Constrained Geometry Organolanthanide Catalysts. Synthesis, Structural Characterization, and Enhanced Aminoalkene Hydroamination/Cyclization Activity

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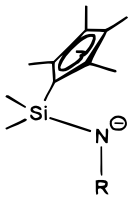
Summary: The synthesis and characterization of a series of $Me_2Si[(\eta^5\text{-}C_5Me_4)(^tBuN)]LnE(TMS)_2$ complexes is described for Ln = Sm, Nd, Yb, Lu; E = CH, N. As precatalysts for aminoalkene hydroamination/cyclization, they are significantly more active than the corresponding $(C_5Me_5)_2LnE(TMS)_2$ complexes.

Research activity in organo-rare earth catalysis has grown exponentially, and lanthanocenes[1] have been shown to exhibit unique characteristics as catalysts in hydrogenation,[2] oligomerization,[3] polymerization,[4] hydroamination,[5] hydrosilylation,[6] silanolytic chain transfer,[7] and hydroboration.[8] Organolanthanides combine facile ligand exchange and high electrophilicity with thermochemically understandable reaction pathways, while the lanthanide series offers tunable reactivity via variation of metal ionic radius and ancillary ligation.[1] Regarding the latter, the development of sterically less encumbered ancillary ligation which retains thermal stability and solubility is of great current interest.

Intramolecular hydroamination/cyclization of aminoalkenes,[5c,h,i] aminoalkynes,[5c,e−h] and aminoallenes[5a,b] can be mediated by a number of catalyst systems,[9] with lanthanocenes being some of the most efficient and selective discovered to date.[5] Mechanistically, amino alkene hydroamination/cyclization involves turnover-limiting insertion of the olefinic functionality into an Ln−N bond followed by rapid Ln−C protonolysis.[5] The rate is influenced by factors including substrate structure, metal ionic radius, and ancillary ligand "openess". The rate law is usually first-order in [catalyst] and zero-order in [substrate], with the ring-size cyclization rate dependence for aminoalkenes[5i] and -alkynes[5f] being 5 > 6 ≫ 7. These observations raise the intriguing question of whether less sterically/electronically saturated catalysts would effect more rapid hydroamination and conversion of more demanding substrates. In this regard, the silyl-linked amido cyclopentadienyl ligand $[Me_2Si(\eta^5\text{-}C_5Me_4)(^tBuN)]^{2-}$, originally developed for Sc,[10] has recently attracted attention, in group 4, where "constrained geometry catalysts" (e.g., **I**) exhibit impressive olefin polymerization characteristics.[11] We



I

report here a new series of constrained geometry organolanthanide $[Me_2Si(C_5Me_4)(^tBuN)]LnE(TMS)_2$ catalysts (E = N or CH; R = ^{t}Bu) and their significantly enhanced activity for aminoalkene hydroamination/cyclization.

$[Me_2Si(C_5Me_4)(^tBuN)]LnN(TMS)_2$ and $[Me_2Si(C_5Me_4)(^tBuN)]LnCH(TMS)_2$ complexes were synthesized by reaction of the corresponding homoleptic amides or alkyls with $Me_2Si(C_5Me_4H)(^tBuNH)$.[12] Unlike salt elimination reactions, the amine and alkane elimination

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(12) See Supporting Information for synthetic and characterization details.

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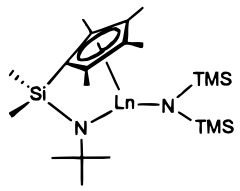
reactions proceed cleanly in hydrocarbon solvents, affording salt- and solvent-free products. However, amine elimination does not lie completely to the right and must be driven to completion by $HN(TMS)_2$ removal (eq 1).[12] When Ln = Sm, the bis-chelated complex [$Me_2Si(\eta^5$-$C_5Me_4)(^tBuN)$]Sm[$Me_2Si(\eta^5$-$C_5Me_4)(^tBuNH)$] (**2**) is also isolated in small quantities (eq 2). The separation of **1** from **2** is achieved by recrystallization, while complex **4** is purified by recystallization and complex **3** by vacuum sublimation.

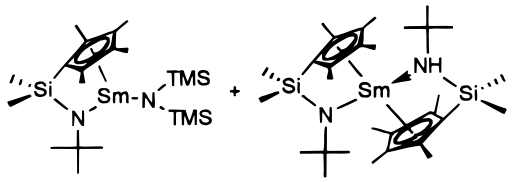
$$Ln[N(TMS)_2]_3 + Me_2Si(C_5Me_4H)(^tBuNH) \xrightarrow[\text{reflux}]{\text{toluene}} [-2\,NH(TMS)_2]$$

Ln = Nd(**3**), 24 % yield
Lu (**4**), 32 % yield



(1)

$$Sm[N(TMS)_2]_3 + Me_2Si(C_5Me_4H)(^tBuNH) \xrightarrow[\text{reflux}]{\text{toluene}}$$



major
1, 22 % yield

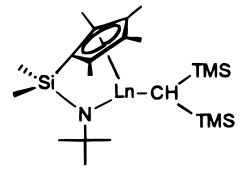
minor
2, 2.2 % yield

(2)

In contrast to amine elimination, alkane elimination is a more efficient synthetic route. The reaction is likely more exothermic,[13] and Ln−C bonds are protonolytically more reactive.[1] In situ NMR reveals that Ln[$CH(TMS)_2$]$_3$ complexes first undergo reaction with the N−H functionality of $Me_2Si(C_5Me_4H)(^tBuNH)$ to release 1.0 equiv of $CH_2(TMS)_2$, and heating is necessary to subsequently activate the tetramethylcyclopentadiene C−H group. Complexes **5** and **6** are readily synthesized via this route (eq 3).[12] However, thermal instability of the early lanthanide trialkyls has precluded synthesis of the Nd and Sm analogues.

$$Ln[CH(TMS)_2]_3 + Me_2Si(C_5Me_4H)(^tBuNH) \xrightarrow[\text{reflux}]{\text{toluene}} [-2\,CH_2(TMS)_2]$$

Ln = Yb (**5**), 49 % yield
Lu (**6**), 36 % yield



(3)

Complexes **1**−**6** were characterized by NMR, elemental analysis, and mass spectroscopy,[12] and **1**, **2**, and **5** by X-ray diffraction (Figures 1, 2).[12] Despite the lower formal coordination numbers, the Sm−$N(TMS)_2$ bond distance of 2.320(4) Å in complex **1** is significantly (>3σ) *longer* than those found in other samarocene bis(trimethylsilyl) amides, e.g., $(C_5Me_5)_2$Sm−$N(TMS)_2$ (2.301(3) Å),[14] (*S*)-[$Me_2Si(C_5Me_5)$((+)-neomenthylCp)]Sm−$N(TMS)_2$ (2.300(5) Å),[15] (*S*)-[$Me_2Si(C_5Me_5)$((−)-menthylCp)]Sm−$N(TMS)_2$ (2.302(9) Å).[15] However, the Sm−cent(Cp) distance (2.371 Å) is substantially *shorter* than in $(C_5Me_5)_2$Sm−$N(TMS)_2$ (Sm−cent(Cp1) = 2.479 Å, Sm−cent(Cp2) = 2.470 Å).[15] In **1**, the Sm−N(^{t}Bu) bond distance (2.257(4) Å) is shorter than the Sm−$N(TMS)_2$ bond distance (2.320(4) Å), presumably a consequence of the chelate structure. A close Ln−CH_3-Si contact of 2.657(5) Å is also observed in **5**. This "multicenter" Ln···Me−Si interaction[16] has been observed in numerous organolanthanide−$CH(TMS)_2$ complexes, e.g., (C_5Me_5)Y(OAr)$CH(TMS)_2$,[16a] (C_5Me_5)La-$[CH(TMS)_2]_2$,[15] $(C_5Me_5)_2$Ln$CH(TMS)_2$ (Ln = Ce,[17] Nd[2d]), [$Me_2Si(C_5H_5)(C_5Me_4)$]Lu$CH(TMS)_2$,[18] (*R*/*S*)-[$Me_2Si(C_5$-$Me_4)$((+)-neomenthylCp)]−Y$CH(TMS)_2$,[15] and (*R*)-[Me_2-$Si(C_5Me_4)$((−)-menthylCp)]YCH−$(TMS)_2$.[15]

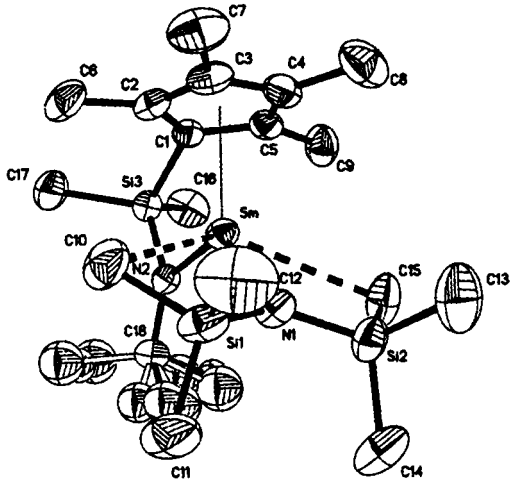


Figure 1. Molecular structure of complex **1**. Selected bond lengths (Å) and angles (deg): Sm−N(1), 2.320(4); Sm−N(2), 2.257(4); Sm−C(1), 2.600(5); Sm−C(2), 2.642(5); Sm−C(3), 2.697(5); Sm−Cent, 2.371; Sm···C(10), 3.308; Sm···C(15), 3.045. Sm−C(4), 2.709(5); Sm−C(5), 2.641(5). N(2)−Sm−N(1), 126.4(2); C(1)−Si−N(2), 97.1(2) [Cent is the centroid of Cp C(1)−C(5)].

Complexes **1**, **3**, **5**, and **6** are significantly more active for aminoalkene hydroamination/cyclization than conventional $(C_5Me_5)_2$LnR catalysts. Tables 1, 2 summarize results for CH_2=$CHCH_2C(CH_3)_2CH_2NH_2$ (**7**) and CH_2=

(13) Bond enthalpies from: (a) Nolan, S. P.; Stern, D.; Hedden, D.; Marks, T. J. *ACS Symp. Ser.* **1990**, *428*, 159. (b) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844.

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(19) Estimated from activation parameters in ref 5i.

(20) At longer conversions, some deviation is observed in the cases of the larger ionic radius lanthanides. This type of behavior has been observed before.[5h]

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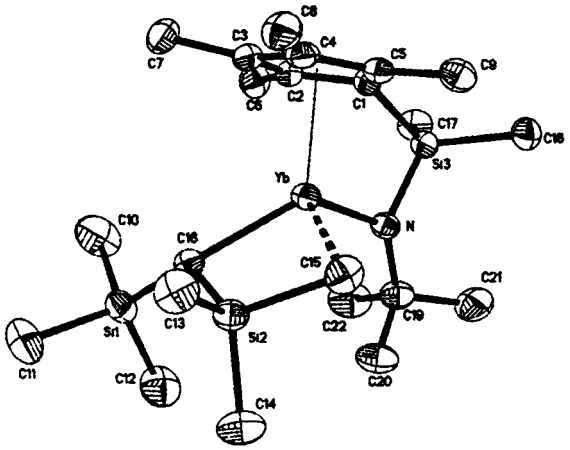
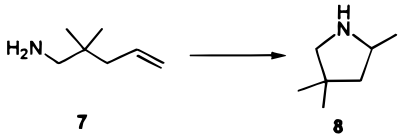


Figure 2. Molecular structure of complex **5**. Selected bond lengths (Å) and angles (deg): Yb−N, 2.164(4); Yb−C(16), 2.378(1); Yb−C(15), 2.657(5); Yb−C(1), 2.482(4); Yb−C(2), 2.528(4); Yb−C(3), 2.629(4); Yb−C(4), 2.625(4); Yb−C(5), 2.544(4); Yb−Cent, 2.254. N−Yb−C(12), 129.6(1); C(15)−Yb−C(16), 73.7(2) [Cent is the centroid of Cp C(1)−C(5)].

Table 1. Ancillary Ligation Effects on the Intramolecular Hydroamination/Cyclization of $CH_2{=}CHCH_2C(CH_3)_2CH_2NH_2$ (7)[a]



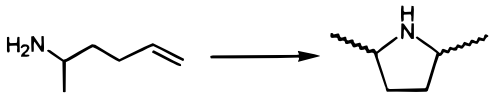
7 **8**

catalyst	N_t (h^{-1}), °C
$[Me_2Si(C_5Me_4)(^tBuN)]SmN(TMS)_2$ (**1**)	181 (25 °C)
$[Me_2Si(C_5Me_4)(^tBuN)]NdN(TMS)_2$ (**3**)	200 (25 °C)
$[Me_2Si(C_5Me_4)(^tBuN)]YbCH(TMS)_2$ (**5**)	10 (25 °C)[b]
$[Me_2Si(C_5Me_4)(^tBuN)]LuCH(TMS)_2$ (**6**)	90 (25 °C)
$(C_5Me_5)_2LaCH(TMS)_2$	95 (25 °C)[c]
$(C_5Me_5)_2SmCH(TMS)_2$	48 (60 °C)[c] 4.8 (25 °C)[d]
$(C_5Me_5)_2LuCH(TMS)_2$	< 1 (80 °C)[c] < 0.03 (25 °C)[d]
$Me_2Si(C_5Me_4)_2LuCH(TMS)_2$	75 (80 °C)[c]

[a] Conditions: [substrate]/[catalyst] = 50−300/1; [catalyst] = 0.70−2.0 mM in toluene-d_8. [b] NMR integration less accurate due to paramagnetism. [c] From ref 5k. [d] Estimated from activation parameters in ref 5k.

$CHCH_2CH_2CH(CH_3)NH_2$ (**9**). Comparison of turnover frequencies (N_t; h^{-1}) under the same reaction conditions demonstrates the far greater activity of the $[Me_2Si(C_5Me_4)(^tBuN)]LnE(TMS)_2$ catalysts. For example, in the cyclization of **7**, complex **1** mediates the transformation with $N_t = 181\ h^{-1}$ at 25 °C vs $N_t = 48\ h^{-1}$ at 60 °C and $N_t \sim 4.8\ h^{-1}$ at 25 °C[20] for $(C_5Me_5)_2SmCH(TMS)_2$.[5i] Furthermore, complex **6** ($N_t = 90\ h^{-1}$, at 25 °C) is dramatically more active than $(C_5Me_5)_2LuCH(TMS)_2$ ($N_t < 1\ h^{-1}$, 80 °C;. 0.03 h^{-1} at 25 °C[25]).[5i] For cyclization of **9**, complex **1** is more active than $(C_5Me_5)_2SmN(TMS)_2$ ($N_t = 24\ h^{-1}$ vs 9.1 h^{-1} at 25 °C), and complex **6** is moreactive than $(C_5Me_5)_2LuCH(TMS)_2$ ($N_t = 28\ h^{-1}$ vs 0.5 h^{-1} at 25 °C). Regarding mechanism, the rate law for the $[Me_2Si(C_5Me_4)(^tBuN)]$Ln-mediated hydroamination/cyclizations examined is[20] zero-order in substrate concentration, suggesting turnover-limiting olefin insertion, and in accord with analogous lanthanocene-mediated processes. Finally, **1** has been successfully employed in the total synthesis of the alkaloid natural product (3*S*,5*R*,8*S*)-3-heptyl-5-methylpyrrolizidine [(+)-xenovenine] (Scheme 1).[21] A crucial transformation is catalytic stereoselective tandem **A** → **B** bicyclization. While conventional catalysts yield only monocyclic product (**A** → **C**), **1** mediates rapid and regioselective bicyclization.

Table 2. Ancillary Ligand Effects on the Intramolecular Hydroamination/Cyclization of $CH_2{=}CHCH_2CH_2CH(CH_3)NH_2$ (9)[a]

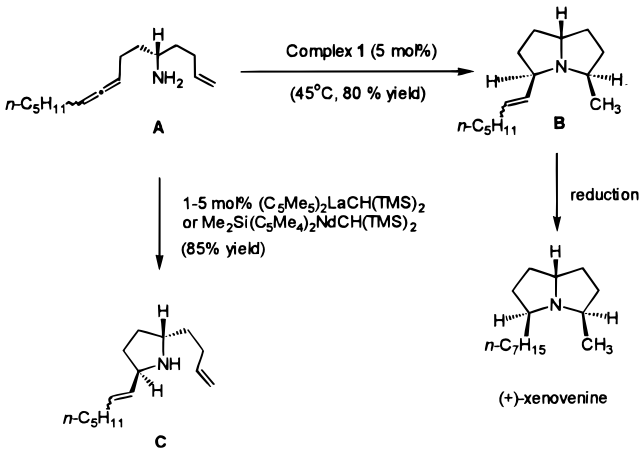


9 **10**

catalyst	N_t (h^{-1}), °C	product *trans*/*cis* ratio
$[Me_2Si(C_5Me_4)(^tBuN)]SmN(TMS)_2$ (**1**)	24 (25 °C)	10
$[Me_2Si(C_5Me_4)(^tBuN)]NdN(TMS)_2$ (**3**)	24 (25 °C)	10
$[Me_2Si(C_5Me_4)(^tBuN)]YbCH(TMS)_2$ (**5**)	34 (25 °C)	21
$[Me_2Si(C_5Me_4)(^tBuN)]LuCH(TMS)_2$ (**6**)	28 (25 °C)	17
$(C_5Me_5)_2LaCH(TMS)_2$	45 (25 °C)[b]	5[b]
$(C_5Me_5)_2SmN(TMS)_2$	9.1 (25 °C)	
$(C_5Me_5)_2LuCH(TMS)_2$	0.5 (25 °C)	

[a] Conditions: [substrate]/[catalyst] = 40−130; [catalyst] = 0.70−2.0 mM in toluene-d_8. [b] From ref 5k.

Scheme 1. Organolanthanide-Catalyzed Aminoallene Cyclization Processes, from Ref 21



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Supporting Information Available: Details describing synthesis and characterization of complexes **1**−**6** and details of structure determinations, including final coordinates, thermal parameters, bond distances and bond angles; figures giving representative kinetics plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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