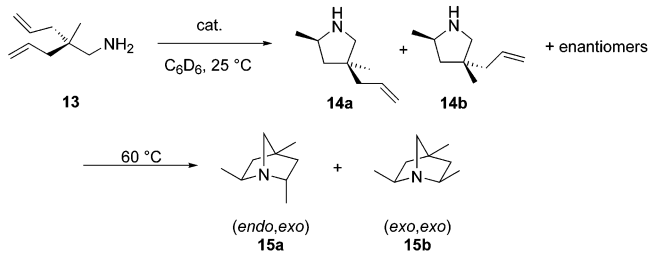
[a] Reaction conditions: C_6D_6, Ar atm. [b] Diastereomeric ratios were determined by ^1H NMR spectroscopy after vacuum transfer.

(**9**) (Table 1, entries 15, 16, and 20−23) than complex **4a** or **4b**. NMR spectroscopic data suggest protolytic loss of diamidoamine ligand in these reactions when complex **4a** is employed, while the more acidic dichlorophenyl-substituted diamidoamine ligand remains coordinated. Coincidently, the homoleptic rare earth metal trisamido complexes [Ln{$N(SiMe_3)_2$}$_3$] (Ln = Y, La) also show very low activity for these substrates (Table 1, entries 17, 18, and 24).[27] Addition of substrate **7** to the [Ln{$N(SiMe_3)_2$}$_3$] catalyst solution results in the formation of a solid gel, suggesting the formation of a polymeric coordination network. In the case of the lanthanum complex this solid gel liquefies gradually upon conversion. It is also interesting to note that [Y(*o*-$C_6H_4CH_2NMe_2)_3$] and [Y{$N(SiHMe_2)_2$}$_3$$(THF)_2$] display significantly lower catalytic activity for ring-closing of aminoalkene **5** than [Y{$N(SiMe_3)_2$}$_3$] (Table 1, entries 12−14).

The observed rate law for complexes **2a** and **4a** was found to be zero-order in substrate and first-order in catalyst for substrates **5** and **11** (Figures 6−9), although a slight curvature was found in the cyclization of **5**. This observation is in accordance with previous findings

(27) These catalytic activities for [Ln{$N(SiMe_3)_2$}$_3$] are slightly higher than reported in ref 9c.

Table 3. Catalytic Hydroamination/Cyclization of 2-Allyl-2-methylpent-4-enylamine (13)[a]



entry	rxn[b]	cat.	[cat.]/[s] (mol %)	*T* (°C)	time	conv (%)	TOF (h^{-1})	dr[c] (a:b)
1	**13** → **14**	**2a**	3	25	34 min	91	>55	1.3:1
	14 → **15**			60	39 h	95		1.3:1
2	**13** → **14**	**2b**	3	25	37 min	>98	>55	1.3:1
	14 → **15**			60	30 h	93		1.4:1
3	**13** → **14**	**4a**	9	25	180 min	>98		1.2:1
4	**13** → **14**	**4c**	3	25	228 min	97	9.2	1.2:1
5	**13** → **14**	[Y{N(SiMe$_3$)$_2$}$_3$]	3	25	34 min	>98	>60	1.3:1
	14 → **15**			60	4 h	>98		1:1
6	**13** → **14**	[La{N(SiMe$_3$)$_2$}$_3$]	3	25	100 min	>98		1.4:1
	14 → **15**			25	45 h	72		1:1.5
				60[d]	7.5 h	94		1.1:1

[a] Reaction conditions: C_6D_6, Ar atm. [b] Reaction mixtures were heated to 60 °C after all **13** had disappeared (according to ^{1}H NMR spectroscopic analysis) in order to facilitate bicyclization. [c] Diastereomeric ratios were determined by ^{1}H NMR spectroscopy. [d] The sample was heated to 60 °C after it had been left at 25 °C for 45 h.

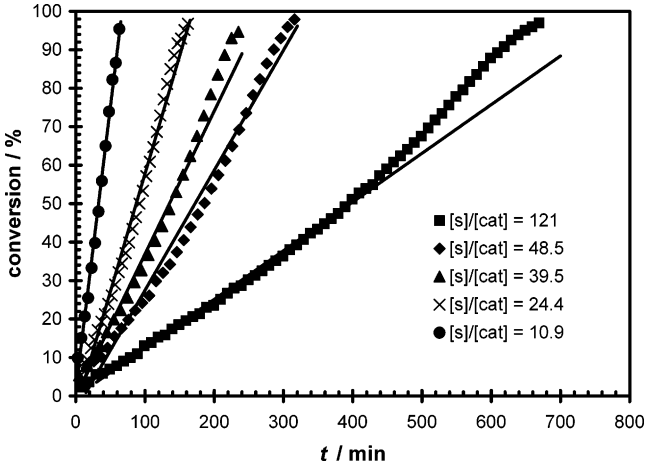


Figure 6. Conversion versus time for the hydroamination/cyclization of **5** ([s] = 0.74 mmol mL^{-1}) with **4a** at 25 °C in C_6D_6. The lines through the data points represent the least-squares fit for the linear part of the data.

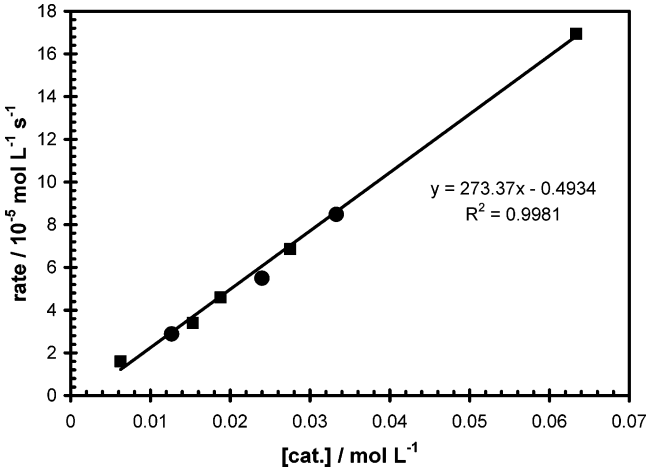


Figure 7. Dependence of catalyst concentration on observed rate for the hydroamination/cyclization of **5** with **2a** (●) and **4a** (■) at 25 °C in C_6D_6. The line through the data points represents the least-squares fit for all data obtained with catalyst **4a**.

using lanthanocene catalysts involving olefin insertion into the rare earth metal amide bonds during the rate-determining step.[8c] Deviation from linearity at high conversions can be attributed to inhibition caused by competitive coordination of the pyrrolidine hydroamination product.[8f] The solvated complex **1** shows significant deviation from zero-order kinetics in substrate and can be better described by a first-order rate law in substrate (Figure 10).

Both mesityl-substituted diamidoamine complexes, **2a** and **4a**, show significantly higher catalytic activity in the presence of THF than complex **1** (Table 1, entries 4, 8, and 9), which is only slightly decreased when compared to their activity in the absence of THF. Additionally, the reactions remain zero-order in substrate in the presence of THF.

Ring-closing of 1-methylpent-4-enylamine (**11**) with catalysts **2a**,**b** and **4a**,**b** proceeds with good activity at room temperature with high *trans* selectivity (Table 2, entries 1, 2, 4, and 6),[28] whereas [Y(*o*-$C_6H_4CH_2NMe_2$)$_3$] and [La{N(SiMe$_3$)$_2$}$_3$] require high temperatures and display low diastereoselectivity (Table 2, entries 8 and 9).[29] The *trans* selectivity for catalyst **4c** is somewhat smaller than that for complex **4a**, which is most likely due to less steric hindrance around the yttrium metal center when exchanging mesityl for 2,6-dichlorophenyl substituents. However, catalysts **2b** and **4b** with increased steric bulk around yttrium give diastereoselec-

(28) Preliminary experiments using a sample of the lanthanum complex **3a** contaminated with 16% [La{N(SiMe$_3$)$_2$}$_3$] showed diminished catalytic activity (2 h^{-1} at 25 °C) and diastereoselectivity (5:1 *trans*:*cis*) in the ring-closing reaction of **11**. [La{N(SiMe$_3$)$_2$}$_3$] requires elevated temperatures for the cyclization of **11** (see Table 2, entry 9; see also refs 9b,d) and is catalytically inactive at 25 °C.

(29) This is in accordance with observations made with [Ln{N(SiMe$_3$)$_2$}$_3$] (Ln = Y, Nd), see refs 9b,d.

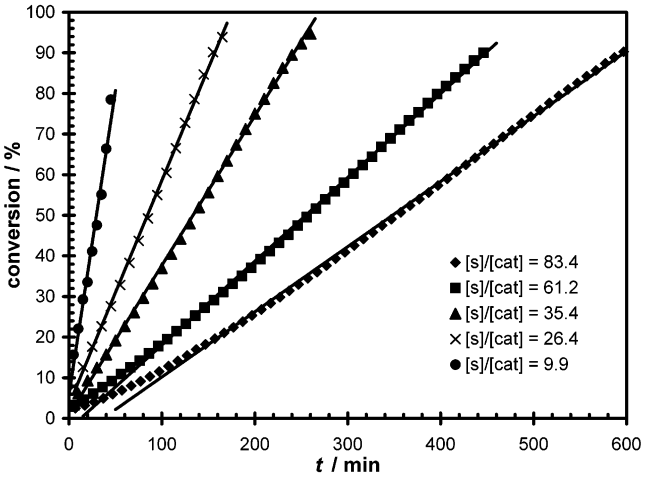


Figure 8. Conversion versus time for the hydroamination/cyclization of **11** with **4a** at 25 °C in C_6D_6. The lines through the data points represent the least-squares fit for the linear part of the data.

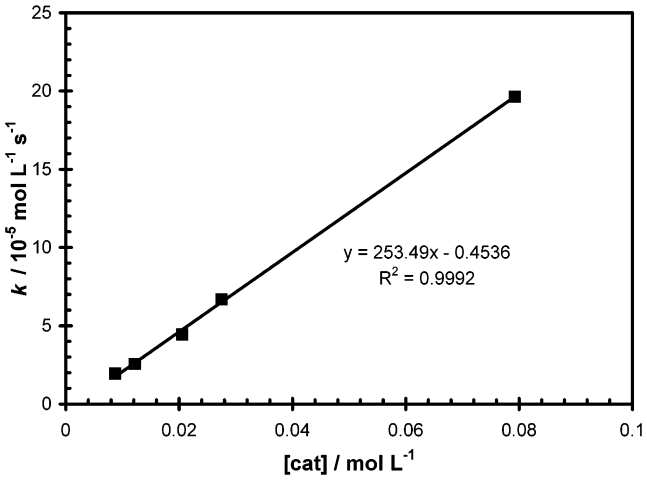


Figure 9. Dependence of catalyst concentration on observed rate for the hydroamination/cyclization of **11** with **4a** at 25 °C in C_6D_6. The lines through the data points represent the least-squares fit for all data.

tivity similar to that of **2a** and **4a**. Diastereoselectivity for substrate **13**, on the other hand, is rather low for all catalysts. Although the relative orientation of the two isomeric pyrrolidines of **14** cannot be confirmed, it is believed that the major isomer **14a** has the methyl group in the 2-position and the sterically slightly more demanding allyl substituent in the 4-position with *cis* orientation relative to each other. This interpretation would be in accordance with the observed slight preference for the formation of *cis*-2,4-dimethylpyrrolidine in the cyclization of 2-methylpent-4-enylamine.[8c,9d] The second allyl group reacts very slowly at room temperature, preferentially to give the *exo*,*exo*-isomer **15b** (Table 3, entry 6). However, facile bicyclization of **14** to a mixture of *endo*,*exo*- and *exo*,*exo*-2,4,6-dimethyl-1-azabicyclo[2.2.1]heptane[30] can be achieved upon heating to 60 °C (Table 3). Similar to the first cyclization step, the bicyclization proceeds rather unselectively to yield the two diastereomers in essentially 1:1 ratio.

Discussion

As recent investigations by Livinghouse have shown, even simple catalyst systems such as $[Ln\{N(SiMe_3)_2\}_3]$[9b]

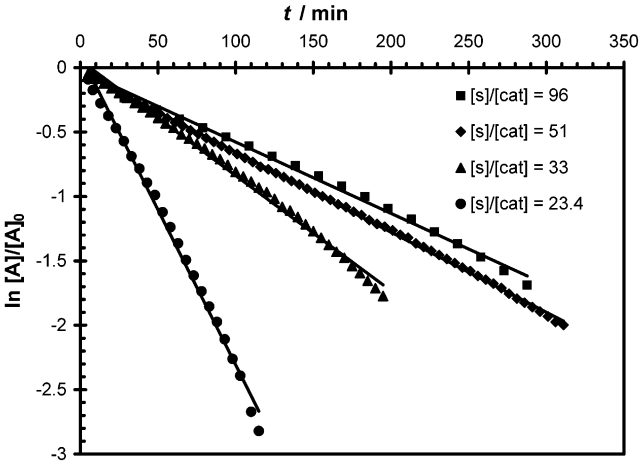


Figure 10. First-order plot for the hydroamination/cyclization of **5** with **1** at 60 °C in C_6D_6. The lines through the data points represent the linearization by least-squares analysis of all data.

or systems derived thereof by addition of a chelating diamine[9d,g,15] show good catalytic activity and often high selectivity. In this study several different diamidoamine ligand based rare earth metal complexes have been prepared. An attractive feature of these systems is the straightforward ligand synthesis, allowing easy ligand modifications.[31] The complexes can be prepared in a single step from readily available trisamido or trisaryl complexes. From a synthetic point of view, the pentacoordinate yttrium amido complex $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ is the better starting material for complex synthesis when compared with $[Y\{N(SiMe_3)_2\}_3]$, because product formation proceeds cleanly under mild conditions without formation of unwanted side products. This result is not unprecedented, as rare earth metal amido complexes $[Ln\{N(SiMe_3)_2\}_3]$ have been shown to often yield polymeric material or undesired side products or failed to give the desired product at all in a number of examples.[9f,32] However, complexes with the bis(dimethyldisilyl)amido are inferior catalysts for hydroamination/cyclization due to sluggish initiation (vide infra). Additionally, we have employed $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$, which can be conveniently synthesized in large quantities from cheap starting materials, as a new and valuable starting material for catalyst synthesis.[18] $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ is the better starting material for the synthesis of complexes with the dichlorophenyl-substituted ligand, because **4c** precipitates in high yield and purity directly from the toluene reaction mixture, whereas the bis(trimethylsilylamido) complex **2c** requires further purification and was obtained in lower yield. The only disadvantage of $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$ as a starting material is the thermal sensitivity of the diamidoamine

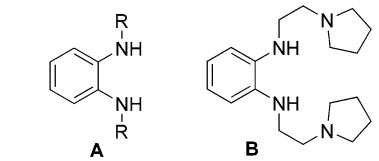
(30) Assignment of stereochemistry is based on H,H-COSY, C,H-COSY, and 2D-NOESY experiments. For the synthesis of analogous 1-aza-bicyclo[2.2.1]heptane derivatives via reverse Cope elimination see: Ciganek, E. *J. Org. Chem.* **1995**, *60*, 5803.

(31) Even simple modifications to the ligand structure of cyclopentadienyl ligands can require tedious multistep procedures, see for example: (a) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965. (b) Halterman, R. L. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, p 455.

(32) (a) Runte, O.; Priermeier, T.; Anwander, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1385. (b) Görlitzer, H. W.; Spiegler, M.; Anwander, R. *Eur. J. Inorg. Chem.* **1998**, 1009. (c) Dash, A. K.; Razavi, A.; Mortreux, A.; Lehmann, C. W.; Carpentier, J.-F. *Organometallics* **2002**, *21*, 3238.

complex **4a**. Decomposition of **4a** gives multiple products according to NMR spectroscopic analysis, suggesting a rather unselective decomposition process. However, the facts that **4b** is thermally more stable than **4a** and complex **4c** is resistant to thermal decomposition suggest that decomposition of **4a** most likely occurs via initial intra- or intermolecular C−H activation of the methyl groups on the mesityl substituents, followed by secondary decomposition reactions. Analogous diamidoamine zirconium alkyl cation complexes have been shown to decompose via C−H activation of the mesityl methyl group with first-order kinetics.[12c,d]

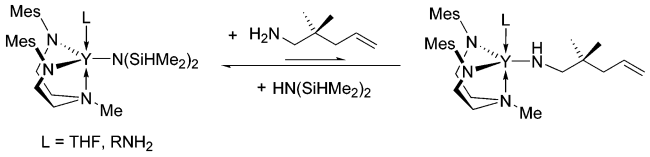
The activity for catalytic hydroamination/cyclization of complexes **2** and **4** is comparable to homoleptic trisamido catalysts [Ln{N(SiMe$_3$)$_2$}$_3$] for substrates **5** and **13**, in addition to higher activity for substrates **7**, **9**, and **11**. This contrasts with results from the Livinghouse system generated from [Y{N(SiMe$_3$)$_2$}$_3$] and *N*,*N*′-disubstituted-benzene-1,2-diamines **A**, which gave inferior activity for aminoalkene **5** compared to [Y{N(SiMe$_3$)$_2$}$_3$] itself.[9b] The diamidoamine catalysts seem to have comparable activity to the [Y{N(SiMe$_3$)$_2$}$_3$]/chelating diamine in situ systems reported by Livinghouse[9d,g] in the ring-closing of 1-methylpent-4-enylamine (**11**), although our reactions with diamidoamine catalysts were generally performed at ambient temperature and the Livinghouse systems were generally used at 60 °C. Interestingly, a catalyst system prepared from [Y{N(SiMe$_3$)$_2$}$_3$] and *N*,*N*′-disubstituted-benzene-1,2-diamine **B**, incorporating two additional pyrrolidine donor functionalities, displayed reduced activity when compared to a system lacking these additional amine donors. Although the structure of this system and catalyst integrity under the catalytic conditions have not been established, it seems reasonable to conclude that the two additional donors hamper substrate accessibility to the metal center by blocking two coordination sites. The diamidoamine systems presented herein leave one coordination site open for binding of the substrate.



When compared with well-established lanthanocene complexes,[8c] the catalytic activity of complexes **2** and **4** for aminoalkene **5** falls between [Cp*$_2$LaCH(SiMe$_3$)$_2$] (95 h^{-1} at 25 °C) and [Cp*$_2$LuCH(SiMe$_3$)$_2$] (<1 h^{-1} at 80 °C). Catalytic activity for the chiral aminoalkene **11** is lower than observed with [Cp*$_2$LaCH(SiMe$_3$)$_2$] (45 h^{-1} at 25 °C); however diastereoselectivity is higher (5:1 *trans*:*cis* ratio at 25 °C for [Cp*$_2$LaCH(SiMe$_3$)$_2$]; this ratio could be increased to 50:1 when 3 equiv of *n*-propylamine was added[8c]). Comparable diastereoselectivities were observed when using *ansa*-lanthanocenes [Me$_2$Si(C$_5$Me$_4$)$_2$NdCH(SiMe$_3$)$_2$] (20:1 at 25 °C) or [Me$_2$Si(C$_5$H$_4$)(C$_5$Me$_4$)YCH(SiMe$_3$)$_2$] (18:1 at 25 °C).[8c]

One serious potential problem of diamido and diamidoamine complexes is the loss of ligand during the catalytic hydroamination reaction by protolytic cleavage. This can result in significantly reduced catalytic activity and diastereoselectivity (e.g., for substrates **7** and **9**). Loss of ligand during catalysis would be even more detrimental to enantioselective hydroamination reactions using chiral amido ligands or other types of chiral ligand. As our results using catalysts **2c** and **4c** have shown, this protolytic loss of ligand can be largely prevented by employing more electron-withdrawing substituents such as 2,6-dichlorophenyl, resulting in a less basic anilido group.

Scheme 2



The low catalytic activity of **1**, in comparison to the THF adducts of complex **2a** and **4a**, has to be attributed mainly to the lower basicity of the bis(dimethylsilyl)-amido ligand as compared to the bis(trimethylsilyl)-amido ligand [i.e., the higher acidity of the conjugated acid tetramethyldisilazane (pK_a(HN(SiHMe$_2$)$_2$) = 22.8)[23a] versus hexamethyldisilazane (pK_a(HN(SiMe$_3$)$_2$) = 25.8)].[33] As a consequence of this difference in basicity of the amido ligands, the equilibrium between precatalyst and the catalytically active species is shifted toward precatalyst in the case of the less basic bis(dimethylsilyl)-amido ligand in complex **1**, which results in a sluggish initiation process (Scheme 2).

While low catalytic activity of [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] could be expected, based on the low activity of complex **1**, the lower activity of [Y(*o*-C$_6$H$_4$CH$_2$NMe$_2$)$_3$] compared to [Y{N(SiMe$_3$)$_2$}$_3$] was unexpected, because both complexes should give the same catalytic active species. This implies that some of the hexamethyldisilazane, formed in the protonolysis of [Y{N(SiMe$_3$)$_2$}$_3$] by the substrate, interacts with the catalytically active species during the catalytic cycle. Additional evidence that these "homoleptic" catalyst systems are more complicated than generally perceived comes from the fact that catalytic hydroaminations, involving [Y{N(SiMe$_3$)$_2$}$_3$] as a catalyst, are generally not zero-order in substrate.[34]

Conclusion

The diamidoamine ligand provides a good steric and electronic environment for the catalytic hydroamination reaction. Less steric hindrance could lead to deactivated oligomeric species with bridging amido ligands. More electron-deficient ligands could result in a stronger binding of the product heterocycle, thereby hampering their substitution with the substrate. Catalysts derived from the 2,6-dichlorophenyl-substituted ligand display increased catalyst stability and superior catalytic activity for a number of substrates that are problematic when homoleptic trisamido rare earth metal complexes [Ln{N(SiMe$_3$)$_2$}$_3$] or diamidoamine catalysts with mesityl- or 2,6-diethylphenyl-substituted ligands are employed.

(33) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.

(34) (a) Hultzsch, K. C. Unpublished observations. (b) For similar observations for [La{E(SiMe$_3$)$_2$}$_3$] (E = CH, N) made by Marks see ref 9h. See also: Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630.

Finally, preliminary experiments indicate that complexes **2a**−**c** and **4a**−**c** promise to be good candidates for other catalytic reactions, e.g., polymerization, hydrosilylation, and similar organic transformations.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexanes, pentane, benzene, and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous YCl_3 (ALFA) was used as received. $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$,[16] $[Ln\{N(SiMe_3)_2\}_3]$,[17] $[Y(o\text{-}C_6H_4CH_2NMe_2)_3]$,[18] $H_2(Mes_2N_2NMe)$,[12b] $H_2(Ar^{Cl}{}_2N_2NMe)$,[12c] and 2-bromo-1,3-diethylbenzene[35] substrates **5**,[36] **7**,[8c] **9**,[8h] **11**,[37] and **13**[9f] were synthesized as described in the literature. The substrates were dried by distillation from CaH_2, followed by a second distillation from trioctyl aluminum (2 mol % added). All other chemicals were commercially available and used as received unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department.

$(C_6H_3Et_2NHCH_2CH_2)_2NH$. A Schlenk flask was charged with tris(dibenzylideneacetone)dipalladium(0) (21.4 mg, 23.4 μmol), *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (32.0 mg, 51.4 μmol), and toluene (15 mL). This solution was heated to 90 °C for 15 min until a clear, bright orange solution had formed. The catalyst solution was then added to a suspension of sodium *tert*-butoxide (1.35 g, 14.0 mmol) in 2-bromo-1,3-diethylbenzene (2.00 g, 9.38 mmol), diethylenetriamine (482 mg, 4.67 mmol), and toluene (15 mL). The reaction mixture was heated to 100 °C for 24 h. Then diethyl ether (100 mL) was added, and the organic layer was washed with water (10 mL) and brine (10 mL). Drying over magnesium sulfate and removal of the solvent in vacuo furnished 1.67 g (97%) of the crude product as a brown oil, which was sufficiently pure according to ^1H NMR spectroscopy and was used without further purification for the next step. ^1H NMR ($CDCl_3$, 25 °C): δ 7.06 (d, $^3J_{HH}$ = 7.5 Hz, 4H, 3-$C_6H_3Et_2$), 6.96 (m, 2H, 4-$C_6H_3Et_2$), 3.08 (m, 4H, $Ar^{Et}NHCH_2$), 2.91 (m, 4H, CH_2NH), 2.72 (q, $^3J_{HH}$ = 7.5 Hz, 8H, $C_6H_3(CH_2CH_3)_2$), 1.27 (t, $^3J_{HH}$ = 7.6 Hz, 12H, $C_6H_3(CH_2CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 145.0 (1-$C_6H_3Et_2$), 136.3 (2-$C_6H_3Et_2$), 126.6 (3-$C_6H_3Et_2$), 122.6 (4-$C_6H_3Et_2$), 50.1 (CH_2NH), 49.7 ($Ar^{Et}NHCH_2$), 24.3 ($C_6H_3(CH_2CH_3)_2$), 14.9 ($C_6H_3(CH_2CH_3)_2$).

$(C_6H_3Et_2NHCH_2CH_2)_2NMe$ ($H_2(Ar^{Et}{}_2N_2NMe)$). A 100 mL Schlenk flask was charged with $(C_6H_3Et_2NHCH_2CH_2)_2NH$ (1.667 g, 4.51 mmol), potassium carbonate (3.00 g), and acetonitrile (20 mL). The solution was cooled to 0 °C and treated dropwise with methyl iodide (0.29 mL, 650 mg, 4.58 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight. The suspension was treated with water (20 mL) and extracted with pentane (2 × 20 mL). The solvent was removed in vacuo, and the product was purified by column chromatography on silica using hexanes, ethyl acetate, and methanol (4:1:0.4) as eluent to give 601 mg (35%) of $H_2(Ar^{Et}{}_2N_2NMe)$ as a light yellow oil. ^1H NMR ($CDCl_3$, 25 °C): δ 7.05 (d, $^3J_{HH}$ = 7.5 Hz, 4H, 3-$C_6H_3Et_2$), 7.00 (m, 2H, 4-$C_6H_3Et_2$), 3.63 (br s, 2H, NH), 3.09 (t, $^3J_{HH}$ = 7.5 Hz, 4H, $Ar^{Et}NCH_2$), 2.71 (m, 12H, CH_2NMe and $C_6H_3(CH_2CH_3)_2$), 2.33 (s, 3H, NCH_3), 1.26 (t, $^3J_{HH}$ = 7.6 Hz, 12H, $C_6H_3(CH_2CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 145.3 (1-$C_6H_3Et_2$), 135.9 (2-$C_6H_3Et_2$), 126.5 (3-$C_6H_3Et_2$), 122.3 (4-$C_6H_3Et_2$), 58.4 (CH_2NMe), 47.3 ($Ar^{Et}NCH_2$), 41.7 (NCH_3), 24.3 ($C_6H_3(CH_2CH_3)_2$), 14.8 ($C_6H_3(CH_2CH_3)_2$). Anal. Calcd for $C_{25}H_{39}N_3$: C, 78.68; H, 10.30; N, 11.01. Found: C, 78.96; H, 10.45; N, 10.91.

$[Y(Mes_2N_2NMe)\{N(SiHMe_2)_2\}(THF)]$ (1). In the glovebox a Schlenk flask was loaded with $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (630 mg, 1.00 mmol), toluene (10 mL), and then $H_2(Mes_2N_2NMe)$ (354 mg, 1.00 mmol). The flask was sealed and the solution was heated to 50 °C for 48 h. The solvent was then removed in vacuo and the remaining residue recrystallized from hexanes (20 mL) at −30 °C to give 495 mg (77%) of a white crystalline powder. ^1H NMR (C_6D_6, 25 °C): δ 6.94 (s, 4H, aryl-H), 4.91 (br m, 2H, SiH), 3.45 (m, 2H, $MesNCH_2$), 3.23 (m, 2H, $MesNCH_2$), 3.09 (m, 6H, CH_2NMe and α-CH_2, THF), 2.78 (m, 2H, CH_2NMe), 2.53 (s, 12H, 2-aryl-CH_3), 2.50 (s, 3H, NCH_3), 2.23 (s, 6H, 4-aryl-CH_3), 0.85 (m, 4H, β-CH_2, THF), 0.30 (d, $^3J_{HH}$ = 2.5 Hz, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 152.5, 130.4, 129.3, 128.6 (aryl), 70.0 (α-CH_2, THF), 58.0 (CH_2NMe), 51.6 (CH_2NMes), 42.2 (NCH_3), 24.7 (β-CH_2, THF), 21.0 (4-aryl-CH_3), 19.6 (2-aryl-CH_3), 4.4 ($SiCH_3$). Anal. Calcd for $C_{31}H_{55}N_4OSi_2Y$: C, 57.74; H, 8.60; N, 8.69. Found: C, 57.61; H, 8.44; N, 8.58.

$[Y(Mes_2N_2NMe)\{N(SiMe_3)_2\}]$ (2a). In the glovebox a Schlenk flask was loaded with $[Y\{N(SiMe_3)_2\}_3]$ (570 mg, 1.00 mmol), toluene (6 mL), and then $H_2(Mes_2N_2NMe)$ (382 mg, 1.08 mmol). The solution was heated to 120 °C for 22 h. The solvent was then removed in vacuo and the remaining residue recrystallized from pentane (3 mL) at −30 °C to give 385 mg (64%) of a white crystalline powder. ^1H NMR (C_6D_6, 25 °C): δ 6.95 (s, 4H, aryl-H), 3.49 (m, 2H, $MesNCH_2$), 2.97 (m, 4H, $MesNCH_2CH_2NMe$), 2.44 (s, 12H, 2-aryl-CH_3), 2.36 (m, 2H, CH_2NMe), 2.20 (s, 6H, 4-aryl-CH_3), 2.09 (s, 3H, NCH_3), 0.00 (s, 18 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 149.6, 134.2, 131.4, 129.6 (aryl), 58.8 (CH_2NMe), 50.4 (CH_2NMes), 42.5 (NCH_3), 20.9 (4-aryl-CH_3), 19.4 (2-aryl-CH_3), 3.1 ($SiCH_3$). Anal. Calcd for $C_{29}H_{51}N_4Si_2Y$: C, 57.97; H, 8.56; N, 9.32. Found: C, 57.72; H, 8.55; N, 9.27.

$[Y(Mes_2N_2NMe)\{N(SiMe_3)_2\}(THF)]$ (2a·THF). A solution of **2a** (7.9 mg, 13.1 μmol) in C_6D_6 (0.5 mL) was treated with THF (1.3 μL, 16.0 μmol) via microsyringe. The complex was not isolated, but used directly for the catalytic hydroamination reaction. ^1H NMR (C_6D_6, 25 °C): δ 6.92 (s, 4H, aryl-H), 3.45 (br m, 4.8H, 1.2 equiv THF), 3.35 (m, 2H, $MesNCH_2$), 3.15, (m, 2H, $MesNCH_2$), 3.03 (m, 2H, CH_2NMe), 2.65 (m, 2H, CH_2-NMe), 2.51 (s, 12H, 2-aryl-CH_3), 2.35 (s, 3H, NCH_3), 2.22 (s, 6H, 4-aryl-CH_3), 0.24 (s, 18 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 152.8, 135.0, 130.8, 129.4 (aryl), 69.0 (THF), 57.9 (CH_2NMe), 51.4 (CH_2NMes), 41.9 (NCH_3), 25.1 (THF), 20.9 (4-aryl-CH_3), 20.0 (2-aryl-CH_3), 5.7 ($SiCH_3$).

$[Y(Ar^{Et}{}_2N_2NMe)\{N(SiMe_3)_2\}]$ (2b). In the glovebox a Schlenk flask was loaded with $[Y\{N(SiMe_3)_2\}_3]$ (285 mg, 0.50 mmol), toluene (3.5 mL), and then $H_2(Ar^{Et}{}_2N_2NMe)$ (191 mg, 0.50 mmol). The solution was heated to 120 °C for 20 h. The solvent was then removed in vacuo and the remaining residue recrystallized from pentane (3 mL) at −30 °C to give 216 mg (69%) of an off-white crystalline powder. ^1H NMR (C_6D_6, 25 °C): δ 7.18 (d, $^3J_{HH}$ = 7.5 Hz, 4H, 3-$C_6H_3Et_2$), 7.07 (t, $^3J_{HH}$ = 7.5 Hz, 2H, 4-$C_6H_3Et_2$), 3.50 (m, 2H, $C_6H_3Et_2NCH_2$), 3.00 (m, 4H, $C_6H_3Et_2NCH_2CH_2NMe$), 2.89 (m, 8H, $C_6H_3(CH_2CH_3)_2$), 2.37 (m, 2H, CH_2NMe), 2.12 (s, 3H, NCH_3), 1.36 (t, $^3J_{HH}$ = 7.5 Hz, 12H, $C_6H_3(CH_2CH_3)_2$), −0.05 (br s, 18 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 151.0, 140.3, 126.2, 123.3 (aryl), 58.8 (CH_2NMe), 52.0 ($CH_2NC_6H_3Et_2$), 42.6 (NCH_3), 24.9 (br, $C_6H_3(CH_2CH_3)_2$), 15.6 ($C_6H_3(CH_2CH_3)_2$), 3.2 ($SiCH_3$). Anal. Calcd for $C_{31}H_{55}N_4Si_2Y$: C, 59.21; H, 8.82; N, 8.91. Found: C, 58.99; H, 8.90; N, 9.14.

$[Y(Ar^{Cl}{}_2N_2NMe)\{N(SiMe_3)_2\}]$ (2c). In the glovebox a Schlenk flask was loaded with $[Y\{N(SiMe_3)_2\}_3]$ (285 mg, 0.50 mmol), $H_2(Ar^{Cl}{}_2N_2NMe)$ (202 mg, 0.50 mmol), and toluene (5 mL). The solution was heated to 90 °C for 20 h. The solvent was then removed in vacuo and the remaining residue recrystallized from toluene (0.6 mL) at −30 °C to give 189 mg (58%) of a

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(37) (a) House, H. O.; Lee, L. F. *J. Org. Chem.* **1976**, *41*, 863. (b) Harding, K.; Burks, S. R. *J. Org. Chem.* **1981**, *46*, 3920.

white crystalline powder. ^{1}H NMR (C_6D_6, 25 °C): δ 6.92 (d, $^3J_{HH}$ = 7.9 Hz, 4H, 3-$C_6H_3Cl_2$), 6.07 (t, $^3J_{HH}$ = 7.9 Hz, 2H, 4-$C_6H_3Cl_2$), 3.81 (m, 4H, $Ar^{Cl}NCH_2$), 2.41 (m, 2H, CH_2NMe), 2.22 (s, 3H, NCH_3), 2.19 (m, 2H, CH_2NMe), 0.25 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 151.9 (d, $^2J_{YC}$ = 2.2 Hz, 1-$C_6H_3Cl_2$), 129.9 (3-$C_6H_3Cl_2$), 122.9 (2-$C_6H_3Cl_2$), 115.0 (4-$C_6H_3Cl_2$), 58.8 (CH_2NMe), 49.4 (CH_2NAr^{Cl}), 43.7 (NCH_3), 5.2 ($SiCH_3$). Anal. Calcd for $C_{23}H_{35}Cl_4N_4Si_2Y$: C, 42.21; H, 5.39; N, 8.56. Found: C, 42.07; H, 5.39; N, 8.36.

[La(Mes$_2$N$_2$NMe){N(SiMe$_3$)$_2$}] (3a). In the glovebox a Schlenk flask was loaded with [La{N(SiMe$_3$)$_2$}$_3$] (311 mg, 0.50 mmol), toluene (4 mL), and then H_2(Mes$_2$N$_2$NMe) (198 mg, 0.56 mmol). The solution was heated to 115 °C for 16 h. The solvent was then removed in vacuo and the remaining residue recrystallized from pentane (1 mL) at −30 °C to give 110 mg of a off-white powder, which still contained 16% of [La{N(SiMe$_3$)$_2$}$_3$] as impurity. ^{1}H NMR (C_6D_6, 25 °C): δ 6.92 (s, 4H, aryl-H), 3.58 (m, 2H, MesNCH_2), 3.26 (m, 2H, MesNCH_2), 3.06 (m, 2H, CH_2NMe), 2.50 (m, 2H, CH_2NMe), 2.38 (s, 12H, 2-aryl-CH_3), 2.28 (s, 3H, NCH_3), 2.19 (s, 6H, 4-aryl-CH_3), 0.18 (s, 18 H, $SiCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 147.3, 133.9, 131.3, 130.0 (aryl), 59.4 (CH_2NMe), 51.5 (CH_2NMes), 41.9 (NCH_3), 20.9 (4-aryl-CH_3), 19.5 (2-aryl-CH_3), 3.6 ($SiCH_3$).

[Y(Mes$_2$N$_2$NMe)(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] (4a). To a solution of [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (742 mg, 1.51 mmol) in toluene (5 mL) was added H_2(Mes$_2$N$_2$NMe) (583 mg, 1.65 mmol). The solution was stirred at 25 °C for 3.5 h. The solvent was then removed in vacuo and the remaining residue recrystallized from pentane (4 mL) at −30 °C to give 510 mg (59%) of **4a** as a light yellow microcrystalline powder. ^{1}H NMR (C_6D_6, 25 °C): δ 7.97 (d, $^3J_{HH}$ = 6.1 Hz, 1H, 6-C_6H_4), 7.30 (m, 1H, 5-C_6H_4), 7.17 (m, 1H, 4-C_6H_4), 6.86 (s, 4H, $C_6H_2Me_3$), 6.79 (d, $^3J_{HH}$ = 7.6 Hz, 1H, 3-C_6H_4), 3.53 (m, 2H, MesNCH_2), 3.20 (m, 2H, MesNCH_2), 3.07 (m, 2H, CH_2CH_2NMe), 3.05 (s, 2H, NC$H_2C_6H_4$), 2.61 (m, 2H, CH_2CH_2NMe), 2.55 (s, 3H, $CH_2N(CH_3)CH_2$), 2.34 (s, 12H, 2-$C_6H_2CH_3$), 2.18 (s, 6H, 4-$C_6H_2CH_3$), 1.31 (s, 6H, $CH_2N(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 184.6 (d, $^1J_{YC}$ = 56.5 Hz, Y-C$_{ipso}$), 150.1 (1-$C_6H_2Me_3$), 145.8 (2-C_6H_4), 138.1 (6-C_6H_4), 135.5, 131.0 (aryl), 129.3 (3-$C_6H_2Me_3$), 125.9 (4-C_6H_4), 125.6 (3-C_6H_4), 125.4 (5-C_6H_4), 67.2 (NC$H_2C_6H_4$), 58.6 (CH_2CH_2NMe), 51.0 (CH_2NMes), 43.1 ($N(CH_3)_2$), 41.5 ($CH_2N(CH_3)CH_2$), 20.9 (4-$C_6H_2CH_3$), 19.1 (2-$C_6H_2CH_3$). Anal. Calcd for $C_{32}H_{45}N_4Y$: C, 66.89; H, 7.89; N, 9.75. Found: C, 64.78; H, 7.76; N, 10.07.

Decomposition Kinetics of 4a. In the glovebox, a screw cap NMR tube was charged with **4a** (10.2 mg 17.8 μmol), ferrocene (2.7 mg, 14.5 μmol), and C_6D_6 (0.5 mL). The NMR tube was then placed in the thermostated probe (±0.5 °C) of the Bruker Avance 400 spectrometer. The decomposition was monitored by ^{1}H NMR spectroscopy by following the disappearance of the signal of H_6 of *o*-$C_6H_4CH_2NMe_2$ at 7.97 ppm relative to the internal standard ferrocene. NMR spectra were taken in 30 min intervals using the *multizg* script from the Bruker XWinNMR software package. To ensure accurate integration, a 10 s delay between 30° pulses was utilized (number of scans = 8, acquisition time = 4 s). The data were linearized by a first-order logarithmic plot (Figure 1) and were fit by least-squares analysis (all data) to give the half-life from the slope. After complete decomposition of **4a**, aminoalkene **5** (40.0 mg, 0.353 mmol) was added and the catalytic hydroamination kinetics was monitored as described below.

[Y(Ar$^{Et}_2$N$_2$NMe)(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] (4b). To a solution of [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (250 mg, 0.51 mmol) in toluene (3 mL) was added $H_2(Ar^{Et}{}_2N_2NMe)$ (197 mg, 0.52 mmol). The solution was stirred at 25 °C for 3 h. The solvent was then removed in vacuo and the remaining residue recrystallized from hexanes (2 mL) at −30 °C to give 220 mg (72%) of **4b** as an off-white microcrystalline powder. ^{1}H NMR (toluene-d_8, −30 °C): δ 7.93 (d, $^3J_{HH}$ = 6.6 Hz, 1 H, 6-C_6H_4), 7.28 (pt, $^3J_{HH}$ = 6.9 Hz, 1H, 5-C_6H_4), 7.15 (dt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, 4-C_6H_4), 7.03−7.12 (br m, 4H, 3-$C_6H_3Et_2$), 6.98 (pt, $^3J_{HH}$ = 7.4 Hz, 2H, 4-$C_6H_3Et_2$), 6.78 (d, $^3J_{HH}$ = 7.4 Hz, 1H, 3-C_6H_4), 3.54 (m, 2H, $Ar^{Et}NCH_2$), 3.25 (m, 2H, $Ar^{Et}NCH_2$), 2.88−3.05 (m, 6H, CH_2CH_2-NMe and $C_6H_3(CH_2CH_3)_2$, obscured by other signal), 2.93 (s, 2H, NC$H_2C_6H_4$), 2.68 (m, 2H, $C_6H_3(CH_2CH_3)_2$) 2.55 (m, 7H, $CH_2N(CH_3)CH_2$, $C_6H_3(CH_2CH_3)_2$, and CH_2CH_2NMe), 1.38 (t, $^3J_{HH}$ = 7.5 Hz, 6H, $C_6H_3(CH_2CH_3)_2$), 1.15 (s, 6H, $CH_2N(CH_3)_2$), 1.05 (t, $^3J_{HH}$ = 7.5 Hz, 6H, $C_6H_3(CH_2CH_3)_2$). ^{13}C{^{1}H} NMR (toluene-d_8, −30 °C): δ 184.0 (d, $^1J_{YC}$ = 57.1 Hz, Y-C$_{ipso}$), 151.6 (1-$C_6H_3Et_2$), 145.8 (2-C_6H_4), 142.6 (2-$C_6H_3Et_2$), 140.7 (2-$C_6H_3Et_2$), 138.2 (6-C_6H_4), 126.7 (3-$C_6H_3Et_2$), 125.9 (4-C_6H_4), 125.8 (3-$C_6H_3Et_2$), 125.6 (3-C_6H_4), 125.4 (5-C_6H_4), 122.9 (4-$C_6H_3Et_2$), 67.0 (NC$H_2C_6H_4$), 58.5 (CH_2CH_2NMe), 52.7 ($Ar^{Et}NCH_2$), 43.2 ($N(CH_3)_2$), 41.6 ($CH_2N(CH_3)CH_2$), 25.1 ($C_6H_3(CH_2CH_3)_2$), 25.0 ($C_6H_3(CH_2CH_3)_2$), 16.5 ($C_6H_3(CH_2CH_3)_2$). Anal. Calcd for $C_{34}H_{49}N_4Y$: C, 67.76; H, 8.19; N, 9.30. Found: C, 66.40; H, 8.13; N, 9.51.

[Y(Ar$^{Cl}_2$N$_2$NMe)(*o*-C$_6$H$_4$CH$_2$NMe$_2$)] (4c). A mixture of [Y(*o*-$C_6H_4CH_2NMe_2)_3$] (495 mg, 1.01 mmol) and $H_2(Ar^{Cl}{}_2N_2$-NMe) (404 mg, 0.99 mmol) was dissolved in toluene (5 mL) with vigorous stirring. The solution was stirred at 25 °C for 4 h, during which the product precipitated from the reaction mixture. The solvent was then removed in vacuo and the remaining residue recrystallized from toluene at −30 °C to give 566 mg (91%) of an off-white microcrystalline powder. ^{1}H NMR (C_6D_6, 25 °C): δ 8.05 (d, $^3J_{HH}$ = 6.6 Hz, 1H, 6-C_6H_4), 7.28 (pt, 1H, 5-C_6H_4), 7.22 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, 4-C_6H_4), 6.96 (d, $^3J_{HH}$ = 7.9 Hz, 4H, 3-$C_6H_3Cl_2$), 6.94 (d, 1H, 3-C_6H_4, obscured by other signal), 6.09 (t, $^3J_{HH}$ = 7.9 Hz, 2H, 4-$C_6H_3Cl_2$), 3.83 (t, $^3J_{HH}$ = 5.2 Hz, 4H, $Ar^{Cl}NCH_2$), 3.38 (s, 2H, NC$H_2C_6H_4$), 2.64 (dt, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, CH_2CH_2NMe), 2.42 (dt, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, CH_2CH_2NMe), 2.06 (s, 3H, $CH_2N(CH_3)CH_2$), 1.84 (s, 6H, $CH_2N(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 185.5 (d, $^1J_{YC}$ = 48.2 Hz, Y-C$_{ipso}$), 153.2 (d, $^2J_{YC}$ = 2.2 Hz, 1-$C_6H_3Cl_2$), 145.7 (2-C_6H_4), 138.5 (6-C_6H_4), 129.6 (3-$C_6H_3Cl_2$), 125.8 (4-C_6H_4), 125.4 (5-C_6H_4), 124.8 (3-C_6H_4), 124.0 (2-$C_6H_3Cl_2$), 114.7 (4-$C_6H_3Cl_2$), 69.7 (NC$H_2C_6H_4$), 58.9 (CH_2CH_2NMe), 50.1 (CH_2NAr^{Cl}), 46.2 ($N(CH_3)_2$), 44.0 ($CH_2N(CH_3)CH_2$). Anal. Calcd for $C_{26}H_{29}$-Cl_4N_4Y: C, 49.71; H, 4.65; N, 8.92. Found: C, 49.27; H, 4.69; N, 8.66.

Crystallography. Clear, colorless crystals of **1** and **4b** suitable for X-ray diffraction analysis were obtained by cooling of a concentrated solution of **1** in toluene and also a solution of **4b** in pentane to −30 °C. Data were collected on a Nonius KappaCCD area detector. Crystal data for **1**: $C_{31}H_{55}N_4OSi_2Y$, M_r = 644.88, monoclinic, space group $P2_1$, a = 9.7470(2) Å, b = 14.6052(4) Å, c = 12.8195(3) Å, β = 101.1230(10)°, V = 1790.66(7) Å^3, Z = 2, ρ_{calcd} = 1.196 g cm^{-3}, F(000) = 688, Mo Kα radiation (λ = 0.71073 Å), μ = 1.722 mm^{-1}, crystal dimensions 0.25 × 0.20 × 0.10 mm, T = 173(2) K, 6948 independent reflections for 2.8° ≤ θ ≤ 27.5°, GOF = 1.050, R ($I > 2\sigma(I)$) = 0.0379, wR_2 (all data) = 0.0918, absolute structure parameter = −0.014(5), largest difference peak and hole 0.278 and −0.474 e·Å^{-3}. Crystal data for **4b**: $C_{34}H_{49}N_4Y$, M_r = 602.68, orthorhombic, space group $Pna2_1$, a = 13.7353(3) Å, b = 23.7396(8) Å, c = 9.8481(3) Å, V = 3211.18(16)) Å^3, Z = 4, ρ_{calcd} = 1.247 g cm^{-3}, F(000) = 1280, Mo Kα radiation (λ = 0.71073 Å), μ = 1.844 mm^{-1}, crystal dimensions 0.35 × 0.35 × 0.20 mm, T = 173(2) K, 6884 independent reflections for 2.7° ≤ θ ≤ 27.5°, GOF = 1.024, R ($I > 2\sigma(I)$) = 0.0450, wR_2 (all data) = 0.1206, absolute structure parameter = 0.511(8) (racemic twin), largest difference peak and hole 0.566 and −0.497 e·Å^{-3}. Cell parameters for **1** and **4b** were obtained from 10 frames using a 10° scan and refined with 4006 reflections for **1** and 3762 reflections for **4b**. Lorentz, polarization, and empirical absorption corrections were applied.[38a,b] The space groups were determined from systematic absences and subsequent least-squares refinement. The structures were solved

(38) (a) "Collect" data collection software, Nonius, B. V. 1998. (b) "Scalepack" data processing software: Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276* (Macromolecular Crystallography, Part A), 307. (c) Sheldrick, G. M. *SHELX-97*, Program for the refinement

by direct methods, and the structure of complex **4b** was solved and refined as a racemic twin. The parameters were refined with all data by full-matrix least-squares on F^2 using SHELXL-97.[38c] Non-hydrogen atoms were refined anisotropically. C2a, C2, and C3 in **4b** were disordered and were refined with two independent positions (occupation ratio 49:51%). Hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[38d] Graphical representations were prepared with ORTEP-III for Windows.[38e]

General Procedure for NMR-Scale Catalytic Hydroamination/Cyclization Reactions. In the glovebox, a screw cap NMR tube was charged with 10 μmol of the catalyst, C_6D_6 (0.5 mL), and the substrate (0.33 mmol) in that order. The NMR tube was then placed in a pretempered oil bath and conversion followed by ^{1}H NMR spectroscopy (for acquisition parameters see below). Final conversion was determined by ^{1}H NMR spectroscopy (disappearance of olefinic signals) and by GC analysis. Diastereomeric ratios of pyrrolidines **12** and **14** were determined by vacuum-transfer of all volatiles and subsequently ^{1}H NMR spectroscopic analysis of characteristic signals (3.15, 2.93, 1.75, and 1.65 ppm for **12**; 2.73, 2.56, 2.42, 1.62, and 1.39 ppm for **14**). For NMR spectroscopic characterization of known substrates and pyrrolidines **5**−**9**, **11**, **12**, and **14** in C_6D_6 see Supporting Information. For NMR spectroscopic data of pyrroline **10** in C_6D_6 see ref 8h; for aminoalkene **13** see ref 9f.

2,4,6-Trimethyl-1-aza-bicyclo[2.2.1]heptane (15). Following the general procedure for NMR-scale catalytic hydroamination/cyclization reactions, cyclization of **13** at room temperature was monitored by NMR spectroscopy. The sample was heated to 60 °C after all **13** had been consumed. Final conversion and diastereomeric ratios where determined after vacuum transfer. *endo*,*exo*-Isomer (**15a**): ^{1}H NMR (C_6D_6, 25 °C): δ 3.09 (m, 1H, C*H*(CH_3)), 3.00 (m, 1H, C*H*(CH_3)) 2.31 (dd, 1H, $^3J_{HH}$ = 9.5 Hz, $^4J_{HH}$ = 2.3 Hz, bridging CH_2), 2.00 ("dt", 1H, $^3J_{HH}$ = 9.4 Hz, $^4J_{HH}$ = 2 Hz, bridging CH_2), 1.34 (ddd, $^3J_{HH}$ = 11.2 Hz, $^3J_{HH}$ = 10.1 Hz, $^4J_{HH}$ = 3.4 Hz, 1H, C*H*$_2$CH(CH_3)), 1.13 (m, 1H, C*H*$_2$CH(CH_3), obscured by other signal), 1.03−1.10 (m, 9H, CH_3, obscured by signals of other isomer), 0.80 (m, 1H, C*H*$_2$CH(CH_3)), 0.37 (ddd, $^3J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 2.2 Hz, 1H, C*H*$_2$CH(CH_3)). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 63.5 (bridging CH_2), 59.9 (*C*HCH_3), 51.1 (*C*HCH_3) 48.5 (*C*(CH_3)), 47.8 (*C*H$_2$CH(CH_3)), 44.3 (*C*H$_2$CH(CH_3)), 23.2, 23.0 (C(*C*H_3), either isomer), 17.74, 17.72, 17.1 (CH(*C*H_3), either isomer). *exo*,*exo*-Isomer (**15b**): ^{1}H NMR (C_6D_6, 25 °C): δ 2.57 (m, 2H, C*H*(CH_3)), 2.05 (s, 2H, bridging CH_2), 1.13 (m, 2H, C*H*$_2$CH(CH_3), obscured by signals of other isomer), 1.03−1.10 (m, 9H, CH_3, obscured by signals of other isomer), 0.74 (m, 2H, C*H*$_2$CH(CH_3)). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 62.6 (*C*HCH_3), 57.5 (bridging CH_2), 46.9 (*C*(CH_3)), 45.6 (*C*H$_2$CH(CH_3)), 23.2, 23.0 (C(*C*H_3), either isomer), 17.74, 17.72, 17.1 (CH(*C*H_3), either isomer). Anal. Calcd for the hydrochloride salt C_9H_{18}ClN: C, 61.52; H, 10.33; N, 7.97. Found: C, 61.45; H, 10.22; N, 8.18.

Preparative-Scale Procedure for Hydroamination/Cyclization Reactions. 2,4,4-Trimethylpyrrolidine Hydrochloride (6·HCl). In the glovebox, a flask was fitted with a stirring bar and was charged with **4a** (7.0 mg, 12.2 μmol), benzene (0.5 mL), and 2,2-dimethylpent-4-enylamine (114 mg, 1.01 mmol) in that order. The solution was then stirred at room temperature for 19 h. All volatiles were then vacuum-transferred, diluted with pentane (2 mL), and treated with hydrochloric acid (1.3 mL, 1 M in Et_2O, 1.3 mmol) at 0 °C. After 30 min, the suspension was brought to room temperature and solvent was removed in vacuo. The white precipitate was washed with diethyl ether and then dried in air to give 140 mg (94%) of a white powder. ^{1}H NMR ($CDCl_3$, 25 °C): δ 9.87 (br s, 1H, NH_2Cl), 9.47 (br s, 1H, NH_2Cl), 3,79 (m, 1H, C*H*(CH_3)NH_2Cl), 3.07 (m, 1H, C*H*$_2NH_2Cl$), 2.95 (m, 1H, C*H*$_2$-NH_2Cl), 1.87 (dd, 1H, $^2J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 6.5 Hz, C*H*$_2$CH-(CH_3)NH_2Cl), 1.53 (dd, 1H, $^2J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 11.2 Hz, C*H*$_2$CH(CH_3)NH_2Cl), 1.48 (d, $^3J_{HH}$ = 6.5 Hz, CH(C*H*$_3$)NH_2Cl), 1.16 (s, 3H, C(CH_3)$_2$), 1.11 (s, 3H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 56.3 (CH_2NH_2Cl), 55.3 (*C*H(CH_3)NH_2Cl), 46.9 (*C*H$_2$CH(CH_3)NH_2Cl), 38.7 (*C*(CH_3)$_2$), 27.22 (C(*C*H_3)$_2$), 27.19 (C(*C*H_3)$_2$), 18.0 (CH(*C*H_3). Anal. Calcd for C_7H_{16}ClN: C, 56.18; H, 10.78; N, 9.36. Found: C, 56.01; H, 10.66; N, 9.33.

2,5-Dimethylpyrrolidine Hydrochloride (12·HCl).[39] In the glovebox, a flask was fitted with a stirring bar and was charged with **4a** (11.1 mg, 19.3 μmol), benzene (0.5 mL), and 1-methylpent-4-enylamine (99 mg, 1.00 mmol) in that order. The solution was then stirred at room temperature for 22 h. All volatiles were then vacuum-transferred, diluted with pentane (3 mL), and treated with hydrochloric acid (1.3 mL, 1 M in Et_2O, 1.3 mmol) at 0 °C. After 30 min, the suspension was brought to room temperature and solvent was removed in vacuo. The white precipitate was washed with diethyl ether and then dried in air to give 125 mg (92%) of a white powder. *trans*-Isomer: ^{1}H NMR ($CDCl_3$, 25 °C): δ 9.50 (s, 2H, NH_2Cl), 3.79 (br m, 2H, C*H*NH_2Cl), 2.18 (br m, 2H, CH_2), 1.63 (br m, 2H, CH_2), 1.48 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 54.9 (CHNH), 32.2 (CH_2), 18.1 (CH_3).

General Procedure for Kinetic Catalytic Hydroamination/Cyclization Reactions. In a glovebox, a screw cap NMR tube was charged with 10 μmol of the catalyst, 6.0 mg of ferrocene (32.3 μmol), C_6D_6 (0.5 mL), and the substrate (0.33 mmol) in that order. The NMR tube was then placed in the thermostated probe (±0.5 °C) of the Bruker Avance 400 spectrometer. The conversion was monitored by ^{1}H NMR spectroscopy by following the disappearance of the olefinic signals of the substrate relative to the internal standard ferrocene. NMR spectra were taken in appropriate time intervals (e.g., 5, 10, 15, or 30 min) using the *multizg* script from the Bruker XWinNMR software package. To ensure accurate integration, a 10 s delay between 30° pulses was utilized (number of scans = 4, acquisition time = 4 s). Substrate and catalyst concentration was verified by comparison of the integrals of characteristic signals (olefinic signals for substrates; N(CH_3) or Si(CH_3) signals for liberated *N*,*N*-dimethylbenzylamine and for hexamethyldisilazane, and for catalyst **1** the total integration of Si(CH_3) signals). The linear part of the data (minimum two half-lives) were fit by least-squares analysis, and the turnover frequency (TOF) was determined from the slope *a*.

$$\mathrm{TOF} = a \times [\mathrm{subst.}]_0/[\mathrm{cat.}]$$

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Supporting Information Available: NMR spectroscopic characterization of known substrates and pyrrolidines **5**−**9**, **11**, **12**, and **14** as well as tables of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **1** and **4b** are available free of charge via the Internet at http://pubs.acs.org.

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