β -SiH-Containing Tris(silazido) Rare-Earth Complexes as Homogeneous and Grafted Single-Site Catalyst Precursors for Hydroamination

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S Supporting Information

ABSTRACT: A series of homoleptic rare-earth silazido compounds and their silica-grafted derivatives were prepared to compare spectroscopic and catalytic features under homogeneous and interfacial conditions. Trivalent tris-(silazido) compounds $Ln{N(SiHMe_2)tBu}_3$ (Ln = Sc (1), Y (2), Lu (3)) are prepared in high yield by salt metathesis reactions. Solution-phase and solid-state characterization of 1– 3 by NMR and IR spectroscopy and X-ray diffraction reveals Ln - H - Si interactions. These features are retained in solventcoordinated 2·Et₂O, 2·THF, and 3·THF. The change in spectroscopic features characterizing the secondary interac-



tions (ν_{SiH} , $^{1}J_{\text{SiH}}$) from the unactivated SiH in the silazane HN(SiHMe₂)tBu follows the trend $3 > 2 > 1 \approx 2 \cdot \text{Et}_{2}\text{O} > 2 \cdot \text{THF} \approx 3 \cdot \text{THF}$. Ligand lability follows the same pattern, with Et₂O readily dissociating from $2 \cdot \text{Et}_{2}\text{O}$ while THF is displaced only during surface grafting reactions. 1 and 2 · THF graft onto mesoporous silica nanoparticles (MSN) to give Ln{N(SiHMe₂)tBu}_n@MSN (Ln = Sc (1@MSN), Y (2@MSN)) along with THF and protonated silazido as HN(SiHMe₂)tBu and H₂NtBu. The surface species are characterized by multinuclear and multidimensional solid-state (SS) NMR spectroscopic techniques, as well as diffuse reflectance FTIR, elemental analysis, and reaction stoichiometry. A key ${}^{1}J_{\text{SiH}}$ SSNMR measurement reveals that the grafted sites most closely resemble Ln THF adducts, suggesting that siloxane coordination occurs in grafted compounds. These species catalyze the hydroamination/bicyclization of aminodialkenes, and both solution-phase and interfacial conditions provide the bicyclized product with equivalent cis:trans ratios. Similar diastereoselectivities mediated by catalytic sites under the two conditions suggest similar effective environments.

INTRODUCTION

Complexes containing only one type of ligand (MX_n) , known as homoleptic compounds, represent the simplest systems for characterizing the nature of metal-ligand interactions because all ligands equivalently contribute electronic and steric effects. The resulting complexes often have intriguing structural and spectroscopic features that are associated with secondary metal-ligand interactions and non-VSEPR geometries.¹⁻⁵ In addition, homoleptic compounds in high oxidation states are often electronically and/or coordinatively unsaturated, giving highly electrophilic metal centers and geometric distortions to counterbalance low electron counts. The nature of the M-X bond is also important to their reactivity; for example, selective substitution of these groups with ancillary ligands (LX) provides routes to reactive complexes, including catalysts. While the rich chemistry of surface-supported organometallic compounds indicates that alkyl species are desirable,⁶ work with grafted early-metal amides suggests their emerging potential in catalysis.⁷⁻¹³ In rare-earth chemistry, homoleptic organometallic and pseudo-organometallic compounds are particularly

important starting materials, but their large ionic radii and low numbers of X-type ligands (either two or three) add to the challenge of preparing reactive monometallic species.¹⁴

As a result, disilazido groups, such as hexamethyldisilazide and tetramethyldisilazide, are the primary N-based ligand types to support monometallic homoleptic rare-earth compounds. Trivalent Ln{N(SiMe₃)₂}₃^{15–17} and Ln{N(SiHMe₂)₂}₃^{18,19} and divalent¹⁹ compounds are prevalent starting materials for a range of rare-earth chemistries, including as homogeneous catalysts.^{20–23} and as precursors for single-site supported rareearth catalysts.^{18,24–28} Such surface-grafted materials catalyze alkyne dimerization,²⁷ Tishchenko aldehyde dimerization,^{26,27} hydroamination (the addition of amines and olefins),²⁸ and polymerization.^{26,29} However, a downside of disilazido complexes as catalyst precursors is that HN(SiMe₃)₂ and especially HN(SiHMe₂)₂ can be poor leaving groups due to their relatively high acidity, with pK_a values of 25.7 and 22.6,

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respectively.³⁰ Disilazanes are effective silylating agents, and grafting of $Ln\{N(SiHMe_2)_2\}_3$ on silica results in significant surface silylation. In addition, compounds containing the smaller $N(SiHMe_2)_2$ ligand are often multimetallic (e.g., $[La\{N(SiHMe_2)_2\}_3]_2)$.³¹ Thus, the basicity of the bulkier silazido ligand $N(SiMe_3)tBu$ was invoked for reactions of $Ln\{N(SiHMe_2)_2\}_3$ (Ln = Y, La) as a precursor to homogeneous hydroamination catalysts.³² Still, the SiH group in $N(SiHMe_2)_2$ provides a valuable spectroscopic handle for both NMR and IR analysis,¹⁸ stabilization of coordinatively and electronically unsaturated metal centers through labile secondary interactions, ^{18,30,33,34} and a site for reactivity.^{35–38}

The silazide N(SiHMe₂)tBu incorporates a number of these desired features: enhanced steric protection, a more basic amide group, and the SiH moiety. This silazido ligand has been underutilized as a supporting ligand in homoleptic compounds in comparison to the disilazido ligands, despite the early promise of the only trivalent homoleptic Er{N(SiHMe2) ${}^{39}_{tBu}$ and the rich chemistry of Cp₂Zr{N(SiHMe₂)*t*Bu}X (X = hydride, halide, alkyl). ${}^{33,34,40-42}$ Both of these systems, as well as the main-group compound $[Mg{N(SiHMe_2)tBu}_2]_2^{43}$ exhibit structural and spectroscopic features associated with multicenter M←H-Si interactions, including short M…H distances and small ∠M-N-Si angles in X-ray diffraction studies, low-energy $\nu_{\rm SiH}$ bands in infrared spectra, upfield $\delta_{\rm SiH}$ signals in ¹H NMR spectra, and low ¹J_{SiH} values in ²⁹Si and ¹H NMR spectra. The NMR properties, however, have not been evaluated for $Er{N(SiHMe_2)tBu}_3$ because of its paramagnetism, although the solid-state structure and infrared spectra established that all three SiH groups interact with the rare-earth center.³⁹ Thus, the N(SiHMe₂)tBu ligand could provide useful precursors for catalysis, such as hydroamination.

Despite the high reactivity of disilazido rare-earth compounds as precatalysts for this process,⁴⁴ examples of grafted single-site rare-earth hydroamination catalysts are limited.²⁸ Moreover, those examples suggested that silica-supported catalysts are diminished in activity in comparison to the homogeneous analogues. A number of additional challenges face the development of the catalytic hydroamination reaction, including functional group tolerance, catalytic efficiency for intermolecular additions, and control over selectivity.

The selectivity and activity in catalytic conversions of aminodialkenes could provide a means for examining the effect of surface and pore environment on hydroamination processes; because both mono- and bicyclization products are possible, each product has cis and trans diastereomers (Scheme 1) and the diastereoselectivity is sensitive to reaction conditions. For example, we recently reported that substrate concentration affected the cis:trans ratio in an enantioselective Zr-catalyzed

Scheme 1. Cis and Trans Diastereomers Accessible from Monocyclization and Bicyclization of Aminodialkenes



monocyclization reaction of aminodialkenes and aminodialkynes to give optically active pyrrolidines.⁴⁵ In addition, Marks and co-workers showed in their seminal study that diastereoselectivity in $Cp*_2LaCH(SiMe_3)_2$ -catalyzed hydroaminations of chiral aminoalkenes is also influenced by concentration.⁴⁶ Rare-earth compounds and a few zirconium catalysts give hydroamination/bicyclization products through a two-step process in which the second cyclization requires conditions more forcing than those in the first.^{32,47-51,48-50}

Ligand-metal or surface-metal center interactions might provide control over selectivity in the hydroamination of aminodialkenes. Experiments are needed to test for surface effects on (a) monocyclization vs bicyclization of aminodialkenes and (b) cis:trans selectivity of the products to elucidate factors that ultimately control selectivity in such C–N bond forming reactions. Controlling selectivity in these reactions has synthetic value in terms of additional transformations of the olefin-substituted heterocycles.⁵² In addition, the azabicyclo[2.2.1]heptane product contains motifs found in natural products and biologically active substances, and the exo and endo selectivity is also important for their applications.^{53–55}

Thus, homoleptic monometallic compounds of the type $Ln{N(SiHMe_2)tBu}_3$ may be effective precatalysts and precursors for single-site heterogeneous catalysts. The present study describes our efforts to synthesize a series of homoleptic rare-earth silazido compounds. The NMR, IR, and structural properties of $Ln{N(SiHMe_2)tBu}_3$ and their ethereal solvent adducts were analyzed to provide molecular models for surfacebonded species. Such surface-supported analogues are obtained by grafting on mesoporous silica nanoparticles (MSN). Characterization of MSN-supported rare-earth silazido materials via IR and solid-state NMR spectroscopy provides a molecular picture of the surface sites. With this picture and the spectroscopic comparison between solution-phase homoleptic vs grafted species in hand, we studied their catalytic reactivity (activity and selectivity) in hydroamination/cyclization of aminoalkenes and aminodialkenes.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of Ln{N(SiHMe₂)tBu₃ and Ln{N(SiHMe₂)tBu₃L. Reactions of three equiv of [LiN(SiHMe₂)tBu] and LnCl₃ (Ln = Y, Lu) or $LnCl_3THF_3$ (Ln = Sc, Lu) in THF or Et_2O provide $Ln{N(SiHMe_2)tBu}_3$ or $Ln{N(SiHMe_2)tBu}_3L$, as outlined in Scheme 2 (Ln = Sc (1), Y (2, 2. Et_2O , 2. THF), Lu (3, 3. THF)). Compound 1 is isolated as a light yellow sticky solid, and neither Et₂O nor THF is retained in the scandium's coordination sphere. The solvent-free Y compound may be obtained by subliming 2.Et₂O or by performing the synthesis under concentrated conditions (0.46 M). The solvent-free Lu compound is obtained from the reaction of LuCl₃ in Et₂O. The complexes 2.Et₂O, 2.THF, and 3.THF are isolated as white sticky solids from pentane crystallization or precipitation. Sublimation of the sticky solids of 2. THF and 3. THF affords analytically pure powders while retaining the THF ligand. While the ¹H NMR spectrum of 2. THF is not altered by sublimation, the ν_{SiH} region of the infrared spectra is slightly sharper after this treatment (see the Supporting Information).

The infrared spectra of the series of compounds contained bands attributable to Si–H stretching modes, ranging from 2019 to 1849 cm⁻¹ (Figure 1 and Table 1; see the Supporting Information for full IR spectra). Spectra for 1-3 and 2·Et₂O







Figure 1. Infrared spectra of $HN(SiHMe_2)tBu$, $[LiN(SiHMe_2)tBu]$, 1, 2·Et₂O, and 2·THF (before sublimation) corresponding to Si–H stretching modes. Full spectra are shown in the Supporting Information.

revealed a single strong band assigned to bridging $Ln \leftarrow H-Si$ groups, with the tricoordinated scandium complex's peak

Tab	le	1.	Spe	ectros	copic	Data	for	Silazid	lo Co	mpound	s
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appearing at higher energy than the signal for the ethercoordinated yttrium species. The signal for the $\nu_{\rm SiH}$ band of 3 (1849 cm⁻¹) appeared with the lowest energy of the series, which follows the trend 3 < Er{N(SiHMe_2)tBu}₃ (1858 cm⁻¹)³⁹ < 2 < 1. In contrast, the $\nu_{\rm SiH}$ region for nonsublimed 2• THF contained two peaks at 2019 and 1967 cm⁻¹ at notably higher energy; once it was sublimed, a signal at 2117 cm⁻¹ was detected due to sharpening of the broad 2019 cm⁻¹ band. The signals for the SiH group in the lutetium THF adduct were observed around 2000 cm⁻¹. For comparison, the SiH stretching frequencies of the silazane HN(SiHMe_2)tBu and lithium silazido [LiN(SiHMe_2)tBu] appeared at higher energy in comparison to those of the rare-earth silazido compounds.

Room-temperature ¹H NMR spectra suggested that the homoleptic rare-earth species are C_{3v} symmetric on the basis of three resonances, which were assigned to the SiH, SiMe₂, and *t*Bu groups in equivalent silazido ligands. The ³J_{HH} coupling in SiHMe₂ is small and resolved clearly as doublets (3 Hz) for the Me in **2**, **2**•**THF**, **3**, and **3**•**THF**. The ¹J_{SiH} values (Table 1) vary depending on the rare-earth element and the coordinated THF or Et₂O ligands but are generally low and suggest Ln—H–Si bonding motifs. The ¹J_{SiH} values in HN(SiHMe₂)*t*Bu (192 Hz) and [LiN(SiHMe₂)*t*Bu] (168 Hz) are larger than those in the rare-earth compounds. At low temperature (190 K), the SiMe₂ signals in the ¹H NMR spectra of **1**, **2**•**THF**, and **3**•**THF**

compound	$\delta_{ m SiH}$, ppm	¹ J _{SiH} , Hz	$\delta_{\mathrm{S}i\prime}$ ppm	$\delta_{ m N}$, ppm	$\nu_{\rm SiH}$, cm ⁻¹
$Sc{N(SiHMe_2)tBu}_3(1)$	4.18	125	-22.9	-208	1893
$Y{N(SiHMe_2)tBu}_3$ (2)	4.26	124	-24.8	-221	1860
2·Et ₂ O	4.30	126	-25.9	-222	1864
2·THF	4.59	143	-30.5	-231	2019, 1967
$Lu{N(SiHMe_2)tBu}_3$ (3)	4.42	121	-20.5	-221	1849
3·THF	4.63	137	-28.7	-232	1988
HN(SiHMe ₂)tBu	4.83	192	-18.8	-329	2135, 2104
[LiN(SiHMe ₂)tBu]	4.87	168	-23.1	-301	2055

appeared as two signals of equal intensity, implying lowtemperature C_3 -symmetric structures. Interestingly, the SiH chemical shift and coupling constants were identical in spectra acquired down to 190 K, and this observation suggested that the fluxional process did not involve disruption of the secondary Ln-H-Si interactions. In contrast, the ¹H NMR spectra of **2**, **2**·Et₂**O**, and **3** merely broadened at 190 K in toluene- d_8 .

The ²⁹Si NMR spectra vary from -20.5 to -30.5 ppm depending on the identity of the rare-earth element, and these were slightly upfield in comparison to HN(SiHMe₂)tBu. A similar trend was observed in the ²⁹Si NMR spectra of the rareearth disilazido compounds $Ln\{N(SiHMe_2)_2\}_3THF_n$, which are ca. 10 ppm upfield in comparison to the disilazane HN- $(SiHMe_2)_2$ (-11.1 ppm).¹⁸ In addition, ¹H-¹⁵N HMQC experiments (at natural abundance) revealed cross-peaks between N and tBu signals but not with the SiHMe₂ group. The ¹⁵N NMR chemical shifts were downfield in comparison to those of HN(SiHMe₂)tBu and [LiN(SiHMe₂)tBu] (see Table 1). We also noticed the same trend in the ¹⁵N NMR chemical shifts for Sc{N(SiHMe₂)₂}₃THF (-253 ppm) and Y{N- $(SiMe_3)_2$ (-243.1 ppm), which are downfield of those for $HN(SiHMe_2)_2$ (-365 ppm) and $HN(SiMe_3)_2$ (-354 ppm). Likewise, the ¹⁵N NMR chemical shifts for Cp₂Zr{N(SiHMe₂) tBu}H (-260 ppm) and Cp₂Zr{N(SiHMe₂)₂}H (-292 ppm) are downfield with respect to those of HN(SiHMe₂)tBu (-329 ppm) and HN(SiHMe₂)₂ (-365.3 ppm).³

X-ray Crystallography. Single-crystal X-ray diffraction studies provided solid-state structures of 1 (Figure 2; see the



Figure 2. Rendered thermal ellipsoid plot of $Sc\{N(SiHMe_2)tBu\}_3$ (1) at 50% probability. See the Supporting Information for isostructural yttrium (2) and lutetium (3). H atoms bonded to Si were located objectively in the Fourier difference map and are included in the rendition; all other H atoms are not included for clarity.

Supporting Information for other structures), 2, $2 \cdot \text{Et}_2 O$, $2 \cdot \text{THF}$ (Figure 3), 3, and $3 \cdot \text{THF}$ for comparison to $\text{Er}\{N(\text{SiHMe}_2) t\text{Bu}\}_{3}^{39}$ The molecular structures of 1-3 and the erbium analogue are similarly pseudo- C_3 with the $N(\text{SiHMe}_2)t\text{Bu}$ ligands adopting a propeller-like conformation. All three SiH groups are located (identified objectively on the difference Fourier map) on the same face of the LnN₃ core, and these



Figure 3. Rendered thermal ellipsoid plot (50% probability) of $Y{N(SiHMe_2)_2}_3THF$ (2·THF). See the Supporting Information for solid-state structures of 2·Et₂O and 3·THF. H atoms bonded to Si were located objectively in the Fourier difference map and are included in the rendition; all other H atoms are not included for clarity.

groups are directed toward the rare-earth center. The methyl groups in the $SiMe_2$ are inequivalent in these structures, and this is consistent with the low-temperature ¹H NMR spectrum described above.

The LnN₃ cores of 1-3 adopt similar trigonal geometries distorted by pyramidalization $(\sum_{NLnN}: Sc, 348.62(9)^\circ; Y,$ $351.3(2)^{\circ}$; Lu, $349.0(2)^{\circ}$ (vs Er, 350.42°)). There are three short Ln…H and three short Ln…Si distances. Remarkably, the scandium-silicon distances in 1 (Sc1-Si1, 2.8603(3) Å; Sc1-Si2, 2.8343(4) Å; Sc1-Si3, 2.8557(4) Å) are similar to the distance in the scandium silyl compound Cp₂ScSi(SiMe₃)₃THF $(2.863(2) \text{ Å})^{56}$ and only slightly longer than that in $\text{Cp}*_2\text{ScSiH}_2\text{SiPh}_3$ (2.797(1) Å),⁵⁷ both of which contain bona fide two-center-two-electron Sc-Si bonds. These short distances are complemented by the Sc-N-Si angles, which are much smaller than the 120° expected for a trigonal-planar N center (98.47(4), 97.98(4), and 97.93(4)°). Taking into consideration the short distances to N and Si, the N₃Si₃ atoms form a trigonal prism, with the smaller N3 end-capping triangle twisted from the triangular face composed of Si₃ vertices. The Sc center is 0.41 and 1.02 Å from the N_3 and Si3 planes, respectively. The scandium-hydrogen distances (Sc1-H1s, 2.26(1) Å; Sc1-H2s, 2.20(2) Å; Sc1-H3s, 2.23(1) Å), however, are significantly longer than the calculated distance in ScH₃ (1.82 Å).⁵⁸ For comparison, the homoleptic, solvent-free tris(amido)scandium compound Sc{N(SiMe₃)₂}₃ is pyramidal in the solid state ($\sum_{NScN} = 346.5^{\circ}$) but planar in the gas phase.⁵⁹ In that compound, the solid-state and gasphase Sc-N distances (2.047(2) and 2.02(3) Å, respectively) are slightly shorter than those in 1 (Sc1-N1, 2.0656(6) Å; Sc1-N2, 2.063(1) Å; Sc1-N3, 2.071(2) Å). The Sc-N distances in 1, however, are similar to those in the four-coordinate THF adduct $Sc{N(SiHMe_2)_2}_3THF$.¹⁸ As expected, the Ln-N, Ln...Si, and Ln...H distances in 2 and 3 are longer than those in 1 (see the Supporting Information). The Y-N distances (2.223(2), 2.223(2), and 2.227(2) Å) are slightly

Scheme 3. Surface Grafting Reactions and Proposed Surface-Supported Homoleptic Silazido Rare-Earth Compounds Formed from MSN_{550} or MSN_{700} and $Sc{N(SiHMe_2)tBu}_3$ (1) or $Y{N(SiHMe_2)tBu}_3THF$ (2·THF)



longer than the Er–N distances (2.206(2) Å),³⁹ while the Lu–N distances (2.174(2), 2.177(2), and 2.178(2) Å) are shorter.

The yttrium species 2, 2. Et₂O, and 2. THF are further compared because the last two compounds have distinct $\nu_{\rm SiH}$ IR bands and ${}^{1}J_{\text{SiH}}$ values that suggest inequivalent structures. At the same time, the coordination numbers of 2 and 2.Et₂O are inequivalent, although their spectroscopic features are similar. **2·THF** contains two crystallographically unique molecules (Z =8) per unit cell, whereas 2 and 2·Et₂O crystallize with only one (Z = 4). All three crystallographically unique molecules of 2·L are four-coordinate on the basis of the YN₃O core, with the YN₃ part flattened ($\sum_{NYN} = 344.7(3)^{\circ}$ (2·Et₂O), 346.4(3) and $347.9(3)^{\circ}$ (2·THF)) in comparison to the sum of three angles of an ideal tetrahedron ($\Sigma = 327^{\circ}$). In addition, one of the N– Y-O angles is ca. 90° in each of the structures (i.e., the molecules lack even a pseudo- C_3 axis). All three Si-H groups point toward the Y center, and each of these H atoms is pseudo-trans to either a silazide or ether ligand (e.g., in 2.Et₂O H1s-Y1-N2 is 175(1)°, H2s-Y1-N3 is 152(1)°, and H3s-Y1-O1 is $153(1)^{\circ}$). The Y-O distances for diethyl ether and THF are nearly identical (2·Et₂O, 2.377(3) Å; 2·THF, 2.385(2) and 2.376(2) Å), even though Et_2O is removed during sublimation while THF is not. The similar conformations, as well as the interatomic angles and distances associated with Y-N-Si-H structural motifs of the 2·L yttrium species, are in contrast with the distinguishing $\nu_{\rm SiH}$ and ${}^{1}J_{\rm SiH}$ spectroscopic features noted above. The geometry of the lutetium analogue Lu{N(SiHMe₂)tBu}₃THF (3•THF; Figure S24) is similar to that of 2.Et₂O and 2.THF, yet the SiHcentered spectroscopic features are between those of the two yttrium species (Table 1). Thus, the trends of Ln…H and Ln… Si distances do not correlate one to one with energies and coupling constants indicated by the spectroscopic signatures, although the features are consistently present in all the compounds.

Synthesis and Characterization of Ln{N(SiHMe₂) tBu_n @MSN. Compounds 1 and 2·THF were stirred with SBA-type mesoporous silica nanoparticles (MSN) previously heated under vacuum either at 550 °C (MSN₅₅₀, 1.5 mmol of OH/g) or 700 °C (MSN₇₀₀, 0.9 mmol of OH/g) to graft the rare-earth species on the material, as depicted in Scheme 3.

These rare-earth elements were initially chosen for study because Anwander and co-workers showed that grafted yttrium complexes are more active in hydroamination/cyclization than the corresponding grafted lanthanide catalysts,²⁸ and we also wished to compare mild conditions for cyclization with diastereoselective Zr-catalyzed hydroamination (see below).⁴⁵ Micromole-scale grafting reactions were performed in benzene d_6 and monitored by ¹H NMR spectroscopy, while preparativescale syntheses were performed in pentane at room temperature for 20 h. The former experiments provided an initial estimate of loading and possible surface species on the basis of reaction stoichiometry (Table 2). For example, a micromole-

Table 2. Stoichiometry of Surface Grafting Reactions

preparation	amt of Ln consumed (mmol)	amt of <i>t</i> BuNH ₂ measd (mmol)	amt of silazane measd (mmol)
1 + MSN ₅₅₀	0.54	0.37	0.46
$1 + MSN_{700}$	0.35	0.14	0.21
2•THF + MSN ₅₅₀	0.48	0.33	0.35
$2 \cdot THF + MSN_{700}$	0.22	0.05	0.15

scale reaction in benzene- d_6 consumed 0.48 mmol of 2·THF and produced 0.33 mmol of $tBuNH_2$ and 0.35 mmol of HN(SiHMe₂)tBu per gram of MSN₅₅₀. In addition, the intensities of THF ¹H NMR signals are not diminished in the spectroscopically monitored grafting experiments, implying that THF dissociates from surface-bonded Y sites and coordinates to or rapidly exchanges with the solvent in 2·

	amt of Ln	amt of Ln	amt of N		amt of C (mmol/	
preparation	$(wt \%)^a$	(mmol/g)	(mmol/g)	N:Ln	g)	C:N
Sc{N(SiHMe ₂)tBu} ₃ + MSN ₅₅₀ (1@MSN ₅₅₀)	2.5	0.56	0.75	1.3	6.1	8.1
$Sc{N(SiHMe_2)tBu}_3 + MSN_{700} (1@MSN_{700})$	1.5	0.33	0.64	1.9	4.3	6.8
$Y{N(SiHMe_2)tBu}_3THF + MSN_{550}$ (2@ MSN ₅₅₀)	4.2 ± 0.1	0.47 ± 0.01	0.86 ± 0.01	1.83 ± 0.05	6.4 ± 0.1	7.5 ± 0.2
$Y{N(SiHMe_2)tBu}_3THF + MSN_{700}$ (2@ MSN ₇₀₀)	2.3	0.26	0.54	2.1	3.4	6.4

^aError is given on the basis of standard deviation determined from four measurements on 2@MSN₅₅₀.

THF. These experiments provide a rough estimate of the yttrium loading (see Table 2, 0.48 mmol/g in this example), the average podality (~1:1 monopodal and bipodal in this example), and the quantity of surface silylation in the grafting experiments. Notably, less rare-earth amide is consumed and less $tBuNH_2$ and $HN(SiHMe_2)tBu$ are formed in reactions with MSN_{700} , while the $tBuNH_2$: $HN(SiHMe_2)tBu$ ratio also decreased in experiments with the high-temperature-treated MSN. The ratio of consumed rare-earth silazide to silazane and amine produced in reactions with MSN_{700} suggests that the grafted species are primarily monopodal in those cases. Systematic and corroborative quantitative analysis with inductively coupled plasma optical emission spectroscopy (ICP-OES) and CHN combustion analysis supports the initial estimates.

In addition, an excess of carbon is present on the surface. The C:N ratio in a N(SiHMe₂)tBu ligand is 5.15:1, whereas the measured C:N ratios are higher for grafted materials (e.g., 1@ MSN_{550} , C:N = 8.1:1). This higher carbon loading is readily rationalized by a silylation of the surface silanols, as reported for disilazanes HN(SiMe₃)₂ and HN(SiHMe₂)₂ and supported by solid-state NMR experiments and IR spectroscopy (see below).^{18,60} The observation of tBuNH₂ in the supernatant is also consistent with such a process. Less surface silylation occurs in grafting reactions involving MSN₇₀₀ in comparison with MSN₅₅₀.

Diffuse reflectance IR spectra of the rare earth silazide treated materials (Figure 4), in comparison to pristine MSN_{550} and MSN_{700} , revealed that isolated silanols are consumed in the grafting reactions and the new surface species contain CH and SiH groups. In all reactions of MSN and rare-earth silazides, the absorption band at 3747 cm⁻¹ assigned to isolated silanol groups^{61,62} disappeared upon grafting; however a broad signal from 3740 to 3280 cm⁻¹ assigned to hydrogen-bonded silanols was apparent in the grafted materials' spectra.^{61,63,64}

These remaining SiOH groups were not readily accessible for reactivity, as demonstrated by the trace amounts of toluene detected upon addition of $Mg(CH_2Ph)_2(O_2C_4H_8)_2$. The SiH region of the diffuse reflectance IR spectra of 2@MSN contained a sharp signal at 2149 cm⁻¹ and a broad signal



Figure 4. Diffuse reflectance infrared spectra of (A) $MSN_{550'}$ (B) $Y\{N(SiHMe_2)tBu\}_3THF$, (C) $Y\{N(SiHMe_2)tBu\}_3THF$ + $MSN_{550'}$ and (D) $HN(SiHMe_2)tBu$ + $MSN_{550'}$. See the Supporting Information for Sc and MSN_{700} analogues.

from 2080 to 1780 cm⁻¹ with a maximum at 1924 cm⁻¹. The former signal was assigned to \equiv SiO-SiHMe₂ surface groups on the basis of comparison with MSN independently treated with HN(SiHMe₂)tBu or HN(SiHMe₂)₂ (at 2152 cm⁻¹; see Figure 4D) and literature reports.¹⁸ The \equiv SiO-SiHMe₂ functionality arises from the reaction of silanols and HN-(SiHMe₂)tBu, the byproduct from grafting of 1 or 2·THF. The broad signal contained features around 2000 and 1900 cm⁻¹ assigned to terminal Si-H and bridging Y-H-Si groups in surface-grafted 2@MSN. The diffuse reflectance IR spectra of the scandium material 1@MSN suggest the surface scandium silazido species also contain bridging Sc-H-Si groups (see Figure S25).

Characterization by Solid-State NMR. The atomic-scale structures of $Ln{N(SiHMe_2)tBu}_n@MSNs$ (Ln = Y, Sc) were further probed by solid-state (SS) NMR spectroscopy. The experimental parameters are given in the figure captions using the following symbols: $\nu_{\rm R}$ denotes the magic angle spinning (MAS) rate, $\nu_{\rm RF}(X)$ is the magnitude of the RF magnetic field at the resonance frequency of the X nucleus, au_{CP} is the crosspolarization (CP) contact time, Δt_1 is the increment of t_1 during 2D acquisition, $\tau_{\rm RD}$ is the recycle delay, and NS is the number of scans (see the Supporting Information for more experimental details). Here, we will report the spectra obtained for 2@MSN₅₅₀ and 2@MSN₇₀₀; the Sc-containing analogues 1@MSN₅₅₀ and 1@MSN₇₀₀ yielded very similar results (Figures S29-S33), to which we will refer when appropriate. The 2D ¹³C-¹H heteronuclear correlation (HETCOR) spectrum of $2@MSN_{550}$ acquired using the indirectly (or ¹H) detected scheme,^{65,66} referred herein as ¹H{¹³C} idHETCOR, is shown in Figure 5A. The spectrum is consistent with the presence of MSN-bound $Y{N(SiHMe_2)tBu}_n$ species



Figure 5. (A) ¹H{¹³C} idHETCOR spectrum of Y{N(SiHMe₂)*t*Bu}_n@MSN₅₅₀ (2@MSN₅₅₀), obtained at 14.1 T using $\nu_{R} = 36$ kHz, $\nu_{RF}(^{1}H 90^{\circ})$, CP) = 100 kHz, $\nu_{RF}(^{13}C 90^{\circ}) = 100$ kHz, $\nu_{RF}(^{13}C CP) = 64$ kHz, $\tau_{CP1} = \tau_{CP2} = 6$ ms, $\nu_{RF}(^{1}H HORROR) = 18$ kHz, $\nu_{RF}(^{1}H SPINAL-64) = 10$ kHz, $\nu_{RF}(^{13}C SPINAL-64) = 100$ kHz, $\tau_{RD} = 1.5$ s, $\Delta t_1 = 27.8 \ \mu s$ (256 rows), and NS = 64. (B) Postulated constitution of MSN-bound surface species. (C) ²⁹Si{¹H</sup> CPMAS spectrum of 2@MSN₅₅₀. (D-F) ¹H{²⁹Si} idHETCOR spectra of SiHMe₂@MSN₅₅₀, 2@MSN₅₅₀, and 2@MSN₇₀₀, respectively. Spectra C-F were obtained at 9.4 T using $\nu_{R} = 18$ kHz, $\nu_{RF}(^{1}H CP) = 83$ kHz, $\nu_{RF}(^{29}Si CP) = 65$ kHz, $\tau_{CP} = 3$ ms (C), $\tau_{CP1} = \tau_{CP2} = 4$ ms (D), $\tau_{CP1} = \tau_{CP2} = 2$ ms (E, F), $\nu_{RF}(^{1}H SPINAL-64) = 83$ kHz, $\nu_{RF}(^{29}Si SPINAL-64) = 68$ kHz (D-F), $\nu_{RF}(^{1}H HORROR) = 18$ kHz (D-F), $\tau_{RD} = 1.3$ s, NS = 10000 (C), $\Delta t_1 = 55.5 \ \mu s$ (D-F), 128 rows (D-F), and NS = 256 (D-F).

shown in Figure 5B. The assignments of 1H and ^{13}C resonances (Table 4) are based on the δ_C values reported for Y{N-

Table 4. Summary of Peak Assignments in the SSNMR Spectra of Y{N(SiHMe₂)tBu}_n@MSN (2@MSN)

resonance	chemical shift (δ , ppm)	assignment
H1	-0.1	$-SiH(CH_3)_2$
H2	1.0	$=NC(CH_3)_3$
H3	4.5	$-SiH(CH_3)_2$
C1	-0.1	$-SiH(CH_3)_2$
C2	35	$=NC(CH_3)_3$
C3	51	$=NC(CH_3)_3$
М	-3	-OSiHMe ₂
Si1	-31	$-OY{N(SiHMe_2)tBu}_2$
Si2′	-13	$(-O)_2$ SiMe ₂
Si2"	-19	$(-O)_2$ <i>Si</i> HMe

(SiHMe₂)tBu₃ (2; Figure S10) and tert-butylamine (H₂N-CMe₃).⁶⁷ The correlations involving Si–H(H3) are suppressed in Figure 5A because the ¹H{¹³C} idHETCOR scheme uses two CP transfers (¹H \rightarrow ¹³C and ¹³C \rightarrow ¹H); however, these protons are quantitatively observed in the ¹H MAS SSNMR spectra of **2@MSNs** (Figure S27). Note that the carbon intensity in dimethylsilyl groups (C1) relative to C2 decreases in the MSN₇₀₀ sample (Figure S28), suggesting that C1 also includes surface-bound –SiHMe₂ groups whose population is reduced on MSNs pretreated at higher temperature (see also the discussion of ²⁹Si spectra below). Importantly, we do not detect any THF ligands in the $2@MSN_{550}$ sample, which would yield ¹³C resonances at 26 and 68 ppm.

The 1D ²⁹Si{¹H} CPMAS spectrum of 2@MSN₅₅₀ (Figure 5C) shows a resonance centered at ~ -105 ppm attributable to the so-called Q^n sites forming the MSN framework and described by the general formula $(\equiv SiO)_n Si(OR)_{4-n}$; here mainly with n = 4, 3, where R = Ln, H (Figure 5B). The Qⁿ sites are underrepresented in the CPMAS spectrum and are almost invisible in the ¹H{²⁹Si} idHETCOR spectra, due to the lack of ¹H nuclei suitable for cross-polarization of these sites. The signal at -3 ppm is assigned to $-OSiHMe_2$ groups directly bound to the silica surface (typically denoted as M sites), on the basis of the ${}^{1}H{}^{29}Si{}$ idHETCOR spectrum of an MSN sample grafted with HN(SiHMe₂)₂, which shows a dominant cross-peak at δ_{Si} –3 ppm and δ_{H} 4.5 ppm (Figure 5D). The Si1 peak in Figure 5E,F correlates strongly to H3 and weakly to H1 and H2, and thus represents the silicon site in yttrium complexes. Importantly, there is a difference of ~0.2 ppm between $\delta_{\rm H}$ values for H3 correlated to M and Si1 (this is clearly seen in Figure 5F where there is a shoulder on the upfield side of H3). This shift may suggest the presence of an Y–H-Si structure in the silica-bound complex, 18,33 which we unambiguously confirmed by the 2D J-resolved experiment (vide infra). Again, the intensity of M sites relative to Si1 is lower in the sample prepared using MSNs pretreated at higher temperature (compare Figure 5E and 5F). The remaining weak peaks Si2' and Si2'', which are only observed in samples grafted with metal species, most likely represent silica-bound $(-O)_2$ SiMe₂ and $(-O)_2$ SiHMe sites formed through processes mediated by the rare earth center (Table 4). The latter assignment is based on the Si value for this peak being close to one measured for $(EtO)_2$ SiHMe (-16.7 ppm), and the fact that Si2'' correlates to H1 and H3, but not to H2 (Figure 5E). The correlation pattern for Si2' in Figure 5E,F is more difficult to discern due to the very low intensity; nevertheless, the assignment to $(-O)_2$ SiMe₂ is based on the fact that Si2' is not correlated to H3 (which is quite apparent in the case of 1@ MSN₅₅₀; Figure S33A,B) and has a δ_{Si} value very similar to that reported earlier for this species (-14.2 ppm).⁶⁸ By comparing parts E and F of Figure 5, we find that the relative ratio between M and Si2 sites is about the same in MSN₅₅₀- and MSN₇₀₀based samples.

The 2D J-resolved ²⁹Si SSNMR spectra of the Y{N(SiHMe₂) tBu}₃ precursor and **2@MSN**₇₀₀ were acquired with the pulse sequence proposed by Lesage et al.,⁶⁹ which used a CP step followed by t_1 evolution under the frequency-switched Lee– Goldburg (FSLG) homonuclear ¹H-¹H decoupling.⁷⁰ The evolution period was interjected by two 180° pulses at the ¹H and ²⁹Si frequencies to ensure that the ²⁹Si magnetization will be only modulated by ¹J_{SiH}. In Figure 6 are shown two traces of



Figure 6. ${}^{J}_{SiH}$ doublets extracted for Si1 from the 2D *J*-resolved spectra of 2 (A) and 2@MSN₇₀₀ (B). The spectra were obtained at 14.1 T using $\nu_{\rm R} = 15$ kHz, $\nu_{\rm RF}({}^{1}$ H CP) = 62.5 kHz, $\nu_{\rm RF}({}^{29}$ Si CP) = 47.5 kHz, $\tau_{\rm CP} = 3$ ms, $\nu_{\rm RF}({}^{1}$ H SPINAL-64) = 83 kHz, $\nu_{\rm RF}({}^{1}$ H 180°, FSLG) = 83 kHz, $\nu_{\rm RF}({}^{29}$ Si 180°) = 83 kHz, $\tau_{\rm RD} = 2$ s, NS = 8 (A), and NS = 1024 (B), $\Delta t_1 = 666.7 \ \mu s$ (64 rows). The quadrature detection in indirect dimension was implemented using the States-TPPI method. The 2D spectra contained center peaks at 0 Hz due to the so-called self-decoupling mechanism,⁷¹ which were removed by deconvolution. The ${}^{1}J_{SiH}$ scale has been corrected by the experimentally determined scaling factor of 0.51.

such 2D spectra, extracted along the ${}^{1}J_{\text{SiH}}$ dimension at the chemical shift corresponding to Si1. In both cases, we observed a doublet with ${}^{1}J_{\text{SiH}} = 122$ Hz for Y{N(SiHMe₂)*t*Bu}₃ and ${}^{1}J_{\text{SiH}} = 141$ Hz for 2@MSN₇₀₀. These values agree well with those measured for yttrium compound 2 in solution (124 Hz, Table 1) and are considerably smaller than that observed for the free HN(SiHMe₂)*t*Bu ligand (192 Hz, Table 1). Acquisition of the spectrum for the supported complex was very challenging (~72 h), but this important result clearly demonstrates that the supported complex retains the Y \leftarrow H-Si feature. We note that the ${}^{1}J_{\text{SiH}}$ coupling constants in four-coordinate 2. THF (143 Hz, solution phase) and surface grafted species are in closer agreement than those in the three-coordinate precursor 2 in either solution or solid-state measurements. From this

observation, the lack of THF in the sample, and the 1:2 elemental ratio of Y to N in $2@MSN_{700}$, we conclude that a surface siloxane group coordinates to the yttrium center to give a four-coordinate surface site as depicted in Scheme 3.

In an attempt to directly confirm the podality of silica-bound yttrium derivatives, we measured the ⁸⁹Y{¹H} CPMAS and ¹⁵N{¹H} CPMAS spectra enhanced by dynamic nuclear polarization (DNP). While both measurements were beyond the sensitivity limits of conventional SSNMR due to low quantities and receptivities of ⁸⁹Y and ¹⁵N and line broadening (in the case of ⁸⁹Y), DNP enabled the acquisition of ⁸⁹Y and ¹⁵N spectra within a few hours. The ⁸⁹Y{¹H} CPMAS spectra of 2@MSN₅₅₀ and 2@MSN₇₀₀ (Figure S34A in the Supporting Information) exhibit broad (>100 ppm) peaks centered at around 200 ppm, which demonstrate the presence of yttrium complexes on the surface. However, these spectra are displaced from that measured for the Y{N(SiHMe₂)tBu}₃THF (**2·THF**) at $\delta_{\rm v} \sim 460$ ppm. The latter value appears to be within the range of nitrogen-based ligands, which suggests that the N(SiHMe₂) tBu ligand may have dissociated from the metal center under the DNP conditions. The ¹⁵N{¹H} DNP CPMAS spectra of both samples (Figure S34B) support this hypothesis. They feature a single narrow peak at δ_N –311 ppm, which better agrees with those of free ligand molecules ($\delta_{\rm N}$ –301 ppm for Li-N(SiHMe₂)tBu and -329 ppm for H-N(SiHMe₂)tBu; see Table 1) than the yttrium precursors (-220 to -230 ppm).

Catalytic Hydroamination/Cyclization and Bicyclization of Aminodialkenes. The bicyclization of aminodialkenes requires C–N bond formation first from a primary amine and then from a secondary amine, and each step generates diastereomers (see Scheme 1). This reaction provides a test to compare the relative reactivity and selectivity of homoleptic homogeneous compounds and their mesoporous silica-grafted analogues as catalyst precursors.

First, the intramolecular hydroamination of 2,2-diphenylpent-4-enylamine (4a) was examined to compare conditions for cyclization of primary aminoalkenes (Table 5). With 1 or 2. THF, quantitative conversion to 4,4-diphenyl-5-methylpyrrolidine (4b) is complete within 10 min at ambient temperature. Although supported $Ln{N(SiHMe_2)tBu}_n@MSN (Ln = Sc, Y)$ requires 2 h at 60 °C for quantitative conversion, 5 mol % of either homogeneous or heterogeneous catalyst gives the cyclized product in high isolated yield (84-88%; Table 5). Moreover, kinetic studies, in which NMR yields of pyrrolidine were determined every 30 min, revealed similar rates (per mole of rare-earth element) for all four combinations of Sc and Y, on MSN₅₅₀ and MSN₇₀₀ (see Table S4 and Figure S37). We also noted a roughly linear relationship between time and yield, indicating zero-order rate dependence on substrate concentration.

Conversion of the soluble or supported rare-earth silazido precatalyst into active species involves protonolytic substitution of N(SiHMe₂)tBu by an aminoalkene reactant. Accordingly, HN(SiHMe₂)tBu was observed in the reaction mixtures and quantified. For example, 2.5 equiv of HN(SiHMe₂)tBu was measured with respect to the **2**•**THF** precatalyst after addition of **4a**, whereas 1.1 and 1.5 equiv of HN(SiHMe₂)tBu were observed for the **2@MSN**₅₅₀ and **2@MSN**₇₀₀ materials, respectively. Note that the greater number of equivalents of silazane per yttrium supported on MSN₇₀₀ vs MSN₅₅₀ is consistent with the former's formulation as primarily monopodal \equiv SiO-Y{N(SiHMe₂)tBu}.

Table 5. Catalytic Hydroamination of Aminoalkenes and Aminodialkenes^a

Reaction	Catalyst	Temp (°C)	Time (h)	Yield (%) ^b	dr ^c	
Cat. NH	Y{N(SiHMe ₂) <i>t</i> Bu} ₃ THF	25	0.1	88	n.a.	
Ph ¹ Ph ² Ph ¹ Ph ¹ Ph ⁴	Y{N(SiHMe ₂) <i>t</i> Bu} _n @MSN ₅₅₀	60	2	84		
cat.	Y{N(SiHMe ₂) <i>t</i> Bu} ₃ THF	25	2	85		
Ph Ph 5a Ph 5b	Y{N(SiHMe ₂) <i>t</i> Bu} _n @MSN ₅₅₀	60	12	84	n.a.	
No. No. No. No. No.	Sc{N(SiHMe ₂) <i>t</i> Bu} ₃	25	2	88	2:1	
$\left(\begin{array}{c} C_{6}H_{5} \\ NH_{2} \end{array}\right) \xrightarrow{\text{cat.}} \left(\begin{array}{c} \\ \end{array}\right) + \left(\begin{array}{c} \\ \\ \end{array}\right)$	Y{N(SiHMe ₂) <i>t</i> Bu} ₃ THF	25	2	92	2:1	
$6a$ C_6H_5 C_6H_5	Sc{N(SiHMe ₂) <i>t</i> Bu} _n @MSN ₅₅	o 60	12	92	2:1	
cis-6c trans-6c	Y{N(SiHMe ₂) <i>t</i> Bu} _n @MSN ₅₅₀	60	12	90	2:1	
$ \begin{array}{c} & \underset{C_{\theta}H_{5}}{\overset{Cat.}{\longrightarrow}} & \overset{N_{1}}{\overset{N_{2}}{\longrightarrow}} & \overset{N_{2}}{\overset{N_{2}}{\longrightarrow}} & \overset{N_{2}}{\overset{N_{2}}{\to} & \overset{N_{2}}{\overset{N_{2}}{\longrightarrow}} & \overset{N_{2}}{\overset{N_{2}}{\to} & \overset{N_{2}}{\overset{N_{2}}{\to} & \overset{N_{2}}{\overset{N_{2}}{\to} & \overset{N_{2}}{\overset{N_{2}}{\to}} & \overset{N_{2}}{\overset{N_{2}}{\to} & \overset{N_{2}}{\overset{N_{2}}{\to}} & \overset{N_{2}}{\overset{N_{2}}{$	Y{N(SiHMe ₂)/Bu} ₃ THF Y{N(SiHMe ₂)/Bu} _n @MSN ₅₅₀	25 60	2 12	81 83	2:1 2:1	
3:1 = cis:trans cis-6c trans-6c (96 % ee) Me cat. H_{+} $H_$	Y{N(SiHMe ₂)/Bu} ₃ THF Y{N(SiHMe ₂)/Bu} _n @MSN ₅₅₀	25 60	2 12	81 84	1:1.2 1:1.2	
$Me \xrightarrow{\text{cat.}} N \xrightarrow{\text{cat.}} + Me \xrightarrow{\text{me}} Me \xrightarrow{\text{me}} K$	Y{N(SiHMe ₂)/Bu} ₃ THF Y{N(SiHMe ₂)/Bu} _n @MSN ₅₅₀	60 80	6 24	81 84	1:1 1:1	
cot d	Y{N(SiHMe ₂) <i>t</i> Bu} _n @MSN ₅₅₀	60	2	96 ^d		
	1 st recycle	60	2	94 ^{<i>d</i>}	n.a.	
$\begin{array}{c} Ph \\ Ph \\ 4a \\ \end{array} \begin{array}{c} Ph \\ Ph \\ 4b \\ \end{array}$	2 nd recycle	60	2	82 ^d		
	3 rd recycle	60	2	70 ^d		

^aCatalytic conditions: 0.1 mmol of catalyst (5 mol % metal basis), 2.0 mmol of aminoalkene, 5 mL of benzene. Only one enantiomer of the (racemic) product is illustrated in mixtures of diastereomers. ^bIsolated yield. ^cdr = cis:trans. ^dNMR yield.

The second step of the bicyclization sequence requires hydroamination of secondary amines, and this reaction was tested separately from the first hydroamination step on the basis of cyclization of the secondary aminoalkene *N*-methyl-2,2-diphenylpent-4-enylamine (**5a**). The desired tertiary amine product forms in 2 h at room temperature using 1 or 2. THF as catalyst or in 12 h at 60 °C with the supported catalysts.

On the basis of the above primary and secondary aminoalkene cyclization studies, the reactivity of supported and homogeneous catalysts for the mono- and bicyclization of a series of aminodialkenes was investigated. As shown in Table 5 and Chart 1 (which shows 2·THF and 2@MSN; see Table S3 in the Supporting Information for a complete list of experiments, conditions, and outcomes), reactions with aminodialkenes provide azabicyclo[2.2.1]heptanes in good yields with both homogeneous and heterogeneous catalysts. As in the monocyclization of primary and secondary aminoalkenes, the supported catalysts require longer reaction times at higher temperatures in comparison to the homogeneous analogues, following the trend established with Y{N(SiMe₃)₂}₃ grafted on SBA-15.²⁸ Significantly, both scandium and yttrium catalysts Chart 1. Products and Diastereoselectivity from Catalytic Cyclization and Bicyclizations with 1, 2·THF, 1@MSN $_{550}$, and 2@MSN $_{550}$



and both interfacial and solution-phase conditions provide the bicyclized product with equivalent diastereoselectivity. For example, the substrate 2-allyl-2-phenylpent-4-en-1-amine (6a) is bicyclized to a mixture of cis-6c and trans-6c (2:1) over 2 h either at room temperature with 1 or 2. THF or over 12 h at 60 °C using the supported Ln{N(SiHMe2)tBu},@MSN (Table 5). The ¹H NMR of the bicyclized product shows cis (exo,exo)⁷² and trans (endo,exo) isomers in a 2:1 ratio. The cis and trans pyrrolidine intermediates (cis- and trans-6b) were observed in the catalytic mixtures prior to quantitative conversion to 6c. Note that the final product 6c forms with the equivalent diastereomeric ratio, regardless of catalyst (Sc or Y), supported vs unsupported species, support pretreatment temperature and surface-bonded structure, and at least a minor variation of the reaction conditions. Unfortunately, the ¹H NMR signals for the intermediates and final products overlapped; therefore, only the selectivity for the final product is reported. Despite this limitation, we investigated a possible relationship between the cis:trans ratio of the pyrrolidine intermediate and that of the final product. Note that the 4C is a stereogenic center in the intermediate 4-allyl-2-methyl-4phenylpyrrolidine (both cis- and trans-6b) and product trans-6c but that carbon is located on a mirror plane in cis-6c. Starting with **6b** prepared with a cis:trans ratio of 3.3:1 (the ee of both diastereomers is 96%) by zirconium-catalyzed monocyclization of 2-allyl-2-phenylpent-4-enylamine,⁴⁵ 6c is obtained with a cis:trans ratio (2:1) equivalent to that obtained directly from bicyclization of the aminodialkene. We conclude that the 4C stereogenic center does not affect the stereoselectivity of bicyclo[2.2.1]heptane formation.

Interestingly, substitutions on the phenyl ring (shown in Chart 1), such as in 2-allyl-(4-bromophenyl)pent-4-en-1-amine (7a), 2-allyl-(p-tolyl)pent-4-en-1-amine (8a), and 2-allyl-2-mesitylpent-4-en-1-amine (9a), provide diastereoselectivities of 2:1, 2.5:1, and 7:1, respectively. More forcing conditions (1 or 2.THF, 60 °C; 1@MSN or 2@MSN, 80 °C) are needed to obtain the bicyclized product 10c (cis:trans = 1:1), whereas lower temperatures provide the pyrrolidine as a mixture of cis and trans isomers (1:1.2). In contrast, the dialkene 11a is monocyclized exclusively to 2-methylpiperidine 11b even after heating at 120 °C.

Unlike the previously reported $\{PhB(Ox^{iPr,Me2})_2C_5H_4\}$ Zr- $(NMe_2)_2$ -catalyzed cyclizations of aminodialkenes or Cp*₂LaCH(SiMe₃)₂-catalyzed hydroamination of chiral aminoalkenes,^{45,46} in which the diastereoselectivity is dependent on the concentration of substrate, these scandium- and yttriumbased catalysts provide the products with cis:trans ratios that are independent of concentration. In conversions of 6a to 6c and of 11a to 11b, equivalent diastereoselectivities are obtained when [6a] or [15a] is varied from 43.5 to 348 mM while the catalyst concentration is kept constant (8.7 mM of 1 or 2. THF or ca. 4.4 mmol of 1@MSN or 2@MSN in 0.5 mL of solvent). Note that the diastereoselectivity in formation of 11b involves desymmetrization by selection of one of two allyl groups and distinguishing the re or si face of the selected olefin, whereas the corresponding conversion of 6b to cis- and trans-6c involves distinguishing the *re* or *si* face of the olefin. The latter process's selectivity is also probably strongly influenced by the conformational preference of the intermediate. In addition, note that soluble catalysts 1 and 2. THF, operating at room temperature or at 60 °C, and the supported catalysts, operating at 60 or 80 °C, all give products with identical diastereoselectivity (for a particular substrate).

The supported catalytic materials were recovered and reused three times for the hydroamination/cyclization, although the product yield diminished after the second and third cycles. Only trace quantities of yttrium were detected in the supernatant from ICP-OES analysis, and conversion stopped after the supported catalyst was separated (by filtration) from the substrate, product, silazane, and solvent. We conclude that catalyst leaching is not responsible for the apparent deactivation. Moreover, the lack of leaching suggests that the similar diastereoselectivities of homogeneous and supported catalysts is not due to the formation of equivalent soluble sites.

CONCLUSION

The silazido ligand $-N(SiHMe_2)tBu$ supports solvent-free homoleptic compounds of small (Sc, six-coordinate ionic radius 0.75 Å) and intermediate-sized (Lu, six-coordinated ionic radius 0.86 Å; Y, six-coordinate ionic radius 0.9 Å) trivalent rare-earth centers, in comparison to the known Er compound (sixcoordinate radius 0.89 Å).73 The homoleptic, solvent-free species are most readily accessible with the smaller rare-earth centers (Sc and Lu), whereas a relatively easily removed Et₂O coordinates to the larger Y center. X-ray crystallography and infrared spectroscopy show that the $Ln{N(SiHMe_2)tBu}_3$ species are isostructural and that the molecules contain three Ln-H-Si (one per silazido ligand) positioned in a fac-like configuration. Coordination of diethyl ether or THF influences the relative location of the secondary interactions in solid-state structures. The NMR spectroscopic properties of Ln{N- $(SiHMe_2)tBu_{3}$ (Ln = Sc, Y) and their ether adducts (Ln = Y, Lu) show that the secondary $Ln \leftarrow H-Si$ interactions, which are indicated by IR spectra and X-ray diffraction of Er{N- $(SiHMe_2)tBu_{3}$, are also maintained in solution. However, the NMR and IR spectroscopic signatures $(\delta_{SiH}, J_{SiH}, \nu_{SiH})$, reactivities, and crystallographic metrics do not show parallel trends. For example, the Y–O distances in 2.Et₂O and 2.THF are identical, yet 2 is accessible from the Et₂O adduct but not the THF adduct. The conformations of the two ether adducts are similar, but the similar spectroscopic properties of 2 and 2. Et₂O are distinct from those of 2. THF.

NMR spectroscopy provides new insight into these compounds' properties. For example, the molecules are fluxional, as often observed in species with secondary interactions. However, the δ_{SiH} and ${}^{1}J_{SiH}$ values are essentially temperature independent, indicating that the fluxional processes do not involve disruption of the secondary interactions, whereas the dimethyl signal indicates equivalent groups at room temperature (fast exchange) and inequivalent groups at low temperature (C_3 symmetry). These spectral changes are rationalized by in-place gyration of the "bidentate" N(SiHMe₂)tBu ligands, through a process that interconverts right- and left-handed propeller configurations. Although this process is distinct from in-place rotation of methyl groups in β agostic molybdenum ethyl compounds proposed to explain the symmetry of ³¹P NMR signals, ⁷⁴ it suggests that the Ln \leftarrow H–Si interactions are greater in strength than the steric interactions between the ligands. This idea is further supported by the lowtemperature ¹H NMR spectra of compounds **2** and **3**, for which coalescence is <190 K (at least in toluene- d_8). In these larger ionic radii rare-earth complexes, interligand interactions would be expected to be diminished, and the barriers of fluxional processes resulting from these interactions would be lower. Note that the apparent equivalence of $N(SiHMe_2)tBu$ ligands in ether adducts 2·Et₂O, 2·THF, and 3·THF is evident at room

temperature and below, even though the solid-state structures are not C_3 symmetric. It is clear from sublimation and synthetic studies that Et₂O readily dissociates from **2·Et₂O**, and IR spectroscopy suggests the coordinated Et₂O barely influences the Ln—H–Si interaction. Importantly, the spectroscopic features (${}^1J_{SiH}$, ν_{SiH}) associated with the Ln—H–Si interaction appear to report on the lability of the Ln—OR₂ coordinative interaction.

The tris(silazido) rare earth compounds react with partially dehydroxylated mesoporous silica to provide Ln{N(SiHMe₂) tBu}, @MSN. Our data, including diffuse reflectance IR, solidstate NMR spectroscopy, and NMR spectra of the solution phase during grafting experiments suggest THF does not coordinate to the surface-grafted yttrium sites. Note that, in contrast to Et₂O, THF does not readily dissociate from 2. THF, and thus the yttrium-silica interaction affects THF coordination. The data also suggest that reactions of $Ln\{N(SiHMe_2)\}$ tBu_{3L} with MSN₇₀₀ provide monopodal rare-earth sites and a greater ratio of \equiv SiOLn{N(SiHMe₂)tBu}_n sites to \equiv SiOSiHMe₂ surface groups in comparison to a mixture of monopodal and bipodal sites and a large amount of \equiv SiOSiHMe₂ sites in grafting reactions onto MSN₅₅₀. While infrared spectroscopy indicates that secondary Ln-H-Si interactions persist in the grafted materials, ${}^{1}J_{SiH} = 141$ Hz measured for Y{N(SiHMe₂)tBu}_n@MSN₇₀₀ more precisely defines the coordination environment on the surface site. Considering the resistance of 2. THF to dissociate THF (even during sublimation), the spectroscopic similarity between surface site and 2. THF suggests that the siloxane-yttrium dative interaction in $Y{N(SiHMe_2)tBu}_n @MSN$ is not labile. That is, the combination of NMR spectroscopy, X-ray structure determination, and reactivity studies on the new molecular precursors with surface SS NMR spectroscopy provides significant insight into the nature of these surface sites.

We examined the catalytic activity of soluble and supported precatalysts in the intramolecular hydroamination/cyclization of aminoalkenes and bicyclization of aminodialkenes. The formation of HN(SiHMe₂)tBu by protonolytic substitution was observed in the hydroamination catalysis, leading to the generation of active species. The soluble and supported amides proved to be catalytically active in intramolecular hydroamination of aminoalkenes and aminodialkenes. In comparison to the homogeneous rare-earth amides $Ln\{N(SiHMe_2)\}$ $tBu_{3}(Solv)_{n}$, the heterogeneous analogues $Ln\{N(SiHMe_{2})\}$ $tBu_n \otimes MSN$ display slower activity and require more vigorous conditions. In contrast, the diastereoselectivities obtained from the homogeneous and supported sites are very similar and are more dramatically influenced by the nature of the substrate than by the reaction conditions. Given our previous observations with zirconium hydroamination catalysts that show substantial effects of conditions on diastereoselectivity, as well as related effects in Cp*2LnR-catalyzed hydroaminations, the present results appear to reflect similar catalytic environments derived from both homoleptic and grafted precursors. This conclusion, in combination with the spectroscopic characterization noted above, is clearly important for systematic modifications to these heterogeneous catalytic sites on the basis of the coordination environment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00956.

Synthesis and characterization of homoleptic compounds, grafting procedures and characterization data, catalytic experiments, and product characterization (PDF)

Crystallographic information files for compounds 1, 2, 2• Et₂O, 2•THF, 3, and 3•THF (CIF)

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Notes

The authors declare no competing financial interest.

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