ORGANOMETALLICS-

Chloro and Alkyl Rare-Earth Complexes Supported by *ansa*-Bis(amidinate) Ligands with a Rigid *o*-Phenylene Linker. Ligand Steric Bulk: A Means of Stabilization or Destabilization?

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Supporting Information

ABSTRACT: ansa-Bis(amidinate) ligands with a rigid ophenylene linker, C_6H_4 -1,2-{NC(tBu)N(2,6-R₂C₆H₃)H}₂ (R = Me (1), *i*Pr (2)), were successfully employed for the synthesis of rare-earth chloro and alkyl species. The reaction of dilithium derivatives of 1 and 2 with LnCl₃ (Ln = Y, Lu) afforded the monomeric bis(amidinate) chloro lanthanide complexes [C_6H_4 -1,2-{NC(tBu)N(2,6-R₂C₆H₃)}₂]Y(THF)(μ -Cl)₂Li(THF)₂ (R = Me (3), *i*Pr (5)) and [C_6H_4 -1,2-{NC(tBu)N(2,6-Me₂C₆H₃)}₂]LuCl(THF)₂ (4). Bis-(amidinate) ligands in complexes 3 and 4 are coordinated to



the metal atoms in a tetradentate fashion, while the bulkier ligand in **5** is tridentate. The alkane elimination reactions of **1** and **2** with equimolar amounts of $(Me_3SiCH_2)_3Ln(THF)_2$ (Ln = Y, Lu) allowed us to obtain the monoalkyl complexes $[C_6H_4-1,2-{NC(tBu)N(2,6-R_2C_6H_3)}_2]Ln(CH_2SiMe_3)(THF)_n$ (Ln = Y, R = Me, n = 1 (6); Ln = Lu, R = Me, n = 1 (7); Ln = Y, R = iPr, n = 2 (8)). The kinetics of thermal decomposition of complexes **6**–**8** were measured, and for **6** the activation energy was obtained from the temperature dependence of the rate constants ($E_a = 67.0 \pm 1.3 \text{ kJ/mol}$). Complexes **6** and 7 turned out to be inert toward H₂ and PhSiH₃. Surprisingly, complex **8** was inert toward H₂ and PhSiH₃ but rapidly cleaved C–O bonds of DME. The reaction resulted in the formation of the methoxy complex { $[C_6H_4-1,2-{NC(tBu)N(2,6-iPr_2C_6H_3)}_2]Y(\mu_2-OMe)]}_2(\mu_2-DME)$ (**9**) and methyl vinyl ether.

INTRODUCTION

The move from metallocene-type to ansa-metallocene-type structures gave a considerable impetus to progress in the organometallic chemistry of rare-earth metals.¹ Considerable opening of the metal coordination sphere and a subsequent increase of accessibility of the metal center lead to the important growth of the catalytic activity of bis-(cyclopentadienyl) alkyl and hydrido species in transformations of unsaturated substrates.² During the past two decades amidinate ligands were successfully employed in organometallic chemistry of rare-earth metals, that allowed for the synthesis and isolation of new series of highly reactive species such as mono- and bis(alkyl), cationic alkyl, and hydrido complexes.³ Alkyl and hydrido lanthanide complexes supported by amidinate ligands proved to be efficient catalysts for olefin polymerization,^{3g,h} isoprene polymerization,⁴ acetylene dimerization,^{3f} olefin hydroboration,⁵ hydrosilylation,⁶ and hydroamination.⁷ The enhanced catalytic activity gained by alkyl and hydrido rare-earth species due to the transposition from a bis(cyclopentadienyl) to a linked bis(cyclopentadienyl) ligation system inspired us to focus on the development⁸ and application⁹ of linked bis(amidinate) ligand systems. Ligand systems containing conformationally rigid linkers seem to be

the most promising ones, able to provide a control over the geometry of the metal center, its coordination and steric saturation, and therefore its stability and reactivity. One of the objectives of this work was to use a bulky bis(amidinate) ligand system as a means of stabilizing monomeric rare-earth hydrido species. Herein we report on the synthesis, structure, and stability of chloro and alkyl yttrium and lutetium species supported by linked bis(amidinate) ligands of different steric bulk containing *o*-phenylene linker.

RESULTS AND DISCUSSION

Bis(amidines) C_6H_4 -1,2-{NC(*t*Bu)N(2,6-R₂C₆H₃)H}₂ (R = Me (1), *i*Pr (2)) (Scheme 1) were prepared according to the general synthetic approach developed by Arnold.¹⁰ The synthesis and characterization of bis(amidines) 2 and C₆H₄-1,2-{NC(*t*Bu)N(2,4,6-Me₃C₆H₃)H}₂ were previously reported by Hill.¹¹ This method was extended to the preparation of 1 without modification. Amidine 1 was isolated as a colorless crystalline solid in 46% yield.

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Scheme 1







Similarly to the bis(amidines) reported by Hill,¹¹ the complexity of the ¹H NMR spectrum of 1 (CDCl₃) identified the various proton environments. Thus, the protons of the CMe₃ and Me fragments are presented by sets of three singlets and two singlets were assigned to the NH protons. This fact obviously indicates the existence of the various stereoisomers of the C=N double bond in solution at room temperature.

Bis(amidines) 1 and 2 can be easily deprotonated by treatment with 2 equiv of *n*BuLi in a THF-hexane mixture at 0 °C. The dilithium derivatives of 1 and 2 obtained after metalation with *n*BuLi were used in situ for reacting with anhydrous LnCl₃ (Ln = Y, Lu) (1/1 molar ratio) in THF at ambient temperature (Scheme 2). Evaporation of THF, extraction of the solid residue with toluene, and subsequent recrystallization of the reaction product from THF-hexane mixtures allowed for the isolation of bis(amidinate) chloro lanthanide complexes 3-5 in 65, 61, and 58% yields, respectively. Complexes 3-5 were obtained as air- and moisture-sensitive pale yellow crystalline solids, readily soluble in THF and toluene and poorly soluble in hexane.

Lutetium derivative 4 is a neutral compound, while yttrium chloro complexes 3 and 5 after an analogous workup were isolated as ate complexes containing $LiCl(THF)_2$ moieties.

Transparent crystals of complexes 3-5 suitable for X-ray diffraction study were obtained by slow condensation of hexane into THF solutions at ambient temperature. Complexes 3-5 crystallize in triclinic $P\overline{1}$ (3) and monoclinic C2/c (4) and $P2_1/n$ (5) space groups. Complex 4 was isolated as a solvate (4·THF). The molecular structures of complexes 3-5 were established by X-ray diffraction studies and are depicted in

Figures 1-3, respectively; the crystal and structure refinement data are given in Table 1 (Supporting Information).



Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of 3 showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)-N(1) = 2.326(3), Y(1)-N(2) = 2.334(4), Y(1)-O(1) = 2.421(2), Y(1)-N(4) = 2.443(4), Y(1)-N(3) = 2.473(4), Y(1)-Cl(2) = 2.606(1), Y(1)-Cl(1) = 2.682(1), N(1)-C(7) = 1.345(6), N(3)-C(7) = 1.335(5), N(2)-C(20) = 1.354(6), N(4)-C(20) = 1.321(5); N(1)-Y(1)-N(3) = 54.8(1), N(2)-Y(1)-N(4) = 54.2(1), Cl(2)-Y(1)-Cl(1) = 84.18(4), N(1)-Y(1)-N(2) = 66.3(1).



Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of 4 showing the atom-numbering scheme. Hydrogen atoms and the carbon atoms of THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)–O(1) = 2.279(2), Lu(1)–N(3) = 2.288(3), Lu(1)–N(2) = 2.316(2), Lu(1)–O(2) = 2.333(2), Lu(1)–N(4) = 2.393(3), Lu(1)–N(1) = 2.397(3), Lu(1)–Cl(1) = 2.5744(8), N(2)–C(7) = 1.337(4), N(1)–C(7) = 1.360(4), N(3)–C(20) = 1.354(4), N(4)–C(20) = 1.343(4); N(3)–Lu(1)–N(4) = 56.04(9), N(1)–Lu(1)–N(2) = 55.78(9), N(1)–Lu(1)–N(3) = 67.54(9).



Figure 3. ORTEP diagram (30% probability thermal ellipsoids) of **5** showing the atom-numbering scheme. Hydrogen atoms, the carbon atoms of the THF molecule, and isopropyl groups of $2,6-iPr_2C_6H_3$ fragments are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)-N(1) = 2.286(2), Y(1)-N(3) = 2.345(2), Y(1)-N(2) = 2.385(2), Y(1)-O(1) = 2.397(2), Y(1)-Cl(1) = 2.6488(6), Y(1)-Cl(2) = 2.6827(6), N(2)-C(7) = 1.325(3), N(1)-C(7) = 1.359(3), N(4)-C(20) = 1.291(3), N(3)-C(20) = 1.386(3); N(1)-Y(1)-N(2) = 55.89(6), N(1)-Y(1)-N(3) = 69.46(6).

The steric demand of the ligand system turned out to be crucial for the structures of the chloro complexes. Thus, the less sterically demanding 1 coordinates to yttrium in 3 as a tetradentate ligand, while the bulkier ligand 2 binds to yttrium in 5 in a rather unusual tridentate fashion. Similarly to 3 in

complex 4 the bis(amidinate) ligand system chelates the lutetium ion in a tetradentate way. In lutetium complex 4 the chloro ligand is terminal, but in the case of yttrium, being a larger ion¹² ($R_{Y(VI)} = 0.900$ Å, $R_{Lu(VI)} = 0.861$ Å), complexes 3 and 5 contain two μ_2 -chloro ligands bridging yttrium and lithium ions. The metal ions in complexes 3 and 4 have a formal coordination number of 7, and in 5 the yttrium atom is six-coordinated. The coordination environments of the metal atoms in 3 and 4 adopt geometries of distorted pentagonal bipyramids. In complex 4 four nitrogen atoms, the metal atom, and the chloro ligand are disposed in the equatorial plane (the maximum deviation of atoms from the plane is 0.06(2) Å). Two oxygen atoms of THF molecules occupy the apical positions. In 3 the equatorial plane is occupied by four nitrogen atoms, the metal atom, and the chloro ligand (the maximum deviation atoms from the plane is 0.09(2) Å), while the apical positions are occupied by one THF and one chloro ligand. The dihedral angles between the two NMN planes in complexes 3 and 4 have values of 172.5 and 176.3°, respectively. The MNCN fragments in complexes 3 and 4 are close to being planar, the dihedral angles between the planes MNM and NCN being 171.4 and 161.6° in 3 and 172.9 and 164.1° in 4. The average Y-N bond length in 3 (2.394(4) Å) is somewhat longer compared to the related values reported for the sevencoordinated yttrium complexes coordinated by linked bis-(amidinate) ligands ($[C_3H_6{NC(Ph)NSiMe_3}_2]YCl(DME)$, 2.369(3) \dot{A}_{j}^{13} [$C_{10}H_{6}$ {NC(*t*Bu)N-2,6-Me₂C₆H₃}/2YCl(DME), 2.350(1) Å^{8a}). The Y-Cl bond length in 3 is comparable to that in $[C_3H_6{NC(Ph)NSiMe_3}_2]YCl(DME)$.¹³ Unfortunately, no examples of seven-coordinated lutetium complexes with NN ligands could be found for comparison. The average Lu-N bond distance in 4 (2.348(3) Å) is similar to that in 3 if the difference in ionic radii of Y and Lu is taken into consideration.¹² The lengths of amidinate N-C bonds in complexes 3 and 4 have similar values, indicating the negative charge delocalization within the NCN fragments.

Unlike the case in complexes 3 and 4, the dianionic bis(amidinate) ligand system in complex 5 is tridentate. One of the amidinate fragments chelates the yttrium ion, while in the second fragment just one nitrogen participates in the metalligand bonding. The second nitrogen is drifted out from the yttrium coordination sphere. The yttrium and three nitrogen atoms are disposed in one plane, and the maximum deviation of atoms from the plane Y(1)N(1)N(2)N(3) is 0.06(2) Å. Similarly to the case for 3 and 4 the YNCN fragment is nearly planar. The value of the dihedral angle between the planes YNN and NCN is 171.37°. The average Y–N bond length in 5 (2.3384(19) Å) falls into the region of distances normally observed for six-coordinated yttrium bis(amidinate) and bis(guanidinate) complexes¹⁴ and is slightly shorter than the related value in 3 (2.394 Å). The C-N bonds within the N(1)-C(13)-N(2) amidinate fragment have close lengths, while in the second NCN group they differ noticeably (N(3)-C(20) = 1.386(3), N(4)-C(20) = 1.291(3) Å). The length of the C(20)-N(4) bond (1.291(3) Å) is close to that of a double C=N bond,¹⁵ and the N(3)–C(20) bond length (1.386(3) Å)corresponds to a single C-N bond.¹⁵ This indicates that the negative charge is localized on the amido N(3) atom and the N(3)-C(24)-N(4) group can be characterized as amidoimino. Unlike the case for 3 and 4, in complex 5 the yttrium atom is formally six-coordinated; however, the presence of short Y(1)-C(22) and Y(1)-H(22A) contacts (2.969(2) and

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2.48(2) Å, respectively) are indicative of an agostic Y(1)…H-(22A) interaction.¹⁶

An alkane elimination reaction was used for the synthesis of alkyl yttrium and lutetium species supported by the linked bis(amidinate) ligands. The NMR-tube-scale reactions of the tris(alkyl) derivatives $Ln(CH_2SiMe_3)_3(THF)_2^{17}$ (Ln = Y, Lu) with amidines 1 and 2 carried out in C_6D_6 under ¹H NMR control showed clear formation of the alkyl complexes $[C_6H_4-1,2-{NC(tBu)N(2,6-R_2C_6H_3)}_2]Ln(CH_2SiMe_3)(THF)_n$ (R = Me, Ln = Y, *n* = 1 (6); R = Me, Ln = Lu, *n* = 1 (7); R = *i*Pr, Ln = Y, *n* = 2 (8)) in quantitative yields and liberation of 2 equiv of SiMe₄ (Schemes 3 and 4). The NMR-tube-scale salt metathesis

Scheme 4



reactions of bis(amidinate) chloro complexes 3-5 with equimolar amounts of LiCH₂SiMe₃ (C₆D₆, 20 °C) indicated the formation of complexes **6–8**.

The preparative-scale synthesis of complexes 6-8 via alkane elimination reactions were carried out in *n*-hexane at 0 °C. Prolonged cooling of the reaction mixtures at -20 °C afforded these complexes in 65, 54, and 50% yields, respectively. Such a decrease of isolated yields of complexes 6-8 compared to those in the NMR-tube-scale experiments is apparently caused by high solubility of these compounds in aliphatic and aromatic hydrocarbons. The colorless (7) or pale yellow (6, 8) crystalline compounds are moisture- and air-sensitive. The complexes are fairly soluble in commonly used organic solvents (THF, toluene, hexane).

The ¹H NMR spectra of **6** and 7 present single sets of signals due to the amidinate ligand, alkyl fragment, and coordinated THF molecules, indicating the presence of an apparent mirror plane within the molecule. The methylene protons of alkyl fragment attached to the metal atoms appear as a sharp doublet

 $({}^{2}J_{\rm YH} = 3.2 \text{ Hz})$ at -0.57 ppm for yttrium complex **6** or as a singlet at -0.74 ppm for lutetium complex 7. The methylene carbon of alkyl group gives rise to a doublet at $33.7 ({}^{1}J_{\rm YC} = 44.0 \text{ Hz})$ in the ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR spectrum of **6**, while in the spectrum of 7 it appears as a singlet at 38.3 ppm. Unlike the case for complexes **6** and 7, in the ${}^{1}\text{H}$ NMR spectrum of **8** the bis(amidinate) ligand gives rise to a complex set of signals, thus reflecting the nonequivalence of the amidinate fragments. The presence of an alkyl group in **8** is proved by a doublet at $-0.45 \text{ ppm} ({}^{2}J_{\rm Y-H} = 3.4 \text{ Hz})$, corresponding to the YCH₂ protons, and a singlet at 0.20 ppm due to SiMe₃ protons. In the ${}^{13}\text{C}$ NMR spectrum of **8** the corresponding carbon atom gives rise to a doublet at 34.5 ppm (${}^{1}J_{\rm Y-C} = 23.7 \text{ Hz}$).

Under an inert atmosphere, complexes 6-8 can be stored in the crystalline state at 0 °C without decomposition for several months. The thermal stability of alkyl complexes 6-8 was evaluated. The lutetium complex 7 proved to be the most stable; at 20 °C its half-life is 830 h. Visible thermal decomposition of 7 started at 60 °C with a half-life of 8 h. Complex 6 also turned out to be rather stable, with a half-life (20 °C) of 290 h, while complex 8 coordinated by a bulkier bis(amidinate) ligand showed somewhat lower stability. It slowly decomposes at ambient temperature (20 °C) in C₆D₆ solution with a half-life of 210 h. Taking into account the data of stability studies, one can conclude that the ansa-bis-(amidinate) ligand system is a suitable coordination environment which allows for the synthesis of rare-earth alkyl complexes possessing enhanced thermal stability. The comparison of stabilities of yttrium complexes 6 and 8 demonstrates that the steric demand of the ligand system should be optimized and in some cases the greater bulkiness of the supporting ligand does not result in higher stability because another coordination mode occurs due to steric overload of the metal coordination sphere.

The decomposition of complexes **6**–**8** is accompanied by the release of an equimolar amount of SiMe₄; nevertheless, the organometallic product could not be identified. ¹H and ¹³C investigations of the decomposition product unambiguously proved that no C–H bond activation of the Me groups of the bis(amidinate) ligand took place. The thermal decomposition of complex **6** was run at four different temperatures under the control of NMR spectroscopy (Figure 4). The reaction was found to follow first-order kinetics, indicative of an intramolecular process (Figure 5). The activation energy $E_a = 67.0 \pm 1.3$ kJ/mol was obtained from the Eyring plot (Figure 6).

In contrast to the settled opinion about the low thermal stability of rare-earth alkyl complexes,¹⁸ a series of new supporting ligand systems which allow for the synthesis of surprisingly stable hydrocarbyl derivatives was reported over the past two decades.¹⁹ Unfortunately, studies on the quantitative evaluation of thermal stability of rare-earth alkyl



Figure 4. Plot of concentration (C/C_0) of complex 6 versus time (min) at different temperatures in C_7D_8 .



Figure 5. First-order plot for the thermal decomposition of 6 at different temperatures in $\mathrm{C_7D_8}.$



Figure 6. Eyring plot for the thermal decomposition of 6 in C_7D_8 .

species still remain scarce. Berg has reported that the value of the activation energy of thermal decomposition of the yttrium complex Y[DAC][CH₂SiMe₃] (DAC = deprotonated 4,13-diaza-18-crown-6) was found from the Arrhenius plot to be 79 kJ mol^{-1,20a} An alkyl yttrium complex coordinated by a cyclopentadienylamido ligand demonstrated high activation parameters of thermal decomposition: $\Delta H^{\ddagger} = 145 \pm 16$ kJ mol⁻¹ and $\Delta S^{\ddagger} = 110 \pm 50$ J K⁻¹ mol^{-1,20b}

Transparent crystals of complexes 6 and 7 suitable for X-ray diffraction studies were obtained by cooling the concentrated hexane solutions to -20 °C. Unfortunately, all our attempts to

prepare crystals of 8 which would allow for X-ray characterization failed. The molecular structure of complex 6 is shown in Figure 7. For the structure of complex 7 see Figure 19S



Figure 7. ORTEP diagram (30% probability thermal ellipsoids) of **6** showing the atom-numbering scheme. Hydrogen atoms and carbon atoms of the THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)-C(33) = 2.387(2), Y(1)-N(1) = 2.321(2), Y(1)-N(3) = 2.349(2), Y(1)-N(4) = 2.369(1), Y(1)-O(1) = 2.393(1), Y(1)-N(2) = 2.405(2); N(1)-Y(1)-N(2) = 55.00(5), N(3)-Y(1)-N(4) = 55.84(5).

(Supporting Information). The structures refinement data are given in Table 1 (Supporting Information). Complexes 6 and 7 crystallize in the monoclinic space group $P2_1/n$ (6) and triclinic $P\overline{1}$ (7) with four molecules in the unit cells. Complex 7 contains two crystallographically independent molecules in the asymmetric unit which have close geometric parameters. X-ray diffraction studies have revealed that complexes 6 and 7 have similar structures. The metal atom is coordinated by four nitrogen atoms of two chelating amidinate fragments, one oxygen atom of the coordinated THF molecule, and one carbon of the alkyl group, thus resulting in a coordination number of 6. Unlike the case for chloro complexes 3 and 4, in alkyl derivatives 6 and 7 the metal atoms noticeably project from the equatorial planes set up by the nitrogen atoms (deviations of the metal atom from N_4 plane are 0.93 Å in 6 and 1.02 Å in 7). The mutual orientation of the amidinate fragments in alkyl complexes is different of that in chloro species 3-5. The values of dihedral angles between two NMN planes in 6 (131.0°) and 7 (122.9°) are much smaller in comparison to those in the related seven-coordinated chloro complexes 3 (173.5°) and 4 (176.3°). The MNCN fragments in complexes 6 and 7 are bent; the dihedral angles between the MNM and NCN planes are 149.9 and 178.9 in 6 and 157.7 and 166.2° in 7. It should be noted that the amidinate fragments in complexes 6 and 7 are located in cis positions with respect to the C(1)-C(6) ring of the linker. The alkyl groups occupy apical positions. The Y–C (2.387(2) Å) and Lu–C bond lengths (2.342(6) Å) in 6 and 7 fall into the intervals of distances typical for six-coordinated alkyl complexes of Y²¹ and Lu.²²

The reaction of complexes 6 and 7 with an equimolar amount of DME was carried out in C_6D_6 at ambient temperature under ¹H NMR control. It results in rapid

replacement of THF molecules in the metal coordination spheres by DME ligands. The DME adducts which form in the reactions proved to be highly stable under these conditions, since no changes in the ¹H NMR spectra of the reaction mixtures were detected over 5 days. Surprisingly, in contrast to the case for 6 and 7, complex 8 turned out to be highly reactive and able to cleave C-O bonds of DME. Dissolution of 8 in DME (20 °C) and subsequent crystallization of the reaction product from benzene at 8 °C afforded, instead of the expected DME adduct of alkyl complex 8, the dimeric bis(amidinate) yttrium methoxide $[o-C_6H_4\{NC(tBu)N(2,6-iPr_2C_6H_3)_2\}Y(\mu_2-$ OMe)]₂(μ_2 -DME) (9) (Scheme 4). The ¹H NMR spectrum of the reaction mixture indicated that the second product of C-O bond cleavage of DME is methyl vinyl ether, which gives a characteristic set of resonances. Moreover, the GC-MS analysis of the volatile reaction products confirmed the presence of methyl vinyl ether (molecular ion m/z 58). Complex 9 was isolated as colorless crystals in 40% yield and was authenticated by NMR spectroscopy, an X-ray study, and microanalysis. The ¹H NMR spectrum of **9** displays a singlet at 1.96 ppm related to the μ_2 -methoxy group, while in the ¹³C NMR the carbon atom of the OMe group gives a resonance at 52.1 ppm.

Transparent crystals of 9 suitable for an X-ray diffraction study were obtained by slow concentration of the benzene solution at 10 °C. Complex 9 crystallizes as a solvate $(9.6C_6D_6)$ in the monoclinic C2/*c* space group. An X-ray diffraction study of 9 revealed that the complex adopts a dimeric structure (Figure 8) with two μ_2 -methoxide groups bridging two [*o*-C₆H₄{NC(*t*Bu)N(2,6-*i*Pr₂C₆H₃)}₂Y] moieties. The dimer formation is also supported by "spanning" coordination of a DME molecule to two yttrium atoms. The bis(amidinate) ligand in 9 is tridentate, and its coordination fashion is similar to that observed in the related chloro complex 5. Apparently such a coordination mode is characteristic for bulky bis-



Figure 8. ORTEP diagram (30% probability thermal ellipsoids) of 9 showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)-O(1) = 2.263(2), Y(1)-O(2) = 2.268(2), Y(1)-N(2) = 2.274(3), Y(1)-N(3) = 2.366(2), Y(1)-O(3) = 2.413(2), Y(1)-N(1) = 2.466(3), Y(1)-Y(2) = 3.6160(5), Y(2)-O(1) = 2.218(2), Y(2)-O(2) = 2.270(2), Y(2)-N(6) = 2.277(3), Y(2)-N(7) = 2.320(3), Y(2)-N(5) = 2.463(2), Y(2)-O(4) = 2.504(2), N(1)-C(7) = 1.331(4), N(2)-C(7) = 1.348(4), N(5)-C(47) = 1.330(4), N(6)-C(47) = 1.329(4), N(3)-C(20) = 1.376(4), N(4)-C(20) = 1.310(4), N(7)-C(60) = 1.379(4), N(8)-C(60) = 1.296(4); O(1)-Y(1)-O(2) = 72.32(8), O(1)-Y(2)-O(2) = 73.12(8), N(2)-Y(1)-N(1) = 55.24(9), N(6)-Y(2)-N(5) = 55.07(9).

(amidinate) ligand 2 in yttrium complexes. The coordination number of yttrium atoms in 9 is 6.

Analysis of the bonding situation within the NCN fragments in **9** indicates that negative charge delocalization takes place in the chelating amidinate groups while the monodentate groups should be classified as amido-imino ligands. The average value of the Y–N bond distance in **9** (2.361(3) Å) is similar to that in **5**. The Y–O bond lengths in **9** (2.270(2), 2.218(2), 2.26392), 2.268(2) Å) have values typical for bridging Y–O bonds in sixcoordinated yttrium alkoxy complexes.²³ Apparently in complex **9**, similarly to **5**, an agostic interaction between Y and the *t*Bu group takes place. The Y–C, Y–H, and Y–Cent_{C–H} distances are 2.929(2)–2.966(2), 2.43(2)–2.59(2), and 2.64–2.72 Å, respectively; the Y–H–C angle falls into the range of values 100.4–111.7°.

With the aim to prepare monomeric yttrium and lutetium hydrido complexes supported by linked bis(amidinate) ligands, we carried out the reactions of **6** and 7 and of **8** with H₂ and PhSiH₃ in hexane at 20 and 40 °C, respectively. However, the starting alkyl complexes were recovered from the reactions of **6** and 7 with H₂ at 20 °C (**6**, 24 h; 7, 120 h) and PhSiH₃ (1/1 molar ratio, 2 h, 40 °C) in high yields (>60%), and no evidence for the formation of hydrido complexes was found. When the reaction time of 7 with H₂ was increased up to 60 days (20 °C), decomposition products which do not contain either alkyl or hydrido groups were obtained. Unfortunately, attempts to characterize the reaction products failed. Surprisingly, complex **8**, which was able to cleave C–O bonds in DME, proved to be inert toward H₂ and PhSiH₃. Complexes 7 and **8** were inert in ethylene, propylene, isoprene, and styrene polymerizations.

CONCLUSION

Two bulky ansa-bis(amidinate) ligand systems containing a rigid o-phenylene linker were successfully employed for the synthesis of a series of chloro and alkyl rare-earth complexes. The ligand bearing 2,6-dimethylphenyl substituents on amidinate nitrogens turned out to be suitable for tetradentate coordination to yttrium and lutetium ions, while the excessive steric demand of the bulkier 2,6-diisopropylphenyl-substituted analogue allowed only for tridentate coordination. Alkyl derivatives supported by amidinate 1 demonstrated remarkable thermal stability for rare-earth complexes. Thus, for lutetium complex 7 a noticeable thermal decomposition starts only at temperatures above 60 °C. Its half-life at 60 °C was found to be 8 h, while at 20 °C the half-life was 830 h. The half-life of the yttrium congener at 20 °C was predictably shorter and is equal to 290 h. The activation energy of thermal decomposition of 6 was estimated ($E_{a} = 67.0 \pm 1.3 \text{ kJ/mol}$). An alkyl yttrium complex coordinated by the bulkier ligand 2 in a tridentate fashion proved to be less stable (half-life at 20 °C of 210 h). Along with their thermal stability, complexes 6-8 demonstrated considerable chemical inertness. All attempts to prepare rare-earth hydrido species by reacting alkyl complexes 6-8 with either H₂ or PhSiH₃, even at elevated temperatures, failed. Despite its inertness toward H₂ and PhSiH₃, complex 8 was able to cleave C-O bonds of DME at ambient temperature. The second product of this reaction was found to be vinyl methyl ether. A comparison of stabilities of yttrium complexes 6 and 8 demonstrates that a greater size of the supporting ligand does not guarantee higher stability.

EXPERIMENTAL SECTION

All experiments were performed in evacuated tubes by using standard Schlenk techniques, with rigorous exclusion of traces of moisture and air. After being dried over KOH, THF was purified by distillation from sodium/benzophenone ketyl; hexane, diethyl ether, and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. C₆D₆ was dried with sodium and condensed in vacuo into NMR tubes prior to use. CDCl3 was used without additional purificational. 2,6-Diisopropylaniline, 2,6-dimethylaniline, and ophenylenediamine were purchased from Acros. Anhydrous YCl₃, $LuCl_3$,²⁴ Me₃SiCH₂Li,²⁵ (Me₃SiCH₂)₃Ln(THF)₂ (Ln = Y, Lu),¹⁷ C₆H₄-1,2-(NC(Cl)*t*Bu)₂, and 2¹¹ were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purifications. NMR spectra were recorded with Bruker Avance DRX-400 and Bruker DRX-200 spectrometers in CDCl₃, C_6D_{61} or C_5D_5N at 20 °C, unless otherwise stated. Chemical shifts for ¹H and ¹³C NMR spectra were referenced internally to the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls with a "Bruker-Vertex 70" instrument. A "Polaris Q GC/MS" spectrometer was used for GS/MS analysis; lanthanide metal analyses were carried out by complexometric titration. The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of C_6H_4 -1,2-{NC(*t*Bu)NH(2,6-Me_2C_6H_3))₂ (1). 2,6-Dimethylaniline (3.87 g, 31.91 mmol) was added to a solution of $C_6H_4-1,2-\{NC(tBu)NH(2,6-Me_2C_6H_3)\}_2$ (4.99 g, 15.91 mmol) and Et₃N (4.4 mL, 31.95 mmol) in toluene (50 mL). The reaction mixture was stirred at 80 °C for 3 days, and the volatiles were removed under vacuum. The resulting off-white solid was dissolved in diethyl ether (100 mL) and was washed with a water solution of Na_2CO_3 (1%, 3 × 100 mL). The ether layer was separated and dried over MgSO₄. After recrystallization from Et₂O 1 was isolated as colorless crystals in 46% yield (3.58 g). Mp: 153-156 °C. MS (EI): m/z 482.3 [M⁺]. Anal. Calcd for C₃₂H₄₂N₄ (482.7): C, 79.62; H, 8.77; N, 11.61. Found: C, 79.28; H, 8.84; N, 11.80. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.25 (s, 7H, C(CH₃)₃), 1.36 (s, 4H, C(CH₃)₃), 1.50 (s, 7H, C(CH₃)₃), 2.04 $(s, 3H, C_6H_3(CH_3)_2)$, 2.13 $(s, 5H, C_6H_3(CH_3)_2)$, 2.15 $(s, 4H, C_6H_3(CH_3)_2)$ $C_6H_3(CH_3)_2$), 5.86 (s, 1H, NH), 6.15 (s, 2H, C_6H_4), 6.39 (t, ${}^{3}J_{HH} =$ 7.27 Hz, 1H, C_6H_4), 6.60–6.82 (m, 4H, $C_6H_3(CH_3)_2$), 6.90 (d, ${}^3J_{H,H}$ = 7.53 Hz, 2H, $C_6H_3(CH_3)_2$), 7.36 (s, 1H, NH), 7.8 (d, ${}^3J_{H,H}$ = 6.95 Hz, 1H, C₆H₄). ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ 18.4, 18.5, 18.9 (C₆H₃(CH₃)₂), 29.2, 29.3, 29.5 (C(CH₃)₃), 39.3, 39.6, 40.7 (C(CH₃)₃), 118.4, 118.8, 119.5, 121.2 (C₆H₄), 119.9, 121.5 124.4, 126.1, 127.5, 128.0 (C₆H₃(CH₃)₂), 131.9, 133.6, 136.5, 147.0, 148.2 (ArC), 154.3, 158.6, 159.7 (NCN). IR (Nujol, KBr; $\overline{\nu}$ (cm⁻¹)): 3392 (m NH), 1643 (s, C=N), 1589 (m), 1261 (w), 1222 (w), 1130 (w), 1087 (w), 1028 (w), 939 (w), 765 (s), 740 (s).

Synthesis of $[C_6H_4-1,2-{NC(tBu)N(2,6-Me_2C_6H_3)}_2]Y(THF)(\mu Cl)_2Li(THF)_2$ (3). To a solution of 1 (0.59 g, 1.22 mmol) in Et₂O (30 mL) was added a solution of nBuLi (1.18 M, 2.1 mL, 2.45 mmol) in hexane at 0 °C, and the reaction mixture was stirred for 1 h. The solvent was removed under vacuum, the resulting solid residue was dissolved in 15 mL of THF, and this solution was added to a suspension of YCl_3 (0.24 g, 1.22 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 12 h and filtered, and the solvent was removed under vacuum. The remaining solid was extracted into toluene (50 mL). After filtration of the toluene extracts the solvent was removed in vacuo at room temperature and the remaining solid was dissolved in THF (10 mL). Slow condensation of hexane into a THF solution afforded light yellow crystals of 3 in 65% yield (0.68 g). Anal. Calcd for C44H64Cl2LiN4O3Y (863.74): C, 61.18; H, 7.47; N, 6.49; Y, 10.29. Found: C, 60.81; H, 7.08; N, 6.18; Y, 10.47. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 1.19 (br s, 18H, C(CH₃)₂), 1.31 (br s, 12H, β -THF), 2.33, 2.50 (br s, each 6H, C₆H₃(CH₃)₂), 3.53 (br s, 12H, α-THF), 6.66–6.87 (m, 2H, ArH), 6.78–6.88 (m, 3H, ArH), 6.86–7.01 (m, 5H, ArH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ 20.5 $(C_6H_3(CH_3)_2)$, 25.2 $(\beta$ -THF), 29.1 $(C(CH_3)_2)$, 41.7 $(C(CH_3)_2)$, 68.4 (α-THF), 120.1, 121.9, 125.3, 137.5, 143.8, 148.8 (ArC), 177.3

(NCN). ⁷Li NMR (155 MHz, C_6D_{62} , 25 °C): δ 0.23. IR (Nujol, KBr; $\overline{\nu}$ (cm⁻¹)): 1647 (s), 1584 (s), 1278 (s), 1254 (w), 1209 (m), 1097 (m), 1043 (s), 1028 (s), 958 (s), 916 (m), 892 (m), 762 (s).

Synthesis of [C₆H₄-1,2-{NC(tBu)N(2,6-Me₂C₆H₃)}₂]LuCl(THF)₂ (4). A synthetic procedure similar to that for 3 was used, with 1 (1.24 g, 2.56 mmol) in Et₂O (30 mL), nBuLi (5.13 mmol, 4.35 mL, 1.18 M in hexane), and LuCl₃ (0.72 g, 2.56 mmol) in THF (5 mL). Pale yellow crystals of 4 were isolated in 61% yield (1.36 g). Anal. Calcd for C₄₂H₆₀ClLuN₄O₂₅ (871.36): C, 57.89; H, 6.94; N, 6.43; Lu, 20.08. Found: C, 57.55; H, 6.69; N, 6.20; Lu, 20.26. ¹H NMR (400 MHz, C_6D_{6} , 25 °C): δ 0.87 (s, 3H, C(CH_3)_3), 1.08 (s, 5H, C(CH_3)_3), 1.26 (br s, together 18H, C(CH₃)₃, β -THF), 1.90 (s, 2H, C₆H₃(CH₃)₂), 2.14 (s, 3H, C₆H₃(CH₃)₂), 2.37 (s, 5H, C₆H₃(CH₃)₂), 2.50 (s, 2H, $C_6H_3(CH_3)_2$, 3.58 (br s, 8H, α -THF), 6.67–6,70 (m, 1H, ArH), 6.73-6.77 (m, 2H, ArH), 6.87-6.90 (m, 2H, ArH), 6.95 (m, 1H, ArH), 7.00 (s, 2H, ArH), 7.02 (s, 1 H, ArH), 7.31 (br s, 1H, ArH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ 19.7, 20.0, 20.4, 20.6 $(C_6H_3(CH_3)_2)$, 25.2 (β -THF), 28.6, 29.0, 29.2 ($C(CH_3)_3$), 41.1, 42.2, 43.3 (C(CH₃)₃), 69.2 (α-THF), 119.3, 121.3, 122.0, 122.2, 122.5, 122.9, 127.6, 127.8 128.2, 128.9, 130.9, 131.7, 142.3, 145.8, 147.8, 148.4, (ArC), 174.6, 177.7, 180.7 (NCN). IR (Nujol, KBr; $\overline{\nu}$ (cm⁻¹)): 1656 (w), 1590 (w), 1568 (w), 1272 (m), 1203 (s), 1164 (s), 1094 (s), 1016 (s), 955 (s), 925 (m), 895 (w), 859 (s), 768 (s), 744 (s).

Synthesis of $[C_6H_4-1,2-\{NC(tBu)N(2,6-iPr_2C_6H_3)\}_2]Y(THF)(\mu Cl)_2Li(THF)_2$ (5). A synthetic procedure similar to that for 3 was used, with 2 (0.51 g, 0.87 mmol in 30 mL Et₂O), nBuLi (1.74 mmol, 1.47 mL, 1.18 M in hexane), and YCl₃ (0.17 g, 0.87 mmol) in 40 mL of THF. A 0.49 g amount of pale yellow crystals of 5 was isolated (yield 58%). Anal. Calcd for $C_{52}H_{80}Cl_2LiN_4O_3Y$ (975.97): C, 63.99; H, 8.26; N, 5.74; Y, 9.11. Found: C, 63.67; H, 8.08; N, 5.34; Y, 9.35. ¹H NMR (400 MHz, $C_6 D_{67}$ 25 °C): δ 0.95 (d, ³ $J_{H,H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 1.01 (d, ${}^{3}J_{H,H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.16 (d, ${}^{3}J_{H,H}$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.2 (d, ${}^{3}J_{H,H}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, ${}^{3}J_{H,H} = 2.2$ Hz, 6H, CH(CH₃)₂), 1.27 (s, 8H, C(CH₃)₃), 1.29 (s, 4H, C(CH₃)₃), 1.34 (d, ${}^{3}J_{H,H} = 7.0$ Hz, 4H, CH(CH₃)₂), 1.36 (s, 6H, $C(CH_3)_3$, 1.40 (br s, 12H, β -THF), 3.06, 3.22 (sept, ${}^{3}J_{H,H} = 6.9$ Hz, each 2H, CH(CH₃)₂), 3.57 (br s, 12H, α-THF), 6.14, 6.26 (br s, each 1H, ArH), 6.57 (dd, ${}^{3}J_{H,H} = 6.0$ Hz, ${}^{3}J_{H,H} = 3.5$ Hz, 1H, ArH), 6.66 (t, ${}^{3}J_{H,H} = 7.6$ Hz, 1H, ArH), 6.78–6.83 (m, 2H, ArH), 6.90–6.97 (m, 1H, ArH), 6.99 (s, 1H, ArH), 7.01 (s, 1H, ArH), 7.10 (s, 1H, ArH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ 21.2, 21.9, 22.3, 22.7, 23.1, 24.1 (CH(CH₃)₂), 25.4 (β-THF), 28.4, 28.5 (CH(CH₃)₂), 29.0, 29.3, 29.5 (C(CH₃)₂), 39.2, 39.7, 41.3 (C(CH₃)₂), 67.6 (α-THF), 119.5, 119.9, 121.1, 122.3, 122.5, 122.6, 122.7, 128.9, 132.7, 134.6, 135.6, 136.3, 137.5 (ArC), 144.2, 145.4, 152.9 (NCN). ⁷Li NMR (155 MHz, C_6D_{67} 25 °C): δ 0.32. IR (Nujol, KBr; $\overline{\nu}$ (cm⁻¹)): 1593 (m), 1554 (s), 1314 (s), 1277 (s), 1250 (s), 1223 (s), 1201 (s), 1172 (s), 1150 (s), 1138 (s), 1102 (m), 1040 (s), 1014 (s), 962 (m), 931 (m), 914 (m), 887 (m), 868 (m), 806 (m), 767 (m), 740 (s), 712 (m), 690 (m).

Synthesis of $[C_6H_4-1,2-{NC(tBu)N(2,6-Me_2C_6H_3)}_2]Y (CH_2SiMe_3)(THF)$ (6). To a suspension of 1 (0.80 g, 1.65 mmol) in hexane (40 mL) was added a solution of (Me₃SiCH₂)₃Y(THF)₂ (0.82 g, 1.65 mmol) in hexane (30 mL) at 0 °C, and the reaction mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and was stirred for an additional 30 min. The solution was concentrated and cooled to -20 °C. Complex 6 was isolated as a pale yellow crystalline solid in 65% yield (0.78 g). Anal. Calcd for C₄₀H₅₉N₄OSiY (728.91): C, 65.91; H, 8.16; N, 7.69; Y, 12.20. Found: C, 65.56; H, 8.00; N, 7.22; Y, 12.48. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ -0.57 (d, ${}^{2}J_{Y,H}$ = 3.2 Hz, 2H, CH₂SiMe₃), 0.23 (s, 9H, CH_2SiMe_3), 0.83 (m, 4H, β -THF) 1.16 (s, 18H, $C(CH_3)_3$), 2.15, 2.46 (s, each 6H, $C_6H_3(CH_3)_2$), 3.02 (br s, 4H, α -THF), 6.83 (t, ${}^{3}J_{H,H} = 7.4$ Hz, 3H, $C_6H_3(CH_3)_2$), 6.89–6.95 (m, 3H, $C_6H_3(CH_3)_2$), 6.96 (dd, ${}^{3}J_{H,H} = 5.9 \text{ Hz}, {}^{3}J_{H,H} = 3.5 \text{ Hz}, 2H, C_{6}H_{4}), 7.39 \text{ (dd, }{}^{3}J_{H,H} = 5.9 \text{ Hz},$ ${}^{3}J_{\rm H,H}$ = 3.5 Hz, 2H, C₆H₄). ${}^{13}C{}^{1}H$ NMR (100 MHz, C₆D₆, 25 °C): δ 3.9 (CH₂SiMe₃), 20.4 (C₆H₃(CH₃)₂), 25.0 (β -THF), 29.4 (C(CH₃)₂), 33.7 (d, ${}^{1}J_{C,Y}$ = 44.0 Hz, CH₂SiMe₃), 42.0 (d, $J_{C,Y}$ = 2.6 Hz, C(CH₃)₂), 69.2 (α -THF), 121.4, 123.9 (C_6H_4), 122.4, 127.9, 128.1 $(C_6H_3(CH_3)_2)$, 130.4, 132.5, 143.5, 149.3 (ArC), 176.3 (d, $J_{CY} = 2.2$ Hz, NCN). IR (Nujol, KBr; $\overline{\nu}$ (cm⁻¹)): 1653 (s), 1579 (s), 1506 (w), 1274 (m), 1246 (m), 1232 (m), 1209 (m), 1168 (m), 1151 (w), 1091 (s), 1037 (m), 1014 (m).

Synthesis of [C₆H₄-1,2-{NC(tBu)N(2,6-Me₂C₆H₃)}₂]Lu-(CH₂SiMe₃)(THF) (7). To a suspension of 1 (0.39 g, 0.80 mmol) in 30 mL of hexane was added a solution of (Me₃SiCH₂)₃Lu(THF)₂ (0.46 g, 0.80 mmol) in hexane (30 mL) at 0 °C, and the reaction mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and was stirred for an additional 30 min. The reaction mixture was concentrated under vacuum. Slow cooling of this solution to -20 °C afforded colorless crystals of 6 (0.35 g, 54%). Anal. Calcd for C40H59LuN4OSi (814.98): C, 58.95; H, 7.30; N, 6.87; Lu, 21.47. Found: C, 58.64; H, 7.05; N, 6.39; Lu, 21.63. ¹H NMR (400 MHz, $C_6 D_{61}$ 25 °C): $\delta = -0.74$ (s, 2H, CH₂SiMe₃), 0.23 (s, 9H, CH₂SiMe₃), 0.84 (br s, 4H, β -THF), 1.15 (s, 18H, C(CH₃)₃), 2.18, 2.46 (s, each 6H, $C_6H_3(CH_3)_2$), 3.00 (br s, 4H, α -THF), 6.82 (t, ${}^3J_{H,H}$ = 7.4 Hz, 3H, $C_6H_3(CH_3)_2$), 6.89–6.95 (m, 3H, $C_6H_3(CH_3)_2$), 6.97 (dd, ${}^3J_{H,H} = 5.9$ Hz, ${}^{3}J_{H,H} = 3.5$ Hz, 2H, C₆H₄), 7.39 (dd, ${}^{3}J_{H,H} = 5.9$ Hz, ${}^{3}J_{H,H} = 3.5$ Hz, 2H, C_6H_4). ¹³C{¹H} NMR (100 MHz, C_6D_6 , 25 °C): δ 3.7 (CH₂SiMe₃), 20.0, 20.1 (C₆H₃(CH₃)₂), 24.2 (β-THF), 29.0 (C-(CH₃)₂), 38.3 (CH₂SiMe₃), 41.9 (C(CH₃)₃), 69.1 (α-THF), 121.0, 123.7 (C₆H₄), 122.3, 127.4, 127.8, 128.1 (C₆H₃(CH₃)₂), 130.5, 132.5, 142.8, 148.8 (ArC), 176.2 (NCN). IR (Nujol, KBr; $\overline{\nu}$ (cm⁻¹)): 1642 (s), 1581 (s), 1514 (s), 1247 (m), 1234 (m), 1211 (m), 1177 (m), 1093 (s), 1039 (m), 1010 (m).

 $[C_6H_4-1,2-{NC(tBu)N(2,6-iPr_2C_6H_3)}_2]Y(CH_2SiMe_3)(THF)_2$ (8). A synthetic procedure similar to that for 6 and 7 was used, with 2 (0.63) g, 1.00 mmol) in hexane (30 mL) and (Me₃SiCH₂)₃Y(THF)₂ (0.53 g, 1.06 mmol) in hexane (30 mL). Complex 8 was isolated as a colorless microcrystalline solid in 50% yield (0.42 g). Anal. Calcd for C48H75N4OSiY (841.13): C, 68.54; H, 8.99; N, 6.66; Y, 10.57. Found: C, 68.26; H, 9.27; N, 6.78; Y, 10.73. ¹H NMR (400 MHz, $C_6D_{6'}$ 25 °C): -0.45 (d, 2H, ${}^2J_{Y-H}$ = 3.4 Hz, CH_2SiMe_3), 0.20 (s, 9H, CH_2SiMe_3), 0.95 (d, ${}^{3}J_{H,H}$ = 6.5 Hz, 1H, $CH(CH_3)_2$), 1.01 (d, ${}^{3}J_{H,H}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 1.13–1.15 (m, 3H, $CH(CH_3)_2$), 1.16 (d, ${}^{3}J_{\rm H,H}$ = 7.0 Hz, 2H, CH(CH₃)₂), 1.2 (d, ${}^{3}J_{\rm H,H}$ = 7.5 Hz, 8H, $CH(CH_3)_2$), 1.25 (d, ${}^{3}J_{H,H}$ = 1.7 Hz, 3H, $CH(CH_3)_2$), 1.27 (s, 14H, C(CH₃)₃), 1.29 (s, 4H, C(CH₃)₃), 1.33-1.39 (m, together 10H, CH(CH₃)₂, β -THF), 1.43 (d, ${}^{3}J_{H,H} = 6.1$ Hz, 3H, CH(CH₃)₂), 3.06, 3.14, 3.23, 3.89 (sept, ${}^{3}J_{H,H} = 6.7$ Hz, 1H, CH(CH₃)₂), 3.4 (br s, 8H, α-THF), 6.78–6.83 (m, 1H, ArH), 6.88–7.11 (m, 8H, ArH), 7.47 (dd, ${}^{3}J_{\text{H,H}} = 6.0 \text{ Hz}, {}^{3}J_{\text{H,H}} = 3.5 \text{ Hz}, 1\text{H}, C_{6}H_{4}$). ${}^{13}\text{C}\{{}^{1}\text{H}\} \text{ NMR}$ (100 MHz, C₆D₆, 25 °C): 3.3 (CH₂SiMe₃), 21.2, 21.9, 22.3, 23.1, 23.3, 24.1, 24.6, 29.0 $(CH(CH_3))_2$, 25.0 (β -THF), 27.5, 28.4, 28.5, 28.5 (CH- $(CH_3)_2$, 29.5, 30.0 $(C(CH_3)_2)$, 34.5 $(d, {}^{1}J_{Y,C} = 23.7 \text{ Hz}, CH_2 \text{SiMe}_3)$, 41.9 (d, $J_{Y,C} = 2.4$ Hz, $C(CH_3)_{2i}$), 68.4 (α -THF), 120.4, 121.1, 122.3, 122.7, 123.2, 123.3, 123.7, 135.7, 136.3, 142.2, 143.9, 145.4, 146.6, 152.9 (ArC), 177.6 (d, $J_{\rm Y,C}$ = 2.2 Hz, NCN). IR (Nujol, KBr; $\overline{\nu}$ (cm⁻¹)): 1655 (s), 1584 (s), 1521 (s), 1491 (s), 1320 (s), 1257 (m), 1223 (w), 1142 (m), 1119 (w), 1099 (w), 1059 (w), 1038 (w), 935 (m), 864 (m), 795 (m), 748 (s).

Synthesis of $\{[C_6H_4-1,2-\{NC(tBu)N(2,6-iPr_2C_6H_3)\}_2]Y-$ (OMe)]]₂(DME) (9). 8 (0.50 g, 0.59 mmol) was treated with DME at room temperature for 1 h. DME was removed under vacuum, and the solid residue was crystallized from benzene at 10 °C. Complex 9 was isolated as colorless crystals in 40% yield (0.39 g). Anal. Calcd for C₁₂₂H₁₆₄N₈O₄Y₂ (1984.43): C, 73.84; H, 8.33; N, 5.64; Y, 8.96. Found: C, 73.52; H, 8.09; N, 5.23; Y, 9.07. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 1.12 (d, ${}^{3}J_{H,H}$ = 6.7 Hz, 14H, CH(CH₃)₂), 1.18 (d, ${}^{3}J_{H,H}$ = 6.8 Hz, 20H, CH(CH₃)₂), 1.27 (d, ${}^{3}J_{H,H} = 6.8$ Hz, 4H, CH(CH₃)₂), 1.31 (d, ${}^{3}J_{H,H} = 7.0$ Hz, 10H, CH(CH₃)₂), 1.34 (s, 18H, C(CH₃)₃), 1.38 (s, 4H, C(CH₃)₃), 1.71 (s, 14H, C(CH₃)₃), 1.96 (s, 6H, µ-OCH₃) 3.17, 3.32 (sept, ${}^{3}J_{H,H} = 7.0$ Hz, each 4H, $CH(CH_{3})_{2}$), 3.25 (s, 6H, (CH₃OCH₂)₂), 3.48 (s, 4H, CH₃OCH₂)₂), 6.39 (br s, 3H, ArH), 6.71 (t, ${}^{3}J_{H,H} = 7.3$ Hz, 2H, ArH), 7.02 (d, ${}^{3}J_{H,H} = 7.7$ Hz, 3H, ArH), 7.06 (d, ${}^{3}J_{H,H} = 7.3$ Hz, 2H, ArH), 7.11 (d, ${}^{3}J_{H,H} = 8.2$ Hz, 2H, ArH), 7.14 (s, 1H, ArH), 7.16 (s, 2H, ArH), 7.14 (s, 1H, ArH), 7.34 (s, 1H, ArH), 7.90 (s, 1H, ArH), 8.75 (d, ${}^{3}J_{H,H}$ = 8.71 Hz, 2H, ArH). ${}^{13}C{}^{1}H$ NMR (100 MHz, C₆D₆, 25 °C): δ 21.8, 22.3, 22.7, 23.0, 24.3, 24.6 $(CH(CH_3)_2)$, 28.5, 28.6 $(CH(CH_3)_2)$, 29.2, 29.4, 29.5 $(C(CH_3)_2)$, 39.8, 40.4, 41.7 (C(CH₃)₂), 52.1 (µ-OCH₃) 58.4 (CH₃OCH₂)₂), 71.8

 $(CH_3OCH_2)_2$, 116.5, 119.3, 120.5, 121.3, 121.9, 122.4, 122.7, 127.5, 128.5, 132.8, 135.7, 136.2, 145.0, 145.7 (ArC), 153.1, 156.2, 159.9 (NCN).

NMR-Tube Reaction of 8 with DME. 8 (15 mg, 17.8 μmol), DME (0.01 mL), and C₆D₆ were placed in an NMR tube at 20 °C. The ¹H NMR (400 MHz, C₆D₆, 20 °C) spectrum along with the signals corresponding to **9** showed the presence of methyl vinyl ether, which gives a characteristic set of resonances: δ 3.80 (s, 3H, CH₂= CHOCH₃), 3.90 (dd, ³J_{HH} = 6.8, 2.1 Hz, 1H, CH₂=CHOCH₃), 4.03 (dd, ³J_{HH} = 14.3, 2.0 Hz, 1H, CH₂=CHOCH₃), 6.44 (dd, ³J_{HH} = 14.2, 6.8 Hz, 1H, CH₂=CHOCH₃). The volatiles were condensed under vacuum and analyzed by GS-MS. MS (EI): m/z 58 [M⁺], 43 [CH₂= CHO⁺].

X-ray Crystallography. X-ray data for 3–7 and 9 were collected on a SMART APEX diffractometer (graphite-monochromated Mo K α radiation, ω -scan technique, $\lambda = 0.710$ 73 Å, T = 100 K). The structures were solved by direct methods and were refined on F^2 using the SHELXTL²⁶ package. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined in the riding model. SADABS²⁷ was used to perform areadetector scaling and absorption corrections. The details of crystallographic, collection, and refinement data are shown in Table 1 (Supporting Information).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC Nos. 879298 (3), 879299 (4), 879300 (5), 879301 (6), 879302 (7), 879303 (9). Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

ASSOCIATED CONTENT

S Supporting Information

Figures, a table, and CIF files giving NMR and IR spectra and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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