1,1,3,3-Tetramethylguanidine solvated lanthanide aryloxides: pre-catalysts for intramolecular hydroalkoxylation†

Thomas E. Janini,[b] Robert Rakosi III,[a] Christopher B. Durr,[a] Jeffrey A. Bertke[a] and Scott D. Bunge*[a]

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The synthesis and structural characterization of six 1,1,3,3-tetramethylguanidine (H-TMG) solvated lanthanide aryloxide complexes are reported. Ln[N{Si(CH$_3$)$_3$}$_2$]$_3$ (Ln = Nd, La) was reacted with two equivalents of both H-TMG and HOAr {HOAr = HOC$_6$H$_2$(CMe$_3$)$_2$-2,6 (H-DBP) or HOC$_6$H$_2$(CMe$_3$)$_2$-2,6-CH$_3$-4 (H-4MeDBP)} and one equivelent of ethanol (HOEt) to yield the corresponding [Nd(H-TMG)$_2$(4MeDBP)$_2$(OEt)] (**1**) and [La(H-TMG)$_2$(DBP)$_2$(OEt)] (**2**). Compounds **1** and **2** were further reacted with 4-pentyn-1-ol {HO(CH$_2$)$_3$C≡CH} to isolate [Nd(H-TMG)$_2$(4MeDBP)$_2${O(CH$_2$)$_3$C≡CH}] (**3**) and [La(H-TMG)$_2$(DBP)$_2${O(CH$_2$)$_3$C≡CH}] (**4**), respectively. Three equivalents of HOAr and one equivalent of H-TMG were additionally reacted with Ln[N{Si(CH$_3$)$_3$}$_2$]$_3$ to generate [Nd(4MeDBP)$_3$(H-TMG)] (**5**) and [La(DBP)$_3$(H-TMG)] (**6**). In order to examine the formation of **1–6**, the interaction of H-TMG and HOAr was further examined in solution and the hydrogen bonded complexes (H-TMG:HOAr), **7** and **8**, were isolated. Upon successful isolation of **1–6**, the utility of **1**, **2**, **4** and **5** as pre-catalysts for the intramolecular hydroalkoxylation of 4-pentyn-1-ol was investigated. The bulk powders for all complexes were found to be in agreement with the crystal structures based on elemental analyses, FT-IR spectroscopy, and ^{1}H and ^{13}C NMR investigations.

Introduction

The development of single-site homogeneous lanthanide-catalysts for organic transformations is driven to a large degree by the quest for increased efficiency and selectivity.[1] Ideally, to shape the microenvironment at the catalytically active lanthanide center, chelating multidentate ligands are utilized to generate a monomeric species with a single reactive site.[2] This is an especially difficult challenge for Group 3 and lanthanide (Ln) complexes; where large coordination spheres, labile ligand interactions, and flexible coordination geometries dominate the chemistry.[3] The use of bulky aryloxide ligands in conjunction with auxiliary Lewis bases has been proven to be a useful strategy for the isolation of well-defined monomeric complexes.[4]

Recently, we reported detailed efforts to outline the stoichiometric reactivity of hetero-ligated zinc and magnesium systems involving alkoxide, aryloxide, and guanidine ligand sets.[5] In these investigations, the use of the bulky aryloxide ligand (H-DBP), in conjunction with 1,1,3,3-tetramethylguanidine (H-TMG) was found to assist in producing well-defined metal alkoxide complexes with a single site for reactions. Previous structural reports of H-TMG complexes are limited.[5,6,7]

Approximately forty years ago, R. Drago and co-workers reported the first examples of H-TMG-solvated metal salts.[8] This pioneering work involved the synthesis of H-TMG adducts of Co(II), Cu(II), Zn(II), Pd(II), Ni(II), and Cr(III). The assignment of the C=N stretching frequency for H-TMG was utilized as an indicator for metal–ligand coordination. More recently, A. Davison and co-workers reported an exciting structurally characterized Tc example utilizing H-TMG as a neutral ligand, [Tc(N)(SC$_6$HMe$_4$)$_2$(H-TMG)$_2$].[9] The scarcity of examples utilizing H-TMG, at the time of this report, was commented upon and rationalized by the lone pair on the bare nitrogen being diffuse and lacking directionality. This diffuseness combined with the steric demands of H-TMG was stated to hinder it from acting as either a nucleophile or as a ligand.[9] Therefore, H-TMG has instead found widespread application in both organic and inorganic syntheses as a non-nucleophilic and non-coordinating base.[10]

Due to our success in isolating Zn and Mg systems, it appeared reasonable to extend this approach to the isolation of Ln complexes. Thus, the intent of this report is to examine the factors that result in the successful formation of H-TMG solvated Ln aryloxides. The subsequent utility of these complexes as pre-catalysts for the cycloisomerization of alkynyl alcohols was also of interest.

Herein, we report the synthesis and characterization of six hetero-ligated aryloxide complexes with the general formulas [Ln(H-TMG)$_2$(OAr)$_2$(OR)] (**1–4**) and [Ln(OAr)$_3$(H-TMG)] (**5** and **6**) (Ln = Nd, La). To examine their utility as pre-catalysts, complexes **1**, **2**, **4** and **5** were subsequently reacted with excess 4-pentyn-1-ol. ^{1}H NMR was utilized to follow the cycloisomerization of the alkynol to the corresponding 2-methylenetetrahydrofuran. Single-crystal X-ray diffraction, elemental analysis, FT-IR, ^{1}H

[a]*Department of Chemistry, Kent State University, Kent, OH, 44242, USA. E-mail: sbunge@kent.edu; Fax: +1 330 6723816; Tel: +1 330 6729445*
[b]*Agricultural Technical Institute, The Ohio State University, Wooster, OH, 44691, USA. E-mail: janini.4@osu.edu; Fax: +1 330 2871333; Tel: +1 330 2871287*

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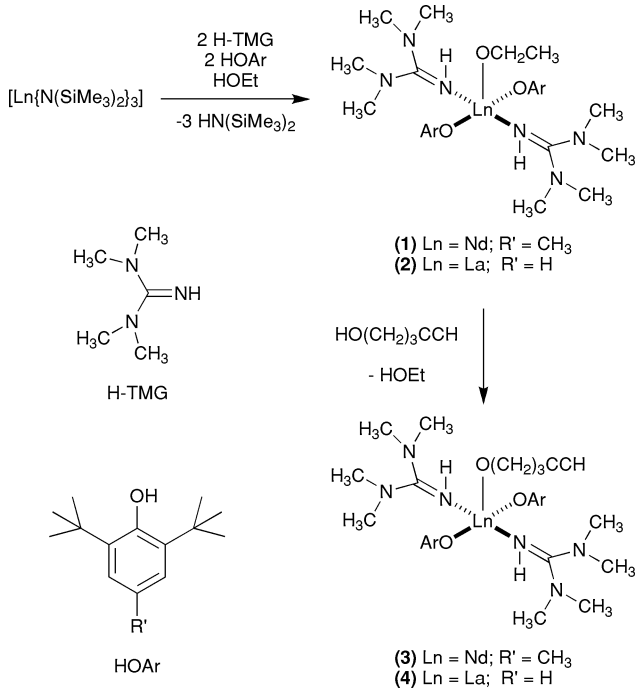
and ^{13}C NMR spectroscopy were performed to characterize the Ln aryloxide complexes.

Results and discussion

Synthesis

Our prior investigations related to the synthesis of Mg and Zn complexes involved the stoichiometric addition of a phenol, H-TMG, and an alcohol to a corresponding organo-magnesium or zinc reagent.[5] Liberation of two equivalents of a volatile alkane drives theses reactions forward and faciliates the isolation of the aryloxide. Following a similar protocol, the synthesis of **1–6** was performed utilizing $Ln[N\{Si(CH_3)_3\}_2]_3$ (Ln = Nd and La). The alcoholysis of a metal amide is generally a straightforward route for isolation of an alkali-metal-free alkoxide.[11]

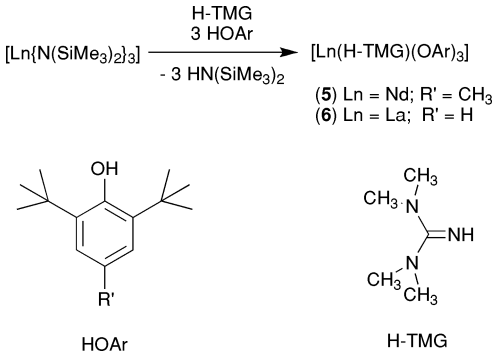
The synthesis of **1–4** is shown in Scheme 1. For the synthesis of **1** and **2**, in a hexanes solution, one equivalent of $Ln[N\{Si(CH_3)_3\}_2]_3$ was reacted with two equivalents of H-TMG, two equivalents of HOAr (H-DBP or H-4MeDBP), and one equivalent of ethanol. A powder precipitated and was re-dissolved through addition of THF to the hexanes solution. Crystals of **1** and **2** were obtained through slow evaporation of the solvent mixture.



Scheme 1 Synthesis of complexes **1-4**.

To accomplish the synthesis of **3** and **4**, **1** and **2** were each dissolved in a (1 : 1) mixture of hexanes and THF. An equivalent of 4-pentyn-1-ol was dissolved in hexanes and then added to each mixture dropwise. The reaction solutions were stirred for 10 min and then allowed to slowly evaporate, liberating EtOH and resulting in the formation of **3** and **4** as crystalline solids.

Scheme 2 depicts the synthesis of **5** and **6**. $Ln[N\{Si(CH_3)_3\}_2]_3$ was dissolved in hexanes and a mixture of three equivalents of HOAr and one equivalent of H-TMG was then added. Analagous to the synthesis of **1** and **2**, a precipitate forms and it is redissolved



Scheme 2 Synthesis of **5** and **6**.

via dropwise addition of THF. Evaporation of the THF : hexanes mixture resulted in crystals of **5** and **6**.

For elemental analysis of **1–6**, re-crystallization was additionally performed by re-dissolving the solids in a hexanes : THF (1 : 1) mixture and then placing the samples at −35 °C for 24 h. Crystalline yields from 37 to 78% were obtained.

In order to determine the origin of the stoichiometric formation of **1–6**, the interaction of HOAr with H-TMG was further investigated in solution and in the solid-state. A hexanes : THF solution of HOAr (OAr = 4MeDBP, DBP) was mixed with an equivalent of H-TMG. The solution was then placed in a −35 °C freezer and colorless crystals of H-DBP·H-TMG (**7**) and H-4MeDBP·H-TMG (**8**).were formed after 24 h.

Structural descriptions

The data collection parameters for **1–6** are presented in Table 2.

[Ln(H-TMG)$_2$(OAr)$_2$(OEt)] (1) and (2). Complexes **1** and **2** crystallized in monoclinic and triclinic space groups, respectively, and are represented by the thermal ellipsoid plot of **1** shown in Fig. 1. A thermal ellipsoid plot of **2** can be seen in ESI Fig. S1.† Both complexes exhibit a slightly distorted square-based pyramidal geometry {τ_5 = 0.13 (**1**), 0.15 (**2**)}.[12] Each Ln is centered ~ 0.6 Å above the N_2O_2 plane generated from the OAr/H-TMG ligand sets. The ethoxide ligand is located at the pyramidal coordination site with a comparatively short Ln–O distance of ~ 2.1 Å *versus* that found for the two bulky aryloxides, Ln–OAr ~ 2.3 Å. Although possessing a unique coordination sphere, the basic metrical parameters of **1** and **2** are similar to previously reported five coordinate Ln aryloxide systems.[13,14] Notably, the square base is composed of alternating H-TMG and aryloxide ligands. However, upon inspection, each complex is void of intramolecular hydrogen bonding interaction between

Table 1 Catalyzed 4-pentyn-1-ol intramolecular hydroalkoxylation in benzene-d_6

Pre-catalyst	Reaction time/h	Conversion (%)	Turnover number, N_t/h^{-1}
(**1**)	23	100	—
(**2**)	48[a]	50	0.19
(**4**)	22[a]	100	0.38
(**5**)	63	100	—
$La[N\{Si(CH_3)_3\}_2]_3$	—	—	4.3[28]

[a] 60 °C, sealed NMR tube, Ph_3SiCH_3 internal standard.

Table 2 Crystal data and structure refinement for **1–6**

Compound number	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{42}H_{77}N_6NdO_3$	$C_{40}H_{73}LaN_6O_3$	$C_{45}H_{79}N_6NdO_3$	$C_{43}H_{72}LaN_6O_3$	$C_{50}H_{82}N_3NdO_3$	$C_{55}H_{92}LaN_3O_5$
M_r/g mol^{-1}	858.37	824.95	896.38	859.98	917.43	1014.23
T/K	100(2)	160(2)	160(2)	160(2)	160(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	17.027(5)	10.8947(19)	17.133(2)	10.108(3)	15.570(11)	14.3312(16)
b/Å	15.239(4)	10.9333(19)	15.229(2)	13.612(4)	16.670(12)	19.335(2)
c/Å	19.483(6)	19.216(3)	19.850(3)	17.232(5)	19.634(14)	20.493(2)
α/°	—	100.912(3)	—	86.866(5)	77.44(10)	—
β/°	111.427(3)	99.102(3)	110.079(2)	87.732(5)	86.895(10)	104.958(2)
γ/°	—	92.317(3)	—	76.967(5)	81.859(10)	—
V/Å^3	4706(2)	2213.4(6)	4864.4(11)	2305.5(12)	4922.7(6)	5486.0(10)
Z	4	2	4	2	4	4
D_{calcd}/Mg m^{-3}	1.211	1.238	1.224	1.239	1.238	1.228
μ/mm^{-1}	1.143	1.005	1.109	0.968	1.096	0.825
Number of reflections (obs)	8346	7756	8625	8103	17405	9700
R_{int}	0.0214	0.0249	0.0373	0.0599	0.0438	0.0460
R_1[a] (%) (all data)	1.85 (2.03)	3.77 (4.03)	3.24 (4.92)	8.71 (24.87)	3.53 (6.04)	5.86 (6.74)
wR_2[b] (%)(all data)	7.38 (7.89)	14.92 (15.27)	4.92 (11.99)	10.56 (25.78)	9.50 (11.94)	14.46 (15.03)
GOF on F^2	0.712	1.292	0.921	1.659	0.769	0.886

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | \times 100$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (w | F_o |^2)^2] 1/2 \times 100$.

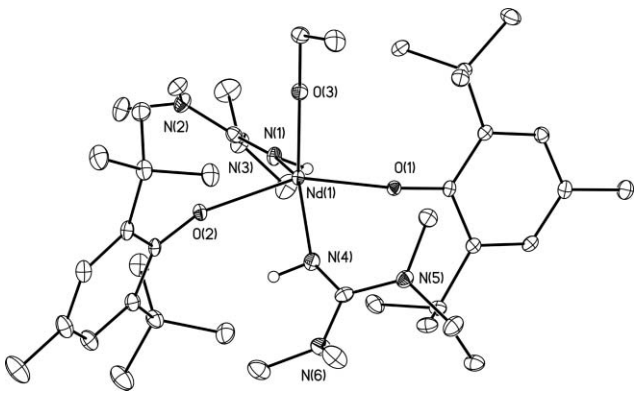


Fig. 1 Thermal ellipsoid plot of **1**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for **1**: Nd(1)–O(3) 2.106(3), Nd(1)–O(2) 2.299(14), Nd(1)–O(1) 2.282(3), Nd(1)–N(1) 2.527(3), Nd(1)–N(4) 2.5203(16), O(3)–Nd(1)–O(1) 100.70(10), O(2)–Nd(1)–O(1) 153.86(10), O(3)–Nd(1)–N(1) 106.66(12), O(2)–Nd(1)–N(1) 97.23(10), O(1)–Nd(1)–N(1) 74.65(11), O(3)–Nd(1)–N(4) 105.60(11), N(1)–Nd(1)–N(4) 147.37(11), O(1)–Nd(1)–N(4) 94.69(10), C(41)–O(3)–Nd(1) 168.9(4), C(5)–O(1)–Nd(1) 157.5(3), C(31)–N(1)–Nd(1) 154.0(3).

the aryloxide and guanidine. The shortest NH $\cdots$ OAr distance is 2.491 Å.

[Ln(H-TMG)$_2$(OAr)$_2${O(CH$_2$)$_3$C≡CH}] (3) and (4). Analagous to **1** and **2**, complexes **3** and **4** contain similar gross structural features and are represented by the plot of **3** in Fig 2. A thermal ellipsoid plot of **4** can be found in ESI Fig. S2.† The geometries of **3** and **4** are square-based pyramidal {$\tau_5 = 0.11$ (**3**), 0.32 (**4**)}.[12] The presence of the {O(CH$_2$)$_3$C≡CH} moiety at the pyramidal site (Ln–O ~ 2.1 Å) indicates successful replacement of the ethoxide ligand. The base is composed of alternating H-TMG and aryloxide ligands and is void of intramolecular hydrogen bonding. The terminal C≡C distance of the alkyne has an average

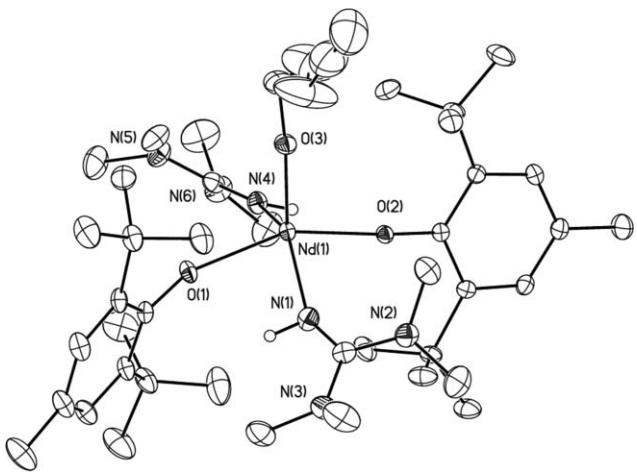


Fig. 2 Thermal ellipsoid plot of **3**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for **3**: Nd(1)–O(3) 2.1079(12), Nd(1)–O(2) 2.265(2), Nd(1)–O(1) 2.2546(13), Nd(1)–N(1) 2.527(3), Nd(1)–N(4) 2.542(3) O(3)–Nd(1)–O(1) 105.93(4), O(3)–Nd(1)–O(2) 101.28(4), O(1)–Nd(1)–O(2) 152.74(5), O(3)–Nd(1)–N(4) 106.13(5), O(1)–Nd(1)–N(4) 96.30(5), O(2)–Nd(1)–N(4) 74.27(5), O(3)–Nd(1)–N(1) 108.69(5), O(1)–Nd(1)–N(1) 78.60(4), O(2)–Nd(1)–N(1) 94.38(4), N(4)–Nd(1)–N(1) 144.87(5), C(31)–N(1)–Nd(1) 146.77(12), C(5)–O(1)–Nd(1) 173.28(10), C(20)–O(2)–Nd(1) 159.09(11).

distance of 1.2 Å, consistent with the presence of a formal carbon–cabon triple bond.[15] Correspondingly, the interaction between the alkyne moiety and the Ln metal center is negligible. The Ln $\cdots$ C distance is 6.1 Å.

[Ln(OAr)$_3$(H-TMG)] (5) and (6). Complexes **5** and **6** are isostructural and are depicted by the thermal ellipsoid plot of **5** in Fig. 3. A thermal ellipsoid plot of **6** can be seen in ESI Fig. S3.† Compound **5** crystalized with two structurally similar

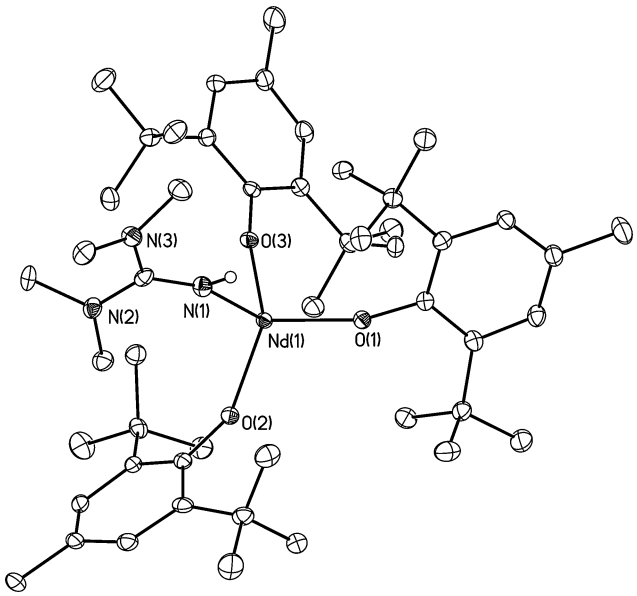


Fig. 3 Thermal ellipsoid plot of **5**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for **5**: Nd(1)–O(3) 2.162(3), Nd(1)–O(1) 2.195(3), Nd(1)–O(2) 2.218(3), Nd(1)–N(1) 2.487(3), O(3)–Nd(1)–O(1) 111.54(10), O(3)–Nd(1)–O(2) 115.70(10), O(1)–Nd(1)–O(2) 115.23(10), O(3)–Nd(1)–N(1) 102.38(11), O(1)–Nd(1)–N(1) 99.32(11), O(2)–Nd(1)–N(1) 10.58(11), C(46)–N(1)–Nd(1) 144.7(3), Nd(1)–N(1)–H(1) 107.6, C(1)–O(1)–Nd(1) 153.4(3).

monomers in the asymmetric unit (one of which is shown in Fig. 3). Both **5** and **6** exhibit trigonal pyramidal geometric character {τ_4 = 0.9 (**5**), 0.9 (**6**)}.[16] The structural features of **5** and **6** closely resemble the previously reported tetrahydrofuran solvated aryloxides, [Ln(OC$_6$H$_2$(CMe$_3$)$_2$-2,6-R-4)$_3$(THF)] {Ln = Dy (R = H), Er (R = Me), Ho (R = OMe), Nd (R = Me, OMe), Sm (R = Me), Yb (R = *t*-Bu)}.[14,17,18] Similar to **1–4**, hydrogen bonding interactions between the aryloxide and guanidine are not present. The shortest NH···OAr distance is 3.38 Å.

HOAr·H-TMG (7) and (8). The data collection parameters for **7** and **8** are presented in Table 3. Both **7** and **8** crystallized in an orthorhombic space group with, respectively, eight and four hydrogen bonded HOAr·H-TMG pairs per unit cell. Thermal ellipsoid plots are shown in ESI Fig. S4 and S5.† A packing diagram of **7** is presented in Fig. 4. Each H-TMG is oriented toward an adjacent phenol {N-HOAr = 173° (**7**), 165° (**8**)}. The N···H and H–O interatomic distances for the shared hydrogen atoms are 1.771, 0.918 (**7**) and 1.907, 0.840 (**8**) Å. This is consistent for the presence of hydrogen bonding interactions between the two molecules.[19]

Spectroscopy

Crystals of **1–6** were dried *in vacuo* to yield bulk powder and used subsequently in the following analyses. All complexes are sparingly soluble in toluene and **2**, **4** and **6** exhibited expected ^{1}H and ^{13}C resonances in the solution NMR spectra. The presence of the N–H bond for the coordinated H-TMG is confirmed by a singlet ($\delta \sim 4$) in the ^{1}H NMR spectra. In the ^{1}H NMR spectrum of **4**, the appearance of peaks at δ = 2.16, 1.85, 1.47, 1.08 and 0.99 ppm are consistent with the replacement of the ethoxide ligand with the 4-pentynoxide. In the ^{13}C NMR spectra, the low field resonance (~160 ppm) for the central carbon atom '*C*N$_3$' of the H-TMG ligand is also an additional distinguishing feature for each compound.

Table 3 Crystal data and structure refinement for **7–8**

Compound number	**7**	**8**
Empirical formula	$C_{19}H_{35}N_3O$	$C_{20}H_{37}N_3O$
M_r/g mol^{-1}	321.50	335.53
T/K	100(2)	100 (2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	$P2_12_12_1$
a/Å	9.654(4)	9.4695(18)
b/Å	16.646(7)	14.576(3)
c/Å	25.314(11)	15.153(3)
α/°	—	—
β/°	—	—
γ/°	—	—
V/Å^3	4068(3)	2091.5(7)
Z	8	4
D_{calcd}/Mg m^{-3}	1.050	1.066
μ/mm^{-1}	0.065	0.066
Number of reflections (obs)	3596	2123
R_{int}	0.0821	0.1016
R_1[a] (%) (all data)	4.68 (7.56)	3.76 (4.84)
wR_2[b] (%)(all data)	12.56 (15.05)	10.40 (11.94)
GOF on F^2	0.916	0.926

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o| \times 100$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w|F_o|^2)^2]1/2 \times 100$.

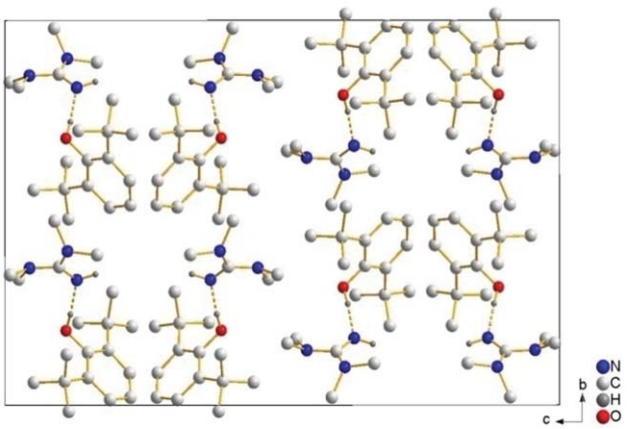


Fig. 4 Unit cell of **7** with packing shown along the *a* axis. Several H atoms have been omitted for clarity.

The FTIR spectra of **1–6** exhibited an absence of stretches associated with –OH ligands, indicative of complete substitution. The expected alkyl and aryl stretches for the aryloxide, alkoxide and guanidine ligands are present for each sample. In **2**, **4** and **6** a strong stretch at 750 cm^{-1} may be assigned to the γ(CH) vibration of the DBP ring. This has been observed previously in the spectra of [Ln(DBP)$_2$(L)] (L = THF or Et$_2$O).[17,20] For **1–6**, the presence of υ(N–H) and υ(C=N) were confirmed by stretching corresponding to peaks around 3300 cm^{-1} and 1580 cm^{-1}, respectively. In addition, for complexes **3** and **4**, a diagnostic peaks around 3637 cm^{-1} and 2117 cm^{-1} can be assigned to the alkyne. Assignment of the Ln–O bands in aryloxides is often difficult owing to the coupling of the C–O and Ln–O modes. Comparisons of the data for **1–6** with data

for HOAr indicates that bands located between 540 and 450 cm^{-1} are most likely associated with the Ln–O bonds.

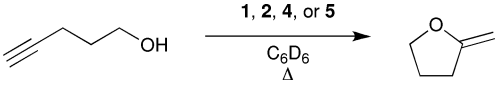
To examine the hydrogen bonding of the phenol and H-TMG in solution, a variable temperature (25 to 65 °C) ^{1}H NMR investigation of a 1 : 1 mixture of H-TMG and H-DBP was performed in C_6D_6. (ESI Fig. S7)† At room temperature, a broad peak integrating for 2 H atoms (assigned to HO and HN functional groups) is located at 6.39 ppm. Indicative of hydrogen bonding in solution, as temperature increases the interaction between these functional groups weakens and the protons become more shielded, resulting in a upfield shift of this peak to 5.80 ppm. Consistent with what is found in the solid-state, the two ligand sets pre-associate in solution prior to addition of the lanthanide amide.

Intramolecular hydroalkoxylation

Producing a catalyst with a single reactive site potentially allows for stereochemical control of the end product. Other groups have been successful in utilizing single-site lanthanide catalysts in polymerization reactions.[21] Oxygen heterocycles are common components of natural products and physiologically active molecules. The ability to efficiently construct these heterocycles has been aided by the application of catalytic methods. A variety of transition metal catalysts have been employed by many groups to cycloisomerize alkynols to enol ethers, in an intramolecular hydroalkoxylation process. Intramolecular oxymercuration of alkynols was initially employed to produce exocyclic enol ethers.[22] Palladium(II) catalyzed variants gave mixtures of *exo*- and *endo-dig* products.[23] Molybdenum pentacarbonyl has been used to catalyze exocyclic alkynol cycloisomerization to the five-membered enol ether.[24]

Alternatively, tungsten hexacarbonyl yielded the corresponding dihydropyran *via* an endocyclic ring closure.[25] Endocyclic enol ethers have been made with chromium, molybdenum and tungsten catalysts in basic solutions.[26] The application of a variety of gold and silver catalysts typically gave the product of an *exo-dig* ring closure.[27] However, oxygen-containing heterocyclic synthesis using lanthanide catalysts has been relatively unexplored. In recent publications by Marks and co-workers, $Ln[N\{Si(CH_3)_3\}_2]_3$ complexes were utilized to carry out hydroalkoxylation reactions with allenyl and alkynyl alcohols acting as substrates.[28,29] However, while kinetic and NMR data were used to characterize the reactions, no structural information was provided about the pre-catalyst complex.

Complexes **1**, **2**, **4**, and **5** were evaluated as pre-catalysts in the cycloisomerization of 4-pentyn-1-ol (see Scheme 3 and Table 1). Conversion of 4-pentyn-1-ol to 2-methylenetetrahydrofuran was followed by ^{1}H NMR spectroscopy. Specifically, the integration of the signal of the methylene hydrogens adjacent to the hydroxyl group of the alkynol at δ 3.6 were compared to the integration of the exo-methylene hydrogen signal at δ 4.6. The product signal, along with the signal of the internal standard's *meta*-aromatic hydrogens, were used to calculate the change in product concentration with time and the turnover number (N_t) for pre-catalysts **2** and **4**. Comparison of the turnover numbers of pre-catalysts **2** and **4** indicate that pre-attachment of the substrate yields a more efficient catalyst.



Scheme 3 Cycloisomerization *via* intramolecular hydroalkoxylation of 4-pentyn-1-ol.

In this particular transformation, the turnover numbers for these pre-catalysts were also lower than the turnover number of the homoleptic pre-catalyst $La[N\{Si(CH_3)_3\}_2]_3$ reported by Marks *et al.*[28,29] This is perhaps caused by the increased steric demand of the aryloxide ligands and the coordination of the H-TMG ligands. While the differences in turnover number for our pre-catalysts as compared to others indicates lower reactivity, no *a priori* inference can be made with regard to the selectivity of our pre-catalysts.[30]

Advantages and disadvantages of the OAr/H-TMG ligand-set

Designing ligands utilizing bioinspired hydrogen bond motifs is currently an active area of research.[31] In this area, intramolecular hydrogen-bonding between monodentate ligands is used to generate a library of bidentate ligands. Hydrogen bonding organizes the ligands in solution and typically remains present upon coordination to the metal.

For the synthesis of **1**–**4**, hydrogen bonding between HOAr and H-TMG is utilized to conveniently generate well-defined Ln systems *via* a "one-pot" approach. However, upon determination of the structure of **1**–**4**, it was found that the hydrogen bonding between ligand sets is no longer present. Thus, disassociation of H-TMG is possible under catalytic conditions of increased temperature and excess alcohol. In order to test this possibility, the synthesis of **5** and **6** was undertaken and **5** was examined as a pre-catalyst for intramolecular hydroalkoxylation. Presumably, due to the steric constraints around the metal center, for **5** and **6**, de-solvation of H-TMG is a necessary pre-requisite prior to coordination and cyclization of substrate.

As shown in Table 1, **5** was successful in converting 4-pentyn-1-ol to 2-methylenetetrahydrofuran. This indicates that the OAr/H-TMG is perhaps not a robust system for tailoring the microenvironment of a Ln center. In support of this finding, in some cases, complexes that were transferred from cold solution and placed under vacuum hindered obtaining satisfactory elemental analysis. This is consistent with possible de-solvation of H-TMG.

Conclusions

The addition of alcohol, H-TMG and HOAr to a solution of $Ln[N\{Si(CH_3)_3\}_2]_3$ is a successful method for synthesizing monomeric five-coordinate lanthanide systems designed with a single site for reactivity. Based on spectroscopic and crystallographic evidence, hydrogen bonding of H-TMG and HOAr in solution may facilitate the remarkable formation of the hetero-ligated products. The structurally characterized complexes have been demonstrated to effectively convert 4-pentyn-1-ol to 2-methylenetetrahydrofuran. Notably, only the furan product from an *exo-dig* ring closure was observed. This conversion also took place when utilizing complexes that were expected to have diminished reactivity due to steric congestion. This is indicative of H-TMG lability and a potential disadvantage in utilizing this combination of ligands.

Experimental

All compounds were handled with rigorous exclusion of air and water using standard glove box techniques. All anhydrous solvents were stored under argon and used as received in sure-seal bottles. H-TMG, H-DBP, H-4MeDBP, ethanol, and 4-pentyn-1-ol were used as received from commercial suppliers. La[N{Si(CH$_3$)$_3$}$_2$]$_3$ and Nd[N{Si(CH$_3$)$_3$}$_2$]$_3$ were synthesized according to literature procedures.[32] FT-IR data was obtained on a Bruker Tensor 27 instrument using KBr pellets under an atmosphere of flowing nitrogen. Melting points were determined on samples in sealed capillary tubes under an atmosphere of argon using an Electrothermal Mel-Temp apparatus and are uncorrected. Elemental analysis was performed on a Perkin-Elmer 2400 Series 2 CHN-S/O Elemental Analyzer. All solution ^{1}H and ^{13}C{^{1}H} spectra were obtained with a Bruker DRX 400 spectrometer at 400 and 100 MHz, respectively.

Preparation of [Nd(H-TMG)$_2$(4MeDBP)$_2$(OEt)] (1) and [La(H-TMG)$_2$(DBP)$_2$(OEt)] (2)

Ln[N{Si(CH$_3$)$_3$}$_2$]$_3$ (Ln = Nd, La), HOAr (OAr = 4MeDBP, DBP), H-TMG, and ethanol were dissolved in hexanes separately. The HOAr, H-TMG, and ethanol were mixed together in one vial and then added dropwise to the stirring Ln[N{Si(CH$_3$)$_3$}$_2$]$_3$ solution. A precipitate formed which upon addition of THF was dissolved. The resulting solution was then stirred for 5 min and left to evaporate overnight. After evaporation of the volatile components, blue crystals of **1** and colorless crystals of **2** were isolated.

[Nd(H-TMG)$_2$(4MeDBP)$_2$(OEt)] (1). Nd[N{Si(CH$_3$)$_3$}$_2$]$_3$ (200 mg, 0.32 mmol), H-4MeDBP (142 mg, 0.64 mmol), H-TMG (74 mg, 0.64 mmol) and HOEt (15 mg, 0.32 mmol) were used. Yield 78% (220 mg, 0.26 mmol) Found: C 59.07, H 8.61, N 8.39%. $C_{42}H_{77}N_6NdO_3$ requires: C 58.77, H 9.04, N 9.79%. Mp = 156 °C. υ_{max}(KBr)/cm^{-1} 3650 (w), 3312 (w), 2954 (s), 1591 (s), 1425 (s), 1260 (m), 1119 (m), 1062 (w), 898 (w), 862 (m), 819 (m), 802 (m), 775 (w), 708 (w), 576 (w), 509 (w), 488 (w), 435 (w).

[La(H-TMG)$_2$(DBP)$_2$(OEt)] (2). La[N{Si(CH$_3$)$_3$}$_2$]$_3$ (200 mg, 0.32 mmol), H-DBP (114 mg, 0.65 mmol), H-TMG (74 mg, 0.64 mmol) and HOEt (15 mg, 0.32 mmol) were used. Yield 66% (180 mg, 0.22 mmol) formed. Found: C 57.30, H 8.79, N 9.69%. $C_{45}H_{79}N_6LaO_3$ requires: C 58.24, H 8.92, N 10.19%. Mp = 126 °C. υ_{max}(KBr)/cm^{-1} 3334 (w), 3070 (w), 2951 (s), 2696 (w), 2527 (w), 2180 (w), 1839 (w), 1567 (s), 1530 (s), 1461 (m), 1404 (s), 1381 (m), 1257 (s), 1199 (m), 1127 (m), 1062 (m), 937 (w), 900 (m), 883 (w), 858 (m), 816 (m), 749 (m), 640 (m), 557 (w), 537 (w), 484 (w), 442 (w). ^{1}H-NMR (C_6D_6): δ = 7.60 (s, 4 H, OC$_6H_3$((C(CH$_3$)$_3$)$_2$-2,6), 6.95 (t, 2 H, OC$_6H_3$((C(CH$_3$)$_3$)$_2$-2,6), 5.48 (s, 2 H, *H*N=C(N((CH$_3$)$_2$)$_2$), 4.47 (q, 2 H, OC*H*$_2$CH$_3$), 2.69, 2.13 (s, 12 H, HN=C(N((C*H*$_3$)$_2$)$_2$), 1.90 (s, 36 H, OC$_6$H$_3$((C(C*H*$_3$)$_3$)$_2$-2,6), 1.58 (t, 3 H, OCH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 165.8 (HN=*C*(N((CH$_3$)$_2$)$_2$), 138.1, 127.2, 124.9, 114.4 (O*C*$_6$H$_3$((C(CH$_3$)$_3$)$_2$-2,6), 39.0 (O*C*H$_2$CH$_3$), 38.4 (OC$_6$H$_3$((C(*C*H$_3$)$_3$)$_2$-2,6), 35.1 (HN=C(N((*C*H$_3$)$_2$)$_2$), 31.4 (OC$_6$H$_3$((*C*(CH$_3$)$_3$)$_2$-2,6), 14.2 (OCH$_2$*C*H$_3$) ppm.

Preparation of [Nd(H-TMG)$_2$(4MeDBP)$_2${O(CH$_2$)$_3$C≡CH}] (3) and [La(H-TMG)$_2$(DBP)$_2${O(CH$_2$)$_3$C≡CH}] (4)

[Ln(H-TMG)$_2$(OAr)$_2$(OEt)] (Ln = Nd, La) was dissolved in a 1 : 1 hexanes : THF mixture. To this solution, 4-pentyn-1-ol, dissolved in hexanes, was added dropwise. The resultant clear solution was stirred for 10 min. This solution was then set out to evaporate overnight. After evaporation, blue crystals of **3** and colorless crystals of **4** formed.

[Nd(H-TMG)$_2$(4MeDBP)$_2${O(CH$_2$)$_3$C≡CH}] (3). [Nd(H-TMG)$_2$(4MeDBP)$_2$(OEt)] (240 mg, 0.28 mmol) and 4-pentyn-1-ol (23 mg, 0.28 mmol) were used. Yield 54% (130 mg, 0.15 mmol). Found: C 60.70, H 8.96, N 8.28%. $C_{45}H_{79}N_6NdO_3$ requires: C 60.30, H 8.88, N 9.38%. Mp = 146 °C. υ_{max}(KBr)/cm^{-1} 3643 (m), 3318 (m), 2956 (s), 2706 (w), 2119 (w), 1752 (w), 1590 (s), 1518 (m), 1415 (s), 1261 (s), 1119 (s), 1063 (m), 1026 (w), 921 (w), 898 (w), 863 (m), 819 (m), 802 (m), 776 (w), 626 (w), 576 (w), 556 (w), 541 (w), 507 (m).

[La(H-TMG)$_2$(DBP)$_2${O(CH$_2$)$_3$C≡CH}] (4). La(H-TMG)$_2$-(DBP)$_2$(OEt) (180 mg, 0.22 mmol) and 4-pentyn-1-ol (18 mg, 0.21 mmol) were used. Yield 59% (110 mg, 0.13 mmol) formed. Found: C 58.98, H 8.20, N 8.52. $C_{43}H_{72}LaN_6O_3$ requires: C 59.84, H 8.76, N 9.74%. Mp = 152 °C. υ_{max}(KBr)/cm^{-1} 3640 (w), 3335 (w), 3300 (m), 3071 (w), 2951 (s), 2704 (w), 2532 (w), 2116 (w), 1587 (s), 1566 (s), 1529 (m), 1467 (m), 1425 (s), 1403 (s), 1382 (s), 1257 (s), 1200 (m), 1102 (s), 1062 (m), 1026 (s), 960 (w), 924 (w), 899 (w), 884 (w), 859 (m), 817 (m), 750 (s), 701 (w), 640 (m), 591 (w), 557 (w), 537 (w), 483 (w), 444 (w). ^{1}H-NMR (C_6D_6): δ = 7.27 (s, 4 H, OC$_6H_3$((C(CH$_3$)$_3$)$_2$-2,6), 6.96 (t, 2 H, OC$_6H_3$((C(CH$_3$)$_3$)$_2$-2,6), 3.49 (s, 2 H, *H*N=C(N((CH$_3$)$_2$)$_2$), 2.60 (s, 24 H, HN=C(N((C*H*$_3$)$_2$)$_2$), 2.16 (t, 2 H, OC*H*$_2$CH$_2$CH$_2$CCH), 1.85 (s, 1 H, OCH$_2$CH$_2$CH$_2$CC*H*), 1.47 (s, 36 H, OC$_6$H$_3$((C(C*H*$_3$)$_3$)$_2$-2,6), 1.08 (t, 2 H, OCH$_2$C*H*$_2$CH$_2$CCH), 0.99 (m, 2 H, OCH$_2$CH$_2$C*H*$_2$CCH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 165.8 (HN=*C*(N((CH$_3$)$_2$)$_2$), 137.9, 135.7, 125.0, 114.3 (O*C*$_6$H$_3$((C(CH$_3$)$_3$)$_2$-2,6), 38.9 (OCH$_2$CH$_2$CH$_2$*C*CH), 38.4 (OCH$_2$CH$_2$CH$_2$C*C*H), 35.2 (HN=C(N((*C*H$_3$)$_2$)$_2$), 34.1 (O*C*H$_2$*C*H$_2$CH$_2$CCH), 31.6 (OC$_6$H$_3$((C(*C*H$_3$)$_3$)$_2$-2,6), 30.2 (OC$_6$H$_3$((*C*(CH$_3$)$_3$)$_2$-2,6), 22.8 (OCH$_2$*C*H$_2$CH$_2$CCH), 14.2 (OCH$_2$CH$_2$*C*H$_2$CCH) ppm.

Preparation of [Nd(4MeDBP)$_3$(H-TMG)] (5) and [La(DBP)$_3$(H-TMG)] (6)

Ln[N{Si(CH$_3$)$_3$}$_2$]$_3$ (Ln = Nd, La), HOAr (H-4MeDBP, H-DBP) and H-TMG were each dissolved in hexanes. HOAr and H-TMG were mixed together in one vial and added dropwise to the Ln[N{Si(CH$_3$)$_3$}$_2$]$_3$ solution. A precipitate formed and was dissolved with THF. Blue crystals of **5** and colorless crystals of **6** were formed after slow evaporation of the respective solutions.

[Nd(4MeDBP)$_3$(H-TMG)] (5). Nd[N{Si(CH$_3$)$_3$}$_2$]$_3$ (200 mg, 0.32 mmol), H-4MeDBP (212 mg, 0.96 mmol) and H-TMG (37 mg, 0.32 mmol) were used. Yield 37% (106 mg, 0.12 mmol). Found: C 64.16, H 8.94, N 3.87%. $C_{50}H_{82}N_3NdO_3$ requires: C 65.46, H 9.01, N 4.58%. Mp = 137 °C. υ_{max}(KBr)/cm^{-1} 3324 (w), 2955 (w), 2916 (m), 2280 (w), 1754 (w), 1710 (w), 1690 (w), 1657 (w), 1563 (m), 1536 (m), 1416 (s), 1384 (w), 1355 (w), 1233 (s),

1121 (m), 1063 (w), 1033 (w), 889 (w), 861 (w), 819 (m), 802 (m), 779 (w), 748 (w), 687 (w), 563 (w), 521 (m), 468 (w), 433 (w).

[La(DBP)$_3$(H-TMG)] (6). La[N{Si(CH$_3$)$_3$}$_2$]$_3$ (200 mg, 0.32 mmol), H-DBP (199 mg, 0.96 mmol) and H-TMG (37 mg, 0.32 mmol) were used. Yield 75% (207 mg, 0.24 mmol). Found: C 64.65, H 9.17, N 5.36%. $C_{47}H_{76}LaN_3O_3$ requires: C 64.88, H 8.80, N 4.83%. υ_{max}(KBr)/cm^{-1} 3312 (m), 3057 (w), 2953 (s), 2802 (w), 2173 (w), 1568 (s), 1519 (m), 1467 (m), 1402 (s), 1382 (m), 1358 (w), 1303 (w), 1234 (s), 1200 (m), 1115 (m), 1063 (w), 1028 (w), 941 (w), 901 (w), 882 (w), 855 (m), 816 (m), 796 (w), 773 (w), 745 (s), 642 (m), 555 (w), 538 (w), 441 (w). ^{1}H-NMR (C_6D_6): δ = 7.43 (d, 6 H, (OC$_6H_3$((C(CH$_3$)$_3$)$_2$-2,6), 6.95 (m, 3 H, (OC$_6H_3$((C(CH$_3$)$_3$)$_2$-2,6), 5.05 (s, 1 H, *H*N=C(N((CH$_3$)$_2$)$_2$), 2.53 (s, 12 H, HN=C(N((C*H*$_3$)$_2$)$_2$), 1.72 (s, 54 H, OC$_6$H$_3$((C(CH$_3$)$_3$)$_2$-2,6) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 166.9 (HN=*C*(N((CH$_3$)$_2$)$_2$), 138.6, 127.8, 125.3, 114.6 (O*C*$_6$H$_3$((C(CH$_3$)$_3$)$_2$-2,6), 39.6 (OC$_6$H$_3$((C(*C*H$_3$)$_3$)$_2$-2,6), 35.9 (HN=C(N((*C*H$_3$)$_2$)$_2$), 32.6 (OC$_6$H$_3$((*C*(CH$_3$)$_3$)$_2$-2,6) ppm.

Preparation of H-DBP·H-TMG (7) and H-4MeDBP·H-TMG (8)

1.96 mmol of HOAr (OAr = 4MeDBP, DBP) was dissolved in a (1 : 1) mixture of hexanes and THF (5 mL). An equivalent of H-TMG was added drop-wise and the mixture was stirred for several minutes. The solution was then placed in a –35 °C freezer and colorless crystals were formed after 24 h.

H-DBP·H-TMG (7). ^{1}H-NMR (C_6D_6, 25 °C): δ = 7.25 (d, 2 H, (HOC$_6H_3$((C(CH$_3$)$_3$)$_2$-2,6), 6.90 (m, 1 H, (HOC$_6H_3$-((C(CH$_3$)$_3$)$_2$-2,6) 6.39 (s, 2 H, *H*OAr·*H*N=C(N((CH$_3$)$_2$)$_2$), 2.41 (s, 12 H, HN=C(N((C*H*$_3$)$_2$)$_2$, 1.55 (s, 18 H, HOC$_6$H$_3$((C(CH$_3$)$_3$)$_2$-2,6) ppm.

Intramolecular hydroalkoxylation (cycloisomerization)

Reaction times were varied to examine conversion and turnover tumber, N_t (h^{-1}).

Preparative scale. 4-Pentyn-1-ol solution (142 mg, 1.69 mmol, 21 equiv.) in C_6D_6 (0.4 mL) was added to a solution of lanthanide pre-catalyst (**1** or **5**) (8.0 mmol, 1.0 equiv.) in C_6D_6 (5.6 mL). Ph_3SiCH_3 (165 mg, 6.0×10^{-1} mmol, 7.5 equiv.) was also included in the solution of pre-catalyst **1**. The mixture was stirred under an argon atmosphere and heated to reflux. The reaction was followed by periodically analyzing aliquots by ^{1}H NMR spectroscopy.

NMR scale. In a glove box, 4-pentyn-1-ol solution (0.30 mL, 0.41 M in C_6D_6, 0.12 mmol, 8.0 equiv.) was added to a solution of lanthanide pre-catalyst (**2** or **4**) (1.5×10^{-2} mmol, 1.0 equiv., 12 mol%) and Ph_3SiCH_3 (30 mg, 1.1×10^{-1} mmol, 7.3 equiv.) in C_6D_6 (1.0 mL) in an NMR tube. The tube was capped with a Teflon valve, removed from the glove box, frozen in liquid nitrogen and attached to a high-vacuum line. The tube was sealed and kept in liquid nitrogen until the cycloisomerization reaction could be followed by ^{1}H NMR spectroscopy.

The turnover frequencies were calculated for pre-catalysts **2** and **4** using a procedure adapted from one used by Marks *et al.*[28] The concentration of the product was measured by integrating the peak from the most downfield methylene hydrogen (δ 4.6) standardized to the peak area of the meta-aromatic hydrogens of the Ph_3SiCH_3 internal standard.

$$[product] = mt \quad (1)$$

$$N_t = \frac{60\,min}{h} \times \frac{m}{[cat]_0} \quad (2)$$

The linear least-squares determined slope m of the line obtained by plotting the product concentration against time (eqn (1)) was used to calculate the turnover frequency, N_t (h^{-1}), using eqn (2), where $[cat]_0$ is the initial concentration of the pre-catalyst.

X-Ray crystallography†

X-Ray crystallography was performed by mounting a crystal of **1–8** onto a thin glass fiber from a pool of Fluorolube™ and immediately placing it under a liquid N_2 cooled N_2 stream, on a Bruker AXS diffractometer. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out using the APEX2 version 1.0-27 software package.[33] Each structure was solved using direct methods. This procedure yielded the heavy atoms, along with a number of the O, N and C atoms. Subsequent Fourier synthesis yielded the remaining atom positions. All atoms, unless otherwise noted, were refined within the XSHELL software.[34] The structures of **1–8** are drawn at 30% probability for clarity and due to disorder in coordinated substrate. Deviations from typical procedures are outlined below. [Nd(H-TMG)$_2$(4MeDBP)$_2$(OEt)] (**1**) H(N) atoms were refined; all other H atoms were refined in riding mode. [La(H-TMG)$_2$(DBP)$_2$(OEt)] (**2**) H(N) atoms refined; all other H atoms were refined in riding mode. [Nd(H-TMG)$_2$(4MeDBP)$_2${O(CH$_2$)$_3$C≡CH}] (**3**) H(N) atoms were refined; all other H atoms were refined in riding mode. The C atoms of the O(CH$_2$)$_3$C≡CH ligand are slightly disordered. [La(H-TMG)$_2$(DBP)$_2${O(CH$_2$)$_3$C≡CH}] (**4**) H(N) atoms were refined; all other H atoms were refined in riding mode. C(42), C(43), and N(6) were disordered over two positions. The C atoms of the O(CH$_2$)$_3$C≡CH ligand are slightly disordered. The structure has had disorder modelled where possible, but significant improvement in refinement was not obtained with additional cycles. [Nd(4MeDBP)$_3$(H-TMG)] (**5**) H(N) atoms were refined; all other H atoms were refined in riding mode. [La(DBP)$_3$(H-TMG)] (**6**) N(1) was disordered and modelled over two positions. Additional disorder was modelled where possible, but significant improvement in refinement was not obtained with additional cycles. The solvent electron density was modelled using PLATON/SQUEEZE (ver. 01-11-99), which located a potential solvent volume of 1218.2 Å^3 and an electron count of 302 electrons/cell, consistent with eight tetrahyrdrofuran molecules/cell. H-DBP·H-TMG (**7**) H(N) and H(O) atoms were refined; all other H atoms were refined in riding mode. H-4MeDBP·H-TMG (**8**) H(N) and H(O) atoms were refined; all other H atoms were refined in riding mode.

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