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Alternatives for Cyclopentadienyl Ligands in Organoyttrium Chemistry: Bis(*N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido)yttrium Compounds

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Reaction of $YCl_3 \cdot THF_{3.5}$ with 2 equiv of $[Me_2Si(NCMe_3)(OCMe_3)]Li$ produces $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}Cl)_2Li \cdot THF_2$ (**1**), which easily loses LiCl to give $[Me_2Si(NCMe_3)(OMe_3)]_2YCl \cdot THF$ (**2**). Salt metathesis of **2** with $LiBH_4$, LiOAr (OAr = O-2,6-$(CMe_3)_2C_6H_3$), $NaN(SiMe_3)_2$, and $LiCH(SiMe_3)_2$ gives the corresponding yttrium bis((alkoxysilyl)amido) derivatives, $[Me_2Si(NCMe_3)(OCMe_3)]_2YR$ (R = $BH_4 \cdot THF$ (**3**), OAr (**4**), $N(SiMe_3)_2$ (**5**), $CH(SiMe_3)_2$ (**6**)). The alkyl compound **6** reacts with H_2 in THF to give an unstable hydride $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}H)\}_2$ (**7**), which was identified by ^1H NMR as a symmetric dimer in solution. Isolation of the hydride **7** appeared not to be possible; the disproportionation product, $[Me_2Si(NCMe_3)(OCMe_3)]_3Y$ (**8**), was obtained instead. With HC≡CR, **6** undergoes protolysis of both the alkyl and the (alkoxysilyl)amido ligands to yield $\{Y(\mu\text{-}C{\equiv}CR)_3\}_n$ for R = $SiMe_3$ (**9**) and CMe_3 (**10**). In contrast, polymerization to polyphenylacetylene was observed for R = Ph. Compound **6** reacts with N≡CMe with metalation of the methyl group under proton transfer to the alkyl ligand to give $CH_2(SiMe_3)_2$. Insertion of another N≡CMe into the new Y−C bond and 1,3-H shift produces $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu(N,N')\text{-}NH{-}CMe{=}CH{-}C{\equiv}N)\}_2$ (**11**). The molecular structures of **6** and **11** show that the bis(*N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido) ligand system is slightly more bulky than the bis(pentamethylcyclopentadienyl) ligand set in compounds Cp^*_2YR. A ROHF INDO/1 semiempirical molecular orbital study on a stripped and symmetrized model of **6**, $[H_2Si(NH)(OH)]_2YCH_3$, shows that the electronic properties of the bis((alkoxysilyl)amido) ligand system are quite different from those of $[C_5H_5]_2YCH_3$ but compare well with those of the bis(benzamidinato) analogue $[HC(NH)_2]_2YCH_3$. The (alkoxysilyl)amido ligand binds dominantly through a strong, ionic Y−N bond, while the ether function coordinates only weakly. Like in the bis(benzamidinato)yttrium system, the (alkoxysilyl)amido and the alkyl ligands accumulate negative charge, resulting in essentially ionic compounds. This high ionicity makes the compounds have little tendency to engage in σ-bond metathesis reactions and (catalytic) insertion chemistry. Because of the absence of charge delocalization within the (alkoxysilyl)amido ligands, these behave as strong Brønsted bases and compete successfully with the Y−C bond in C−H bond activation reactions.

Introduction

The catalytic activity (e.g., in homogeneous Ziegler−Natta type olefin polymerization) of lanthanide, group 3, and isoelectronic cationic group 4 metal carbyl and hydrido derivatives strongly depends on the ancillary ligand system.[1] Until now, most of the research has been carried out on metallocene derivatives,[2] but there is a growing interest in other auxiliary ligands as alternatives for, or in addition to, cyclopentadienyl type ligands.[3] Recently, we have used benzamidinato ligands to stabilize yttrium and group 4 metal carbyl and hydrido complexes and studied catalytic C−C bond formation reactions with these compounds to determine how they differ from the classical metallocene systems.[4]

As a part of a project on new spectator ligands,[4] we explored the bidentate, anionic *N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido ligand for use in organoyttrium chemistry. Both *N*,*N*-bis(trimethylsilyl)benzamidinato and *N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido ligands are hard, basic anions with comparable geometries and steric bulk (Figure 1).

Veith *et al.*[5] were the first to show that the chelating (alkoxysilyl)amido ligand is very useful for stabilizing coordinatively unsaturated main group metal complexes. Later, Edelmann *et al.*[6] reported homoleptic and

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[1] For an overview, see: (a) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (c) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79. (d) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.

[2] (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (b) Jeske, G.; Schock, L. E.; Swepton, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (d) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (e) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. (f) Couglin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606. (g) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.

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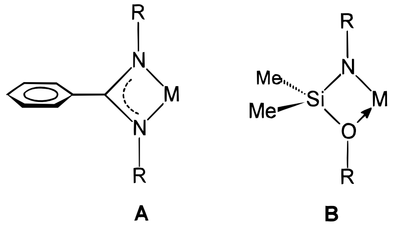


Figure 1. **A**: σ,σ'-Bonded benzamidinato ligand. **B**: σ,σ'-Bonded (alkyoxysilyl)amido ligand.

mixed (alkoxysilyl)amido lanthanoid complexes like ([$Me_2Si(NCMe_3)(OCMe_3)]_3Nd$, [$Me_2Si(NCMe_3)(OCMe_3)]_2$-$Yb{\cdot}(THF)_2$), and [$Me_2Si(NCMe_3)(OCMe_3)]_2Ln(\mu$-$X)_2Li{\cdot}(THF)_2$ (Ln = Yb, X = Cl; Ln = Sm, X = I).

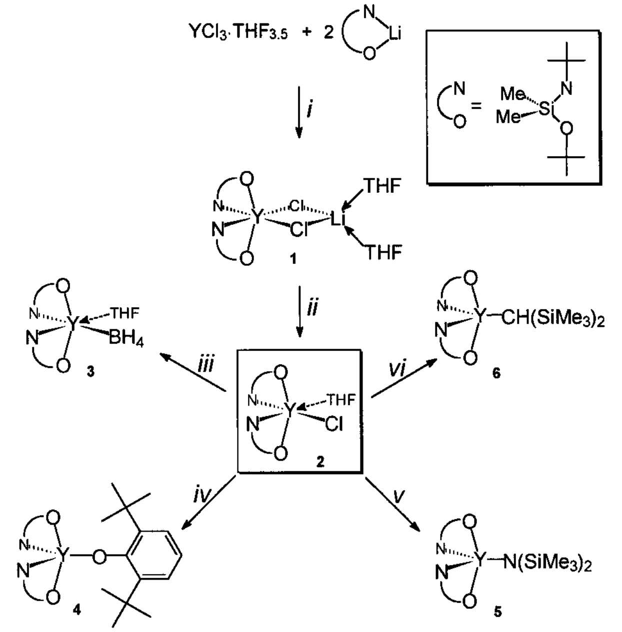
We assumed that, like cyclopentadienyls[1,2] and benzamidinates,[4] (alkoxysilyl)amido ligands could be used to stabilize alkyl or hydride derivatives of the type [$Me_2Si(NCMe_3)(OCMe_3)]_2YR$ (R = alkyl, hydride), which may have attractive catalytic properties, e.g., in C−C bond formation or C−H/C−X bond activation.

In this paper we report the synthesis and characterization of several bis(*N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido)yttrium derivatives, together with an exploratory study of the reactivity of the alkyl derivative [$Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**), the first (alkoxysilyl)amide-stabilized transition metal alkyl. The reactivity will be discussed on the basis of steric aspects and electronic properties derived from RHF INDO/1 calculations on the model system [$H_2Si(NH)(OH)]_2YCH_3$,

Results and Discussion

Synthesis of Bis(*N*,*O*(*tert*-butyl)alkoxydimethylsilylamido)yttrium Complexes. Multigram quantities of the chloride [$Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu$-$Cl)_2$-$Li{\cdot}THF_2$ (**1**) were obtained by reaction of $YCl_3{\cdot}THF_{3.5}$ with 2 equiv of [$Me_2Si(NCMe_3)(OCMe_3)]Li$. This compound is very similar to the related bis((alkoxysilyl)amido) derivatives [$Me_2Si(NCMe_3)(OCMe_3)]_2Ln(\mu$-$X)_2Li{\cdot}THF_2$ (Ln = Yb, X = Cl; Ln = Sm, X = I) reported by Edelmann *et al.*[6] and the bis(benzamidinato)yttrium complex [$PhC(NSiMe_3)_2]_2Y(\mu$-$Cl)_2Li{\cdot}THF_2$.[4]

Scheme 1[a]



[a] (*i*) THF; (*ii*) pentane, reflux; (*iii*) $LiBH_4$, ether; (*iv*) Li−OAr, toluene; (*v*) $NaN(SiMe_3)_2$, toluene; (*vi*) $LiCH(SiMe_3)_2$, toluene.

Like observed for the bis(*N*,*N*′-bis(trimethylsilyl)-benzamidinato) analogue [$PhC(NSiMe_3)_2]_2Y(\mu$-$Cl)_2Li{\cdot}THF_2$,[4] the complexed LiCl can easily be removed by refluxing **1** in pentane to give [$Me_2Si(NCMe_3)(OCMe_3)]_2$-$YCl{\cdot}THF$ (**2**). Attempts to remove the coordinated THF by heating **2** in vacuum were unsuccessful and led to thermal decomposition only. The reactivity of **2** resembles that of its bis(benzamidinato)yttrium analogue [$PhC(NSiMe_3)_2]_2YCl{\cdot}THF$.[4] Chloride metathesis proceeds essentially quantitatively in either ether or toluene (Scheme 1) and forms a convenient synthetic method to various new (alkoxysilyl)amido-stabilized yttrium compounds [$Me_2Si(NCMe_3)(OCMe_3)]_2YR$. Like commonly observed for strong Lewis acidic metal centers, the coordination sphere of the yttrium atom is filled either by incorporation of salt (e.g. **1**) or by complexation of a Lewis base like THF (**2**, **3**). Compounds free of salt and Lewis bases can be made by use of sterically demanding ligands like 2,6-di-*tert*-butyl-phenoxide (**4**), bis(trimethylsilyl)amide (**5**), and bis(trimethylsilyl)-methyl (**6**).

Since our interest primarily concerns the reactivity of the Y−C and Y−H bonds and because the steric bulk of the bis(trimethylsilyl)methyl group severely lowers the reactivity of the alkyl compound, preparation of less bulky and hopefully more reactive alkyl and aryl derivatives was attempted. Unfortunately, all attempts to introduce small carbyl groups (e.g., Me, CH_2CMe_3, CH_2SiMe_3, CH_2Ph, *o*-C_6H_4OMe, *o*-$C_6H_4CH_2NMe_2$) were unsuccessful. Even excess MeLi, which normally leads to very stable “ate” compounds ([Y](μ-$Me)_2Li{\cdot}L_2$; [Y] = [$PhC(NSiMe_3)_2]_2Y$, $Cp^*{}_2Y$, [OEP]Y; OEP = octaethylporphyrin; L_2 = $(Et_2O)_2$, $(THF)_2$, DME, TMEDA),[3d,4b,7] gave intractable mixtures of products.

Characterization of Bis(*N*,*O*(*tert*-butyl)(alkoxydimethylsilyl)amido)yttrium Complexes. Com-

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(3) For example, see: (a) Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 1890. (b) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Organometallics* **1991**, *10*, 2964. (c) Recknagel, A.; Steiner, A.; Noltemeyer, M.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *414*, 327. (d) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968. (e) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124. (f) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (g) Karsch, H. H.; Ferazin, G.; Kooijman, H.; Steigelmann, O.; Schier, A.; Bissinger, P.; Hiller, W. *J. Organomet. Chem.* **1994**, *482*, 151. (h) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (i) Schaverien, C. J.; Orpen, G. *Organometallics* **1994**, *13*, 69.

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(6) Recknagel, A.; Steiner, A.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *415*, 315.

(7) (a) Den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *323*, 181. (b) Schumann, H.; Albrecht, I.; Pickardt, J.; Hahn, E. *J. Organomet. Chem.* **1984**, *276*, C5. (c) Schumann, H. *J. Organomet. Chem.* **1985**, *281*, 95.

plexes **1**−**6** are thermally stable at room temperature though extremely air sensitive. Detailed spectroscopic and analytic data are given in the Experimental Section, and only the more outstanding features and general trends will be discussed here.

With the exception of **4**, the room-temperature ^{1}H NMR spectra of compounds **1**−**6** reveal two distinct resonances for inequivalent methyl substituents on the $SiMe_2$ group. To investigate the fluxional aspects of the bis(*N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido)yttrium system, variable-temperature ^{1}H NMR experiments (−70 to +120 °C) were carried out. For **2**, **5**, and **6**, the coalescence temperatures (T_c) and the $\Delta\nu_c$ of the $Si(CH_3)_2$ groups at the low-temperature extreme[8] allowed calculation of the Gibbs energy for rotation (**2**, $T_c = 67$ °C, $\Delta G^{\ddagger}_{T_c} = 75 \pm 1$ kJ·mol^{-1}; **5**, $T_c = 57$ °C, $\Delta G^{\ddagger}_{T_c} = 73 \pm 1$ kJ·mol^{-1}; **6**, $T_c = 90$ °C, $\Delta G^{\ddagger}_{T_c} = 78 \pm 1$ kJ·mol^{-1}). Compared with the geometrically similar bis(*N*,*N'*-bis(trimethylsilyl)benzamidinatoyttrium amido complex $[PhC(NSiMe_3)_2]_2YN(SiMe_3)_2$ ($\Delta G^{\ddagger}_{T_c} = 57 \pm 1$ kJ·mol^{-1}),[4b] $[Me_2Si(NCMe_3)(OCMe_3)]_2YN(SiMe_3)_2$ (**5**) appears significantly less fluxional.

The single $SiMe_2$ resonance in the room-temperature ^{1}H NMR spectrum of **4** indicates fast fluxional behavior of the ligands in this compound. The coalescence temperature appears to be concentration dependent: for a 0.034 M solution $T_c = -23$ °C; for a 0.34 M solution, $T_c = -31$ °C was observed. The mechanism for the fluxional behavior of **4** must be intermolecular and can be explained by the fact that the 2,6-di-*tert*-butylphenoxide ligand, which is the largest of the ligands R used here, forces an ether function of the (alkoxysilyl)amide to dissociate and engage in a intermolecular exchange. The molecular structures of both **6** and **11** (*vide infra*) show that steric crowding, indeed, results in loosening one of the ether−yttrium interactions. For **6**, it has been found that the coalescence temperature is concentration independent and it is likely that for this compound (and presumably for **2** and **5** as well) the fluxionality is intramolecular and caused by intramolecular cog-wheel type rotation of both (alkoxysilyl)amido ligands, like that proposed for the benzamidinato ligands in the corresponding bis(benzamidinato)yttrium complexes.[4b]

The α-carbon (^{13}C NMR, $\delta = 33.8$ ppm, $^1J_{Y-C} = 30$ Hz) and yttrium resonances (^{89}Y NMR, $\delta = 645$ ppm) of **6** are, compared with those of $Cp^*_2Y(CH(SiMe_3)_2)$ (^{13}C NMR, δ 25.2 ppm, $^1J_{Y-C} = 37$ Hz; ^{89}Y NMR, δ 79 ppm), considerably shifted to low field and correspond more with those of $[PhC(NSiMe_3)_2]_2Y(CH(SiMe_3)_2)$ (^{13}C NMR, δ 43.5 ppm, $^1J_{Y-C} = 30$ Hz; ^{89}Y NMR, δ 721 ppm).[9] Interpretation of these values in terms of differences in electron density is tempting but unreliable since several other factors influence the chemical shift as well.[10] However, the comparable ^{89}Y NMR chemical shifts for $[PhC(NSiMe_3)_2]_2Y(CH(SiMe_3)_2)$[4b] and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**) suggest a close electronic similarity between the two compounds.

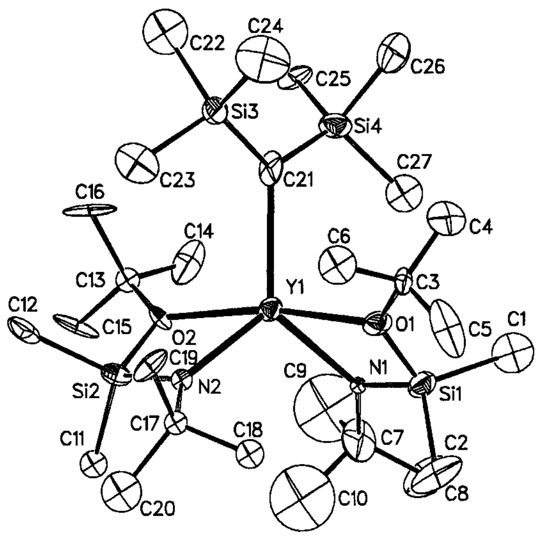

Figure 2. ORTEP drawing of $[Me_2Si(NCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**). Hydrogens are omitted for clarity.

Table 1. Selected Bond Distances and Angles for $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (6)

Distances (Å)			
Y(1)−O(1)	2.307(14)	Y(1)−N(1)	2.316(13)
Y(1)−O(2)	2.504(14)	Y(1)−N(2)	2.195(16)
Y(1)−C(21)	2.558(19)		
Angles (deg)			
Si (1)−Y(1)−Si(2)	131.3(2)	Y(1)−C(21)−Si(3)	119.9(10)
Si(1)−Y(1)−C(21)	116.1(5)	Y(1)−C(21)−Si(4)	119.8(9)
Si(2)−Y(1)−C(21)	112.1(5)	Si(3)−C(21)−Si(4)	119.6(11)
N(1)−Y(1)−N(2)	107.6(5)	O(1)−Y(1)−O(2)	168.8(4)
O(1)−Y(1)−N(1)	63.5(5)	O(2)−Y(1)−N(1)	106.4(4)
O(1)−Y(1)−N(2)	113.2(5)	O(2)−Y(1)−N(2)	63.9(5)
N(1)−Y(1)−C(21)	123.2(6)	O(1)−Y(1)−C(21)	98.9(6)
N(2)−Y(1)−C(21)	128.1(6)	O(2)−Y(1)−C(21)	90.7(6)

An X-ray diffraction study of **6** showed two crystallographically-independent molecules in the unit cell. An ORTEP drawing of one of them is shown in Figure 2. Selected bond lengths and angles (of one independent molecule) are listed in Table 1. Details concerning the data collection and refinement are given in Table 5. The structure of only one independent molecule will be discussed here in detail. There are considerable differences between the two molecules, but the overall picture is the same for both.

Rotational disorder of some of the $C(CH_3)_3$ groups and a long axis hampered the solution of the structure. The positions of the hydrogens could not unequivocally be determined. The heavier atoms near yttrium were reliably localized, providing sufficient relevant information concerning the structure. When considering the (alkoxysilyl)amido ligands to occupy one coordination vertex, the complex can be described as distorted trigonal planar with yttrium in the center (Si(1)−Y(1)−Si(2), 131.3(2)°; Si(1)−Y(1)−C(21), 116.1(5)°; Si(2)−Y(1)−C(21), 112.1(5)°; sum of the angles, 359.5(5)°). As for the corresponding bis(benzamidinato)yttrium bis(trimethylsilyl)methyl complex $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_2Y(CH(SiMe_3)_2)$,[4b] a trigonal-planar geometry seems to be adapted to minimize steric repulsions. With torsion angles of −3.6(6)° (N(1)−Y(1)−O(1)−Si(1)) and 0.9(5)° (N(2)−Y(1)−O(2)−Si(2)), the two (alkoxysilyl)amido ligands form planar four-membered rings with the yttrium atom. Compared with the N−Y−N bite

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[8] (a) Günther, H. In *NMR-Spectroscopy*; Georg Thieme Verlag: Stuttgart, Germany, 1973. (b) Fortman, J. J.; Sievers, R. E. *Coord. Chem. Rev.* **1971**, *6*, 331.

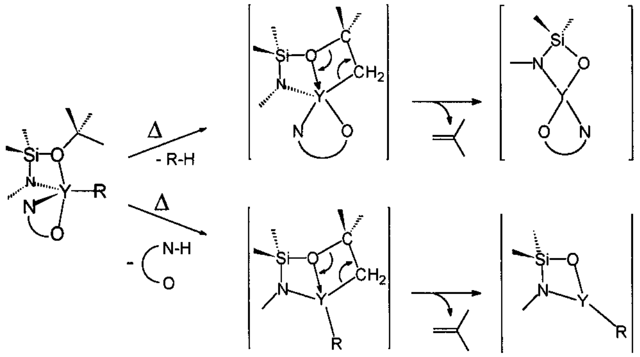
[9] At −10 °C, the ^{1}H NMR spectrum of **6** shows two inequivalent doublets for the α-H ($\delta = -1.05$ ppm, $^2J_{Y-H} = 2.0$ Hz; $\delta = -1.45$ ppm, $^2J_{Y-H} = 1.5$ Hz), indicating the presence of two distinct isomers at low temperature. At 80 °C, these signals are coalescented to one broad signal ($\delta = -1.27$ ppm) for which no yttrium coupling could be observed.

[10] Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861 and references cited therein.

angle (~58°) found in the bis(benzamidinato)yttrium complexes,[4] the corresponding N−Y−O bite angles in **6** (~64°) are considerably larger. The Si−O and Si−N distances (Table 1) are consistent with single bonds and do not indicate significant π-overlap of the N and O lone pairs with empty Si d orbitals. The Y(1)−N(1) (2.316(13) Å) and Y(1)−N(2) (2.195(16) Å) distances are short compared to those in bis(N,N'-bis(trimethylsilyl)benzamidinato)yttrium compounds, $[p\text{-MeOC}_6\text{H}_4\text{C(NSiMe}_3)_2]_2\text{Y(CH(SiMe}_3)_2)$ and $\{[\text{PhC(NSiMe}_3)_2]_2\text{Y}(\mu\text{-R})\}_2$ (R = μ-C≡CH, μ-H), where they range from 2.327(3) to 2.395(4) Å.[4] They resemble more the Y−N distance in $\text{Cp*}_2\text{YN(SiMe}_3)_2$[11] (2.274(5), 2.253(5) Å) and suggest additional π-donation of the nitrogen lone pairs to the electron-deficient yttrium. The Y(1)−O(1) distance (2.307(14) Å) is in agreement with a normal Y←:O dative bond.[12] However, the other ether function (Y(1)−O(2), 2.504(14) Å) is only weakly bonded to yttrium. The Y(1)−C(21) σ-bond (2.558(19) Å) is longer than those in $\text{Cp*}_2\text{Y(CH(SiMe}_3)_2)$ (2.468(7) Å)[11] and $[p\text{-MeOC}_6\text{H}_4\text{C(NSiMe}_3)_2]_2\text{Y(CH(SiMe}_3)_2)$ (2.431(5) Å)[4] and is among the longest, nonbridging Y−C σ-bond known.[13] The planar geometry of the α-carbon of the alkyl group (Table 1) also supports the view that the configuration around the metal is mainly determined by steric interactions. The large Y(1)−C(21)−Si(3) (119.6(11)°) and Y(1)−C(21)−Si(4) (119.8(9)°) angles in **6** exclude agostic interactions (γ, δ) of yttrium with the bis(trimethylsilyl)methyl group, like observed in $\text{Cp*}_2\text{LnCH(SiMe}_3)_2$ (Ln = Y,[11] Ce,[14] Nd[2a]) and $[\text{Me}_2\text{Si(C}_5\text{Me}_4)(\text{C}_5\text{R}_4)]\text{LnCH(SiMe}_3)_2$ (Ln = Nd, R = Me;[2b] Ln = Lu, R = H[2e]). The argument that yttrium in **6** is not very Lewis acidic and therefore does not form agostic interactions is not very convincing, taking into account that (alkoxysilyl)amidos are formally 4-electron donors. Similarly, no agostic interaction was found in other 10-electron species $[p\text{-MeOC}_6\text{H}_4\text{C(NSiMe}_3)_2]_2\text{Y(CH(SiMe}_3)_2)$[4b] and $[\text{OEP}]\text{LuCH(SiMe}_3)_2$.[3d] A possible rationalization of the absence of agostic interactions in **6**, $[p\text{-MeOC}_6\text{H}_4\text{C(NSiMe}_3)_2]_2\text{Y(CH(SiMe}_3)_2)$, and $[\text{OEP}]\text{LuCH(SiMe}_3)_2$ is that the (hard basic) (alkoxysilyl)amido ligands render the complexes significantly more ionic. As a result, the orbitals of the highly positively charged yttrium will be more contracted than those in $\text{Cp*}_2\text{Y(CH(SiMe}_3)_2)$ and therefore less available to effective-overlap with C−H or C−Si electron pairs (*vide infra*).

Thermal Stability of $[\text{Me}_2\text{Si(NCMe}_3)(\text{OCMe}_3)]_2\text{Y(CH(SiMe}_3)_2)$ (6) in Common Solvents. Before the reactivity of **6** was tested, its behavior and thermal stability in common solvents was investigated. At room temperature, **6** is stable for prolonged periods of time in ethers, aromatic solvents, and alkanes. Independent of the solvent used, decomposition starts at higher temperatures (>70 °C), with formation of isobutene (0.8 mol/Y), $\text{H}_2\text{C(SiMe}_3)_2$ (1.0 mol/Y), and $\text{Me}_2\text{Si(N(H)CMe}_3)(\text{OCMe}_3)$ (0.6 mol/Y). From the complicated resonance pattern in the range 2.0−0.0 ppm, it is concluded that a mixture of yttrium containing products has been formed. Identification of the individual components was not attempted. The formation of isobutene indicates the loss of one of the *tert*-butyl substituents of the (alkoxysilyl)amido ligands. The nearly 1:1 formation of $\text{H}_2\text{C(SiMe}_3)_2$ and $\text{Me}_2\text{Si(N(H)CMe}_3)(\text{OCMe}_3)$ suggests that at least two different thermolysis pathways are involved (Scheme 2). Either the $(\text{Me}_3\text{Si})_2\text{CH}$ or $\text{Me}_2\text{Si(NCMe}_3)(\text{OCMe}_3)$ group reacts as a Brønsted base and abstracts a proton from one of the *tert*-butyl groups to form the hydrocarbon $\text{H}_2\text{C(SiMe}_3)_2$ or alkoxysilylamine $\text{Me}_2\text{Si(N(H)CMe}_3)(\text{OCMe}_3)$, respectively (Scheme 2). Subsequent rearrangement of the metalation product by intramolecular C−X (X = N or O)[15] bond activation results in the release of isobutene.[16]

Scheme 2. Schematic Presentation of Proposed Thermolysis Reaction of 2[a]



[a] Attack of the ether function is shown. A similar process can be suggested for attack of the amido function.

Activation of C−H Bonds in Activated Arenes. Aromatic molecules (benzene, toluene, mesitylene; PhX (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, $\text{P(=CH}_2)\text{Ph}_2$); pyridine, α-picoline) are quite readily ortho-metalated by coordinatively unsaturated early transition metal and lanthanide complexes like $\text{Cp*}_2\text{LnR}$ (Ln = Sc, Y, lanthanides),[17] Cp_2TiR,[18] and $[\text{Cp}_2\text{ZrR}\cdot(\text{L})]^+$ [19] (R = H, alkyl, L = Lewis base). This metalation often offers a

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[13] For example, see: (a) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Reingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212. (b) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1989**, *8*, 2454. (c) Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836.

[14] Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495.

[15] Attempts to identify the ligand fragments formed after hydrolysis of the thermolysis product failed. Due to further degradation of the ligand fragments during workup, GC-MS analysis could not answer the question whether the ether or the amido function is involved.

[16] Similar thermolysis was observed for $[\eta^{5}{:}\eta^{1}\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(t\text{-Bu})]\text{TiR}_2$ (R = alkyl) complexes, resulting in the formation of R−H and isobutene, see: Sinnema, P.-J.; Teuben, J. H. To be published. Comparable intramolecular C−H bond activation is well-established in the literature. For example, see: (a) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026. (b) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (c) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *150*, 237. (d) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214. (e) Van Doorn, J. A.; Van der Heijden, H.; Orpen, G. *Organometallics* **1994**, *13*, 4271.

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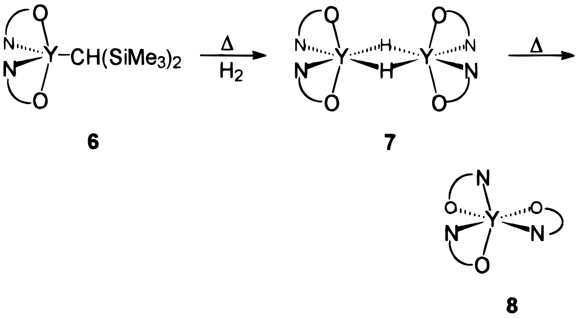
[19] For example, see: Jordan, R. F.; Guram, A. S. *Organometallics* **1990**, *9*, 2116 and references cited therein.

clean route to new alkyl/aryl derivatives and, from a synthetic point of view, is preferred over salt metathesis which often results in mixtures containing complexed salt and solvent molecules.[20] Since the metalation method offers the possibility to generate alkyl/aryl complexes from the easily accessible bis(trimethylsilyl)methyl derivative $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**), it was decided to study its reactivity toward (functionalized) arenes.

Like the bis(*N*,*N'*-bis(trimethylsilyl)benzamidinato)yttrium complexes, $[PhC(NSiMe_3)_2]_2YR$ (R = $CH_2Ph{\cdot}THF$, $CH(SiMe_3)_2$) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$,[4] but unlike the bis(pentamethylcyclopentadienyl) compounds Cp^*_2YR,[17d] heating of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ in aliphatic (hexane) or aromatic solvents (benzene, toluene) does not lead to solvent metalation or H/D scrambling between the yttrium compounds and benzene-d_6.[17d] Degradation of the ligand system (thermolysis) takes place instead.

In an attempt to favor intermolecular C−H bond activation, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ was treated with activated arenes. While no reaction was observed with functionalized arenes, PhX (X = OMe, CH_2NMe_2),[17d] (*ortho*-substituted) pyridines (NC_5H_5, $2\text{-}MeNC_5H_4$, $2,6\text{-}Me_2NC_5H_3$, $2\text{-}EtNC_5H_4$)[17,19] did indeed give the corresponding metalation products. Pyridine gave the pyridyl $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2(C,N)\text{-}2\text{-}NC_5H_4)$ while, interestingly, with α-picoline and 2-ethylpyridine exclusively the α-metalated products $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2(C,N)\text{-}CHR\text{-}2\text{-}NC_5H_4)$ (R = H, Me) were formed. However, concurrent thermolysis of both the starting material **6**, and the metalation products make it difficult to study the process in detail. The metalation reaction and a study of the reactivity of the products are reported in a following article.

Metal−Carbon Bond Hydrogenolysis. In general, hydrido complexes of group 3 metals and lanthanides are much more reactive and better suited to start up a catalytic cycle than the corresponding alkyls. Therefore, priority was given to the synthesis of $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}H)\}_2$ (**7**). Like observed for $[p\text{-}XC_6H_4C(NSiMe_3)_2]_2Y(CH(SiMe_3)_2)$ (X = H, MeO),[4] $[C_5H_4R]_2YCMe_3{\cdot}THF$ (R = H, Me),[21] $Cp^*_2Y(CH(SiMe_3)_2)$,[22] and $Cp^*[OAr]Y(CH(SiMe_3)_2)$,[3i] **6** reacted with dihydrogen under hydrogenolysis of the Y−C bond forming $H_2C(SiMe_3)_2$ and $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}H)\}_2$ (**7**). In THF, the hydride is sufficiently stable to be detected by ^1H NMR spectroscopy but it could not be isolated. The dimer is not broken up, e.g. into a monomeric THF adduct, since, as observed for most yttrium hydrides, the hydride resonance still shows a characteristic $^{89}Y−H$ coupling pattern (δ 6.80, t, $^1J_{Y-H} = 31$ Hz) consistent with a symmetrical dimeric structure in solution. Attempts to prepare the hydride in benzene gave only a disproportionation product $[Me_2Si(NCMe_3)(OCMe_3)]_3Y$ (**8**) and not the hydride $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}H)\}_2$. Apparently, the hydride is unstable and readily undergoes ligand redistribution (eq 1). The reaction of **6** with dihydrogen is quite complicated. When following the hydrogenolysis in THF-d_8 by ^1H NMR spectroscopy, it appeared that resonances of the dimeric hydride never accounted for more than 10% of the yttrium present. The hydrogenolysis is very slow and it required 2 days at 60 °C until all $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**) had reacted. Probably, the hydride causes C−O activation of THF, like observed for $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$,[4] $\{[C_5H_4Me]_2YR{\cdot}THF$ (R = Me, CH_2SiMe_3),[23] and $\{Cp^*_2Ln(\mu\text{-}H)\}_2$ (Ln = Y, La, Ce, Sm).[24] The same argument proposed for the absence of agostic interactions in **6** (*vide supra*) can be used to rationalize the low hydrogenolysis rate. Due to the high positive charge at yttrium, the orbitals may also be too contracted to effectively precomplex substrates like H_2. Furthermore, less effective charge stabilization in the heterolytic transition state[25] and low stability of the initially formed monomeric hydride may be significant. Attempts to synthesize the hydride through alternative methods like thermolysis of *in situ* prepared alkyl compounds (alkyl = *n*-butyl, *t*-butyl)[26] or by salt metathesis of **2** with hydride sources like NaH,[27] $M[BEt_3H]$ (M = Li, K),[28] or $LiAlH_4$[29] invariably resulted in the formation of **8** or intractable oily products.



(1)

Reaction of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (6) with Unsaturated Substrates. (i) Ethene. No reaction was observed at room temperature (benzene-d_6), whereas heating to 70 °C (days) exclusively resulted in thermolysis of **6**. Presumably, the steric bulk of the bis(trimethylsilyl)methyl group blocks incoming ethene molecules, but undoubtedly electronic reasons are important as well (*vide infra*).

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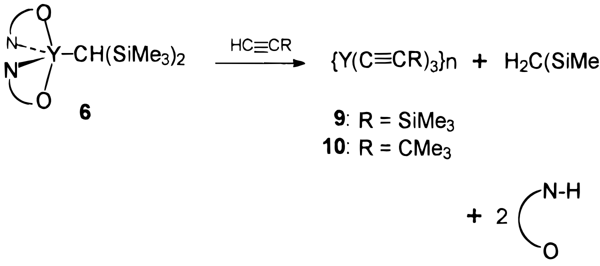
When the reaction was carried out in the presence of dihydrogen (4 atm, benzene-d_6 or THF-d_8), the *in situ* generated hydride $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}H)\}_2$ did not react with ethene either. Analysis of the reaction mixture by NMR spectroscopy and GC gave no indication for oligomerization or hydrogenation of ethene.

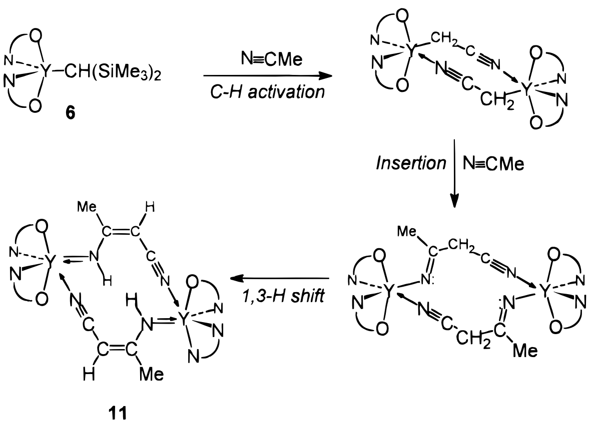
(ii) 1-Alkynes. For compounds $Cp^*{}_2LnR$,[2d,30] Cp*-[ArO]YR,[3i] and $[PhC(NSiMe_3)_2]_2YR$,[4] regioselective, catalytic dimerization of terminal alkynes to 1-buten-3-ynes has been observed. For **6**, the situation is remarkably different compared to the systems mentioned above. Reaction with excess of HC≡CR (R = $SiMe_3$, CMe_3) resulted in quantitative formation of $H_2C(SiMe_3)_2$, $Me_2Si(N(H)CMe_3)(OCMe_3)$ (1:2 ratio), and a white precipitate identified as $\{Y[\mu\text{-}C{\equiv}CR]_3\}_n$ (**9**, R = $SiMe_3$; **10**, R = CMe_3; eq 2). No dimerization of the 1-alkynes was observed. Apparently, the (alkoxysilyl)amido ligands are prone to undergo protolysis, leading to decomposition. This clearly illustrates the much higher Brønsted base character of the (alkoxysilyl)amido ligands compared to benzamidinato ligands.[4]



(2)

Reaction of **6** with an excess of phenylacetylene gives, in addition to $H_2C(SiMe_3)_2$ and $Me_2Si(NHCMe_3)(OCMe_3)$ (1:2 ratio, ^1H NMR), polyphenylacetylene. The final state of yttrium could not be established. The polymer was characterized by IR, ^1H NMR, and GPC techniques. The IR spectrum showed predominantly a *trans*-conformation,[31] while the various olefinic signals in the ^1H NMR spectrum indicate random, head-to-tail and head-to-head, coupling. Apart from a minor fraction, most of the polymer was soluble in chloroform. GPC measurements showed two peaks with $M_w = 780 \pm 20$ g·mol^{-1} ($M_w/M_n = 1.21$) and $M_w = 21\,750 \pm 350$ g·mol^{-1} ($M_w/M_n = 1.7$). The formation of at least three different products indicate that different catalytically active species are involved.

(iii) Acetonitrile. As a follow-up of the reactions with 1-alkynes, which showed dominant protolysis of the (alkoxysilyl)amido ligands, the reactivity of **6** toward the less acidic acetonitrile was studied. Treatment of **6** in THF with excess MeC≡N (2−3 equiv) resulted in an instantaneous reaction, quantitatively affording $H_2C(SiMe_3)_2$ and the crotononitrileamido complex $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu(N,N')\text{−}NH\text{−}CMe{=}CH\text{−}C{\equiv}N)\}_2$ (**11**, eq 3). The (alkoxysilyl)amido ligands were not affected since no $Me_2Si(N(H)CMe_3)(OCMe_3)$ was formed during the reaction. This reaction is strictly analogous to the reaction of the benzamidinato compound $[PhC(NSiMe_3)_2]_2Y(CH(SiMe_3)_2)$ and resembles closely the alkali-metal-catalyzed dimerization of MeC≡N.[32] In contrast, $\{[C_5H_4R]_2Y(\mu\text{-}H)\cdot THF\}_2$ (R = H, Me)[21] and $Cp^*{}_2ScR$ (R = p-MeC_6H_4, Me)[33] selectively insert acetonitrile, yielding the corresponding imido complexes $\{[C_5H_4R]_2Y(\mu\text{-}N{=}C(H)Me)\}_2$ and $Cp^*{}_2ScN{=}C(R)Me$, respectively. Metalation of the nitrile was also observed when $Cp^*{}_2LnCH(SiMe_3)_2$ (Ln = La, Ce) was treated with acetonitrile, affording the cyanomethyl derivative $\{Cp^*{}_2Ln(\mu(C,N)\text{-}CH_2C{\equiv}N)\}_2$.[34] Although no intermediates could be isolated, it is likely that during the formation of **11** the corresponding cyanomethyl derivative $\{[Me_2Si(NCMe_3)(OCMe_3)]Y((\mu\text{-}(C,N)\text{-}CH_2C{\equiv}N)\}_2$ is formed. This then inserts another equivalent of MeC≡N and rearranges via a 1,3-H shift (eq 3).



(3)

The spectroscopic data for **11** are in close agreement with those of Na[NHCMe=CHC≡N][32] and $\{[PhC(NSiMe_3)_2]_2Y(\mu(N,N')\text{-}NH\text{−}CMe{=}CH\text{−}C{\equiv}N)\}_2$.[4c] The IR spectrum shows $\nu_{C\equiv N}$ at 2138 cm^{-1} and additional absorptions at 3250−3450, 2965, and 1643−1599 cm^{-1}, which can be assigned to =NH, =CH, and C=C stretching vibrations, respectively. The low field shift of the *C*(Me)=C resonance (δ = 134.5 ppm) and high field shift of the *C*(H)=C (δ = 49.0 ppm) and C(*H*)=C resonances (δ = 3.32 ppm) in the ^{13}C and ^1H NMR spectra clearly indicate effective charge delocalization within the crotononitrileamido fragment.

To verify the proposed bonding of the crotononitrile fragment, a low-temperature X-ray structure determination of **11** was carried out. The molecular structure is shown in Figure 3. Selected bond lengths and angles are listed in Table 2. Data collection details are given in Table 5. The dimeric structure has a crystallographically imposed center of inversion with two $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$ moieties connected by two crotononitrileamido fragments. Each yttrium atom displays a distorted octahedral geometry formed by the coordination of two (alkoxysilyl)amido and two crotononitrileamido ligands. Like in **6** and $[Me_2Si(NCMe_3)(OCMe_3)]_2Nd(\mu\text{-}Cl)_2Li\cdot THF_2$,[6] both (alkoxysilyl)amido ligands are bonded differently to yttrium (Table 2). The Y(1)−N(2) bond (2.257(4) Å) *trans* to Y(1)−O(1) (2.535(3) Å) is shorter than the Y(1)−N(1) distance (2.279(3) Å) *trans* to Y(1)−N(4) (2.460(4) Å. The Y(1)−N(1) (2.279(3) Å) and Y(1)−N(2) (2.257(4) Å) bonds are very similar to

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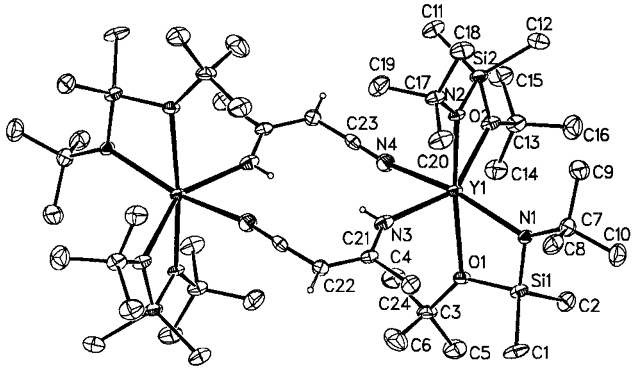

Figure 3. ORTEP drawing of $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu(\boldsymbol{N},\boldsymbol{N'})\text{-}N(H){-}C(Me){=}C(H){-}C{\equiv}N)\}_2$ (**11**). Hydrogens are omitted for clarity.

Table 2. Selected Bond Distances and Angles for $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu(N,N')\text{-}N(H){-}C(Me){=}C(H){-}C{\equiv}N)\}_2$ (11)

Distances (Å)			
Y(1)−O(1)	2.535(3)	Y(1)−O(2)	2.385(3)
Y(1)−N(1)	2.279(3)	Y(1)−N(2)	2.257(4)
Y(1)−N(3)	2.344(4)	Y(1)−N(4)	2.460(4)
N(3)−C(21)	1.331(6)	N(4)−C(23)	1.156(6)
C(21)−C(22)	1.375(7)	C(22)−C(23)	1.393(7)
Angles (deg)			
O(1)−Y(1)−N(1)	63.57(12)	O(2)−Y(1)−N(1)	110.31(12)
O(1)−Y(1)−N(2)	173.76(12)	O(2)−Y(1)−N(2)	65.44(12)
O(1)−Y(1)−N(3)	86.61(11)	O(2)−Y(1)−N(3)	147.44(11)
O(1)−Y(1)−N(4)	94.08(12)	O(2)−Y(1)−N(4)	76.22(12)
N(1)−Y(1)−N(2)	110.20(13)	N(1)−Y(1)−N(3)	111.62(13)
N(1)−Y(1)−N(4)	154.15(14)	N(2)−Y(1)−N(3)	96.51(13)
N(2)−Y(1)−N(4)	91.88(13)	N(3)−Y(1)−N(4)	77.66(14)
O(1)−Y(1)−O(2)	114.25(10	Si(1)−Y(1)−Si(2)	133.96(4)
Y(1)−N(4)−C(23)	167.6(4)	Y(1)−N(3)−C(21)	143.1(3)
N(3)−C(21)−C(22)	126.2(4)	N(4)−C(23)−C(22)	177.8(5)
C(21)−C(22)−C(23)	121.2(4)		

the Y−N distances in $Cp^*{}_2YN(SiMe_3)_2$ (2.274(5), 2.253(5) Å)[11] and suggest additional interaction of the amido lone pairs with the electron-deficient yttrium (*vide infra*). As observed for **6**, one of the ether functions is normally bonded to yttrium (Y(1)−O(2) = 2.385(3) Å) whereas the other is only weakly coordinated (Y(1)−O(1) = 2.535(3) Å). The Si(1)−Y(1)−Si(2) angle (133.96(4)°) is in good agreement with the value observed for **6** (131.3(2)°), indicating that the ligand arrangement around the metal center is comparable in both systems. The short N(3)−C(21) (1.331(6) Å) and C(22)−C(23) (1.393(7) Å) distances and the long C(21)−C(22) bond indicate considerable charge delocalization within the crotononitrileamido fragment[35] and are in good agreement with the spectroscopic data.

Steric and Electronic Properties of the Bis(*N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido) Ligand System. Since both steric and electronic factors influence the stability and reactivity of a system, attempts were made to compare the difference in the effective steric bulk and electronic structure of bis((alkoxysilyl)amido), bis(pentamethylcyclopentadienyl), and bis(benzamidinato) complexes.[4b]

(a) Steric Properties. To compare the steric aspects of bis(*N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido) coordination with the bis(*N*,*N′*-bis(trimethylsilyl)benzamidinato) and bis(pentamethyl)cyclopentadienyl ligand systems,[4b] Brintzinger's[36] approach of coordination aperture and CPK models were used (Figure 4).[37] Space-filling models give a good picture of the relative geometric differences of the various ligand systems. From Figure 4 it is clear that, although quite similar to $Cp^*{}_2Y$, the bis((alkoxysilyl)amido) ligand set is sterically the most demanding, leaving the smallest coordination gap. This is in good agreement with the calculated coordination apertures for $Cp^*{}_2Y$ (72°) and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$ (61°). With a coordination aperture of 84°, the $[PhC(NSiMe_3)_2]_2Y$ system is sterically the least demanding. A consequence of the increase of steric bulk in the order $[PhC(NSiMe_3)_2]_2Y < Cp^*{}_2Y < [Me_2Si(NCMe_3)(OCMe_3)]_2Y$ is the gradual elongation of the Y−C bond in $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_2Y(CH(SiMe_3)_2)$ (2.431(5) Å), $Cp^*{}_2Y(CH(SiMe_3)_2)$ (2.468(7) Å), and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (2.559(19) Å).

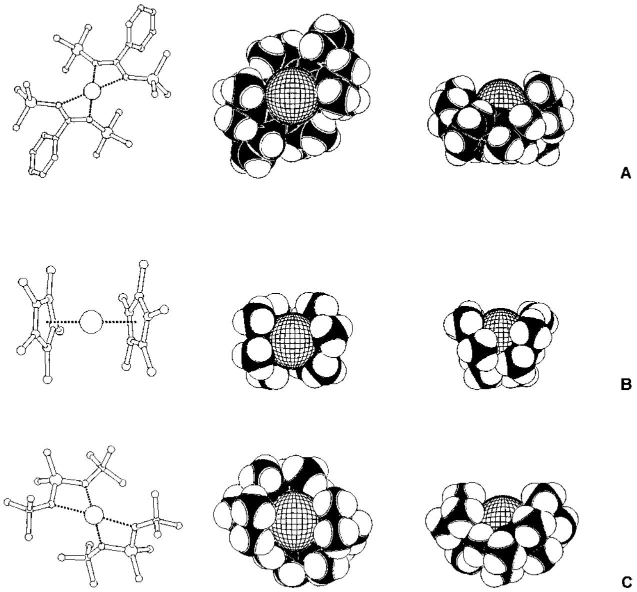

Figure 4. CPK models of $[PhC(NSiMe_3)_2]_2Y$ (A), $Cp^*{}_2Y$ (B), and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$ (C) in two different orientations.

(b) Electronic Properties. For a comparison of the electronic aspects of the three ligand systems under discussion, INDO/1 semiempirical molecular orbital calculations were used as reported earlier.[4b,38] First, ROHF calculations were performed on a stripped version of the (alkoxysilyl)amido ligand $[H_2Si(NH)(OH)]^\bullet$ (Figure 5) to get information about the symmetry and energy of the (alkoxysilyl)amido ligand orbitals available for bonding. Two (N and O) σ-orbitals of the (alkoxysilyl)amido ligand are suitable for σ-interaction with the metal, whereas two (N and O) π-orbitals can provide an additional π-interaction with the metal. An important difference between benzamidinato and (alkoxysilyl)amido ligands is that π-delocalization, leading to a diaza−allylic NCN fragment of the benzamidinato ligands, is not present in the (alkoxysilyl)amido ligand. Hence, the negative charge of the (alkoxysilyl)amido ligands cannot spread out but remains located at the

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[35] Cf.: N−C = 1.40 Å, C−C = 1.46 Å, C=C = 1.34 Å. Burke-Laing, M.; Laing, M. *Acta Crystallogr.* **1976**, 32B, 3216.

[36] Hortmann, K.; Brintzinger, H. H. *New. J. Chem.* **1992**, *16*, 51.

[37] X-ray crystal structure data were used from $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$, ref 4b; $Cp^*{}_2Y(CH(SiMe_3)_2)$, ref 12; and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**). CPK models were prepared using PLUTON-92, see: Spek, A. L. PLUTON-92; University of Utrecht, The Netherlands, 1992.

[38] Zerner, M. C. *ZINDO, a comprehensive semiempirical quantum chemistry package*, University of Florida: Gainesville, FL.

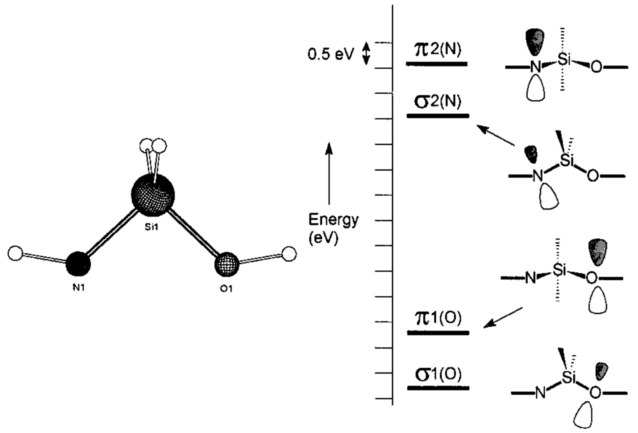

Figure 5. Model for the (alkoxysilyl)amido ligand, $H_2Si(NH)(OH)^•$, used in the INDO/1 calculations, and it frontier orbitals.

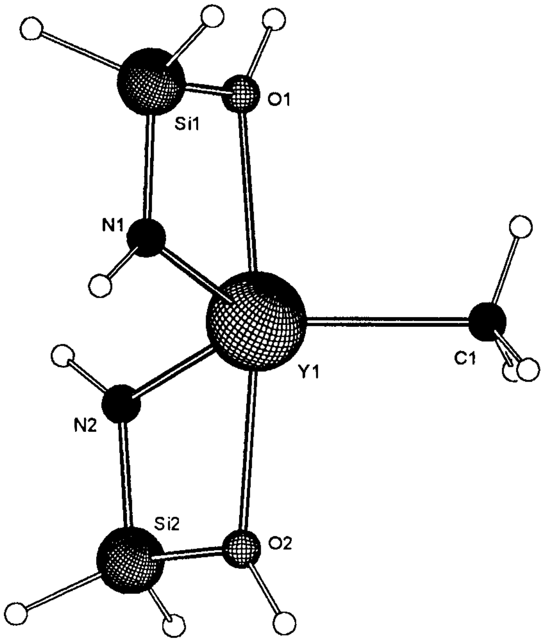

Figure 6. Model for a bis(alkoxysilyl)amido)yttrium alkyl complex, used in the INDO/1 calculations.

nitrogen atom. As a consequence, the (alkoxysilyl)amido ligands are much more basic than benzamidinates: the reactivity differences reflect this. Whereas reaction of $[PhC(NSiMe_3)_2]_2Y(CH(SiMe_3)_2)$ with HC≡CR gives exclusively $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CR)\}_2$,[4a,c] the corresponding complex $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**) shows fast and complete protolysis of the (alkoxysilyl)amido ligands by the acidic alkyne hydrogen instead (*vide supra*).

Following the calculations on the ligand, calculations were carried out on the model compound $[H_2Si(NH)(OH)]_2YCH_3$ (Figure 6). Furthermore, ROHF calculations on the $CH_3^•$ and $[H_2Si(NH)(OH)]_2Y^•$ fragments were performed to estimate the Y−C$_\sigma$ bond strength. Relevant ligand to metal bonding interactions in $[H_2Si(NH)(OH)]_2YCH_3$ are listed in Table 3. To simplify the interpretation of the results, the orbitals were localized. The bonding of cyclopentadienyl ligands has been described elsewhere and will not be discussed here.[39] The bonding in the bis((alkoxysilyl)amido) model $[H_2Si(NH)(OH)]_2YCH_3$ is significantly different from that in the bis(benzamidinato) analogue $[HC(NH)_2]_2YCH_3$ described earlier.[4b] Whereas in $[HC(NH)_2]_2YCH_3$, each nitrogen is bonded to yttrium by one σ-orbital, in $[H_2Si(NH)(OH)]_2YCH_3$ the equatorially-located nitrogens are each bonded by two orbitals: one σ-orbital involving nitrogen (mainly) p_y and yttrium d_{yz} atomic orbitals and a second π-orbital involving nitrogen (mainly) p_z and an orbital constructed of yttrium $p_y + s + d_{(x^2-y^2)}$. In contrast to the benzamidinate nitrogen lone pairs that are involved in π-bonding within the ligand, the nitrogen lone pair on the (alkoxysilyl)amido ligands (for which charge delocalization within the ligand is negligible) is available for additional bonding with the metal. This is supported by the Y−N bond order of 1.11, which suggests a considerably stronger Y−N interaction in $[H_2Si(NH)(OH)]_2YCH_3$ than in $[HC(NH)_2]_2YCH_3$ (Y−N bond order = 0.74−0.78). The axial oxygen atoms (O1, O2) are also bonded to yttrium through two molecular orbitals (one molecular orbital involves yttrium p_x and contributions of the oxygen ($p_y + p_x + s$) orbitals while the other contains yttrium p_x and oxygen (mainly) p_z contributions). However, the Y−O bond order (0.51) clearly indicates that the Y−O interactions are much weaker than those between Y and N. The calculations clearly show that the ether functions do not coordinate strongly to yttrium and suggests that the bidentate bonding of the benzamidinato ligands is much stronger than that of the (alkoxysilyl)amido ligands.

Table 3. Atomic Orbital Contributions (Squares) in Localized Ligand−Metal Bonding Molecular Orbitals of $[H_2Si(NH)(OH)]_2YCH_3$

(contribution)^2 Y		(contribution)^2 ligand		
p_x	0.04	O1, O2	p_y	0.28
			p_x	0.27
			s	0.22
			p_z	0.14
p_x	0.03	O1, O2	p_z	0.48
			s	0.18
			p_x	0.14
			p_y	0.13
d_{yz}	0.05	N1, N2	p_y	0.50
			s	0.19
			p_x	0.06
			p_z	0.06
p_y	0.05	N1, N2	p_z	0.59
s	0.03		s	0.17
$d_{(x^2-y^2)}$	0.03			

The Y−C$_\sigma$ bond in $[H_2Si(NH)(OH)]_2YCH_3$ is very similar to those in $[HC(NH)_2]_2YCH_3$ and $[C_5H_5]_2YCH_3$.[4b] Only the Mulliken charge distributions for the Y−C bonds of these complexes are significantly different (Table 4). Since the observed differences are quite large, the Mulliken population analyses can be used to qualitatively compare the polarity of the Y−C$_\sigma$ bonds. Whereas the charge at the CH_3 group remains practically the same throughout the series of complexes studied, the formal charge on yttrium differs significantly (Table 4). Consequently, the charge separation within the Y−C bond in $[H_2Si(NH)(OH)]_2YCH_3$ (Δq_{Y-C} = 0.98 e) is larger than in $[C_5H_5]_2YCH_3$ (Δq_{Y-C} = 0.73 e) and comparable to that in $[HC(NH)_2]_2YCH_3$ (Δq_{Y-C} = 1.06 e). Hence, the Y−C bond in $[C_5H_5]_2YCH_3$ can be considered to be less polar than that in $[H_2Si(NH)(OH)]_2YCH_3$ and $[HC(NH)_2]_2YCH_3$. It is not only the

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(39) Deelman, B.-J.; Teuben, J. H.; Macgregor, S. A.; Eisenstein, O. *New. J. Chem.* **1995**, *19*, 691 and references cited therein.

Table 4. Y−C σ-Bond: Atomic Orbital Contributions (Squares), Bond Orders (b.o.), Mulliken Formal Charges (*q*) and Calculated Bond Dissociation Enthalpies (kcal·mol^{-1})

complex	(contribution)^2 C		(contribution)^2 Y		b.o.	q_{CH_3}	q_Y	Δq_{Y-C}	q_L	E_{calcd}
$[C_5H_5]_2YCH_3$	p_z	0.459	d_{z^2}	0.142	1.03	−0.25	+0.48	0.73	−0.12	120
	s	0.149	p_z	0.138						
		s	0.108							
$[HC(NH)_2]_2YCH_3$	p_z	0.471	d_{z^2}	0.144	1.03	−0.26	+0.80	1.06	−0.27	120
	s	0.148	p_z	0.118						
		s	0.116							
$[H_2Si(NH)(OH)]_2YCH_3$	p_z	0.472	p_z	0.149	1.01	−0.29	+0.69	0.98	−0.20	116
	s	0.153	d_{z^2}	0.115						
		s	0.105							

Table 5. Details of the X-ray Structure Determination of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (6) and $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu(N,N')\text{-}N(H){-}C(Me){=}C(H){-}C{\equiv}NH)\}_2$ (11)

	6	**11**
formula	$C_{27}H_{67}N_2O_2Si_4Y$	$(C_{24}H_{53}N_4O_2Si_2Y)_2$
mol wt	653.09	1149.58
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1/n$
a, Å	11.422(1)	9.351(1)
b, Å	32.986(1)	32.049(2)
c, Å	11.572(1)	11.384(5)
β, deg	119.67(1)	109.838(5)
V, Å^3	3788.3(6)	3209.2(5)
D_{calcd}, g·mol^{-3}	1.145	1.190
Z	4	2
F(000)	1416	1232
μ(Mo *K*α), cm^{-1}	16.9	19.24
cryst size, mm	0.37 × 0.45 × 0.50	0.25 × 0.36 × 0.40
wavelength, Å	0.710 73	0.710 73
monochromator	graphite	graphite
T, K	130	130
θ range; min max, deg	1.24, 26.5	1.27, 27.0
ω/2θ scan, deg	$\Delta\omega = 0.95 + 0.34 \tan\theta$	$\Delta\omega = 0.85 + 0.35 \tan\theta$
data set	*h*, 0−14; *k*, 0−41; *l*, −14 to 12	*h*, 0−11; *k*, −1 to 40; *l*, −14 to 13
no. of total data	8403	7890
no. of unique data	7988	6951
no. of obsd data ($I \geq 2.5\sigma(I)$)	6068	4684
R1 ($\Sigma(I - \bar{I})/\Sigma I$)	0.079	0.030
R2 ($\Sigma\sigma/\Sigma I$)	0.048	0.048
no. of equiv reflns	790	1358
no. of refined params	560	458
Final agreement factors:		
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.110	0.052
$wR = [\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma w\|F_o\|^2]^{1/2}$	0.096	0.047
weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$	5.336	2.49(2)
m = no. of observations		
n = no. of variables		
residual electron density in final diff Fourier map, e/Å^3	−1.75, 1.20	−1.63, 1.11
max (shift/σ) final cycle	0.1052	0.0506
average (shift/σ) final cycle	0.0635	0.218 × 10^{-2}

Y−C bonds in $[HC(NH)_2]_2YCH_3$ and $[H_2Si(NH)(OH)]_2YCH_3$ which seem to be more polar; the formal charges at $HC(NH)_2$ ($q_L = -0.27$ e) and $H_2Si(NH)(OH)$ ($q_L = -0.20$ e) are also higher than that at C_5H_5 ($q_L = -0.12$ e), rendering these complexes more ionic than $[C_5H_5]_2YCH_3$. The higher negative charge at the benzamidinato and (alkoxysilyl)amido ligands probably originates from the high electronegativity of nitrogen and oxygen. As a consequence of the high positive charge at yttrium in the bis(benzamidinato) and bis((alkoxysilyl)amido)yttrium complexes, the yttrium orbitals are more contracted, which could explain the low tendency to engage in σ-bond metathesis (low hydrogenolysis rate, no solvent metalation, or H/D exchange) and insertion chemistry and the absence of agostic interactions in these molecules. Hence, the bis((alkoxysilyl)amido) systems resemble much more the bis(benzamidinato) than the bis(cyclopentadienyl) system, while the localized negative charge at the nitrogen atoms of the (alkoxysilyl)amido ligands renders them very basic. As a consequence, the (alkoxysilyl)amido ligands are not inert spectators but compete with the Y−C bond in protolysis reactions, a feature that was not observed for benzamidinato or cyclopentadienyl ligands.

Concluding Remarks

This investigation shows that *N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido ligands can be used to stabilize a variety of Y−X (X = C, heteroatom) bonds in the form of compounds $[Me_2Si(NCMe_3)(OCMe_3)]_2YX$. With respect to the shape and fluxionality, the (alkoxysilyl)amido ligands resemble the benzamidinato ligands in $[PhC(NSiMe_3)_2]_2YX$ more closely than the Cp* ligands in bis(pentamethylcyclopentadienyl) compounds Cp^*_2YX. However, reactivity studies on $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**) clearly demonstrate the limited suitability of (alkoxysilyl)amido ligands to be applied as inert spectator ligands in catalysis. They are quite reactive due to their high Brønsted base character. For instance, when weakly acidic hydrogen atoms are available on a substrate molecule, rapid protolysis and loss of alkoxysilylamine, $Me_2Si(N(H)CMe_3)(OCMe_3)$, is observed. Another disadvantage of the (alkoxysilyl)amido ligand is that it is quite labile and is transferred easily to other metal centers, as is illustrated by the disproportionation observed during the hydrogenolysis of **6** which results in formation of the tris((alkoxysilyl)amido)yttrium complex $[Me_2Si(NCMe_3)(OCMe_3)]_3Y$ (**8**). Finally, the (alkoxysilyl)amido ligand has a limited thermal stability since it degrades at elevated temperatures to give isobutene and other so far unidentified products. The low stability of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (**6**) with respect to protolysis, thermolysis, and ligand exchange is mainly due to electronic effects. Calculations show that for the (alkoxysilyl)amido ligands, the negative charge is almost completely located at nitrogen since charge delocalization within the N−Si−O fragment is much less effective than that in the N−C−N fragment of the benzamidinato ligand. Consequently, the (alkoxysilyl)amido ligands behave as classical Brønsted bases, strong enough to activate $C(sp^3)$−H bonds. As calculated for the bis(benzamidinato) series $[PhC(NSiMe_3)_2]_2YX$, the yttrium atom in the bis((alkoxysilyl)amido) compounds has a high positive charge, rendering the system very ionic. The result is that the yttrium orbitals are strongly contracted with, as consequence, a low tendency of (alkoxysilyl)amido-stabilized compounds to engage in σ-bond metathesis reactions (low hydrogenolysis rate, no solvent metalation, or H/D exchange). Also, the absence of agostic interactions, the facile ligand exchange, and the high Brønsted acid base reactivity attributed to the high ionicity of these molecules.

Experimental Section

General Comments. For general aspects of the methods and techniques used, see ref 4b. $YCl_3 \cdot THF_{3.5}$ was prepared by continuous extraction of anhydrous YCl_3[40] with THF. $[Me_2Si(NCMe_3)(OCMe_3)]Li$ was prepared using literature procedures.[5a] ^{89}Y NMR spectra were measured at 25 °C using 10 mm sample tubes containing 2.5 mL of 4.5−5.5 M solutions in benzene-d_6. Because of the negative nuclear Overhauser effect of ^{89}Y, the decoupler was not used. The very long relaxation times observed for ^{89}Y forced us to use delays between $\pi/2$ pulses of 300 s. Data collection is further hindered by acoustic ringing (seen as a rolling base line). Chemical shifts are reported with respect to a 2.0 M sample of YCl_3 in D_2O. To achieve a signal-to-noise ratio of at least 30, 100−300 transients were accumulated.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}Cl)_2Li \cdot THF_2$ (1). At −80 °C, $[Me_2Si(NCMe_3)(OCMe_3)]Li$ (9.5 g, 45.5 mmol) was added to a suspension of $YCl_3 \cdot THF_{3.5}$ (9.9 g, 22.1 mmol) in THF (150 mL). The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was removed *in vacuo*, and the residual sticky solid was extracted with diethyl ether (125 mL). Concentration and cooling to −30 °C afforded **1** as a colorless crystalline material (13.0 g, 18.2 mmol, 82%). IR (KBr/Nujol, cm^{-1}): 1356 (m), 1250 (m), 1181 (m), 1051 (s), 941 (s), 849 (s), 820 (m), 768 (m), 729 (s), 669 (w), 613 (w), 521 (w), 492 (w). ^1H NMR (benzene-d_6, δ, ppm): 3.85 (m, 8H, THF-α-CH_2), 1.54 (s, 18H, $C(CH_3)_3$), 1.49 (s, 18H, $C(CH_3)_3$), 1.38 (m, 8H, THF-β-CH_2), 0.53 (s, 6H, $Si(CH_3)_2$), 0.43 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6, δ, ppm): 77.5 (s, $C(CH_3)_3$), 69.9 (t, THF-α-CH_2, $^1J_{C-H}$ =147 Hz), 52.1 (s, $C(CH_3)_3$), 37.0 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 123 Hz), 32.0 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 126 Hz), 25.3 (t, THF-β-CH_2, $^1J_{C-H}$ = 133 Hz), 8.3 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 117 Hz), 7.5 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd for $C_{28}H_{64}Cl_2LiN_2O_4Si_2Y$: C, 46.99; H, 9.01; Y, 12.42. Found: C, 47.35; H, 9.03; Y, 12.41.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCl \cdot THF$ (2). Compound **1** (1.0 g, 1.40 mmol) was dissolved in pentane (25 mL) and heated to reflux for 1 h, during which time a salt precipitated. The volatiles were removed *in vacuo*, and the product was extracted with pentane (25 mL). Concentration and cooling to −30 °C yielded **2** (0.7 g, 1.16 mmol, 83%) as colorless crystals. IR (KBr/Nujol, cm^{-1}): 1395 (w), 1356 (m), 1246 (m), 1219 (m), 1198 (m), 1181 (m), 1053 (s), 1036 (m), 1020 (m), 941 (s), 910 (m), 851 (s), 822 (s), 766 (m), 731 (s), 655 (w), 613 (w), 521 (w), 492 (w). ^1H NMR (benzene-d_6, δ, ppm): 4.03 (m, 4H, THF-α-CH_2), 1.53 (s, 18H, $C(CH_3)_3$), 1.47 (s, 18H, $C(CH_3)_3$), 1.36 (m, 4H, THF-β-CH_2), 0.50 (s, 6H, $Si(CH_3)_2$), 0.42 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6, δ, ppm): 78.0 (s, $C(CH_3)_3$), 70.9 (t, THF-α-CH_2, $^1J_{C-H}$ = 148 Hz), 52.1 (s, $C(CH_3)_3$), 36.9 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 124 Hz), 31.7 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 126 Hz), 25.0 (t, THF-β-CH_2, $^1J_{C-H}$ 134), 8.0 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 117 Hz), 7.5 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 118 Hz). ^{89}Y NMR (benzene-d_6, δ, ppm): 458. Anal. Calcd for $C_{24}H_{56}ClN_2O_3Si_2Y$: C, 47.94; H, 9.39; Cl, 5.90; Y, 14.79. Found: C, 47.73; H, 9.29; Cl, 6.00;Y, 14.88.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2YBH_4 \cdot THF$ (3). An ether solution (75 mL) of **2** (1.4 g, 2.4 mmol) was stirred for 2 h with excess $LiBH_4$ (0.35 g, 16 mmol) at room temperature and subsequently heated to reflux for 10 min. Then, the volatiles were removed *in vacuo*, and the white residue was extracted with pentane (50 mL). Cooling to −30 °C yielded **3** (1.1 g, 1.9 mmol, 79%) as colorless crystals. IR (KBr/Nujol, cm^{-1}): 2398 (w), 2224 (w), 1395 (m), 1358 (w), 1254 (s), 1196 (s), 1049 (s), 1020 (m), 937 (s), 849 (s), 822 (s), 766 (m), 731 (s), 665 (w), 613 (w), 521 (w), 490 (w). ^1H NMR (benzene-d_6, δ, ppm): 3.73 (m, 4H, THF-α-CH_2), 1.45 (s, 18H, $C(CH_3)_3$), 1.43 (s, 18H, $C(CH_3)_3$), 1.38 (m, 4H, THF-β-CH_2), 1.27 (q, 4H, BH_4, $^1J_{B-H}$ = 84 Hz), 0.42 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6, δ, ppm): 79.0 (s, $C(CH_3)_3$), 68.5 (t, THF-α-CH_2, $^1J_{C-H}$ = 148 Hz), 52.3 (s, $C(CH_3)_3$), 36.8 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 124 Hz), 31.7 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 126 Hz), 25.6 (t, THF-β-CH_2, $^1J_{C-H}$ = 148), 7.8 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 119 Hz). Anal. Calcd for $C_{24}H_{60}BN_2O_3Si_2Y$: C, 49.65; H, 10.42; N, 4.82; Y, 15.31. Found: C, 48.95; H, 10.28; N, 4.89; Y, 15.70.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(O\text{-}2,6\text{-}(CMe_3)_2C_6H_3)$ (4). $2,6\text{-}(CMe_3)_2C_6H_3OH$ (0.59 g, 2.86 mmol) was dissolved in ether (80 mL) and treated with *n*-BuLi (1.2 mL, 2.5 M in hexanes, 3.0 mmol). The white suspension was stirred for 15 min, after which the ether was removed *in vacuo*. The white residue was suspended in toluene (20 mL). At −80 °C, **2** (1.73 g, 2.88 mmol) was added. The mixture was allowed to warm to room temperature and subsequently stirred for 20 h. The toluene was evaporated, and the sticky residue was stripped with 10 mL of pentane. The white solid obtained was extracted with pentane (20 mL), and the washings were concentrated at room temperature until crystallization started. Slow cooling to −30 °C yielded **4** (1.09 g, 1.56 mmol, 55%) as large colorless crystals. IR (KBr/Nujol, cm^{-1}): 3054 (m), 2726 (w), 1643 (w), 1584 (w), 1416 (s), 1381 (m), 1358 (m), 1273 (s), 1252 (s), 1225 (m), 1202 (s), 1177 (m), 1125 (w), 1099 (w), 1059 (s), 1024 (m), 928 (s), 912 (s), 853 (s), 820 (s), 806 (m), 768 (m), 746 (m), 735 (s), 658 (m), 613 (m), 546 (w), 525 (w), 492 (w), 469 (w), 421 (w). ^1H NMR (benzene-d_6, δ,ppm): 7.31 (d, 2H, Ar, $^3J_{HH}$ = 7.7 Hz), 6.77 (t, 1H, Ar, $^3J_{HH}$ = 7.7 Hz), 1.66 (s, 18H, $C(CH_3)_3$), 1.44 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$), 0.45 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6, δ, ppm): 137.0 (s, Ar), 126.7 (d, Ar, $^1J_{CH}$ = 154 Hz), 116.4 (d, Ar, $^1J_{CH}$ = 156 Hz), 78.3 (s, $C(CH_3)_3$), 52.1 (s, $C(CH_3)_3$), 37.3 (q, $C(CH_3)_3$, $^1J_{CH}$ = 123 Hz), 36.3 (s, $C(CH_3)_3$), 34.8 (q, $C(CH_3)_3$, $^1J_{CH}$ = 125 Hz), 32.4 (q, $C(CH_3)_3$, $^1J_{CH}$ = 126 Hz), 8.3 (q, $Si(CH_3)_2$, $^1J_{CH}$ = 118 Hz). ^{89}Y NMR (benzene-d_6, δ, ppm): 399. Anal. Calcd for

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$C_{34}H_{69}N_2O_3Si_2Y$: C, 58.42; H, 9.95; N, 4.01; Y, 12.72. Found: C, 57.89; H, 9.93; N, 3.89; Y, 12.64.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(N(SiMe_3)_2)$ (5). To a solution of **2** (2.92 g, 4.85 mmol) in toluene (50 mL), $NaN(SiMe_3)_2$ (0.891 g, 4.86 mmol) was added at −80 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was evaporated, and the residue was extracted with pentane (50 mL). Concentration to 5 mL and subsequent cooling to −30 °C yielded **5** (1.9 g, 2.9 mmol, 60%) as colorless crystals. IR (KBr/Nujol, cm^{-1}): 2955 (s), 2926 (s), 2855 (s), 1356 (w), 1252 (s), 1225 (w), 1200 (w), 1177 (m), 1132 (w), 1053 (m), 1022 (m), 955 (m), 930 (s), 912 (m), 878 (w), 853 (s), 820 (s), 768 (m), 735 (m), 683 (w), 665 (w), 604 (w), 550 (w), 525 (w), 492 (w). ^1H NMR (benzene-d_6, 80 °C, δ, ppm): 1.42 (s, 36H, $C(CH_3)_3$), 0.41 (s, 12H, $Si(CH_3)_2$), 0.36 (s, 18H, $N(Si(CH_3)_3)_2$). ^{13}C NMR (benzene-d_6, 80 °C, δ, ppm): 78.2 (s, $C(CH_3)_3$), 52.4 (s, $C(CH_3)_3$), 37.2 (q, $C(CH_3)_3$, $^1J_{CH} = 126$ Hz), 32.6 (q, $C(CH_3)_3$, $^1J_{CH} = 125$ Hz), 8.4 (q, $Si(CH_3)_2$, $^1J_{CH} = 119$ Hz), 7.2 (q, $N(Si(CH_3)_3)_2$, $^1J_{CH} = 118$ Hz). Anal. Calcd for $C_{26}H_{66}N_3O_2Si_4Y$: C, 47.74; H, 10.17; Y, 13.59. Found: C, 47.45; H, 10.13; Y, 13.78.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (6). To a toluene (70 mL) solution of **2** (3.0 g, 5.0 mmol), $LiCH(SiMe_3)_2$ (0.80 g, 4.8 mmol) was added at −80 °C. After the reaction mixture was warmed to room temperature, the mixture was stirred overnight. The volatiles were removed *in vacuo*, and the remaining solid was extracted with pentane (70 mL). Concentration and cooling to −30 °C afforded colorless crystals of **6** (2.75 g, 4.2 mmol, 84%). Repeated recrystallization from pentane yielded colorless crystals of **6** suitable for an X-ray diffraction study. IR (KBr/Nujol, cm^{-1}): 1395 (w), 1358 (m), 1252 (s), 1202 (m), 1177 (m), 1055 (s), 1022 (m), 928 (s), 912 (s), 851 (s), 768 (s), 735 (s), 662 (w), 613 (w), 590 (w), 523 (w), 490 (w). ^1H NMR (benzene-d_6, 80 °C, δ, ppm): 1.40 (s, 18H, $C(CH_3)_3$), 1.38 (s, 18H, $C(CH_3)_3$), 0.39 (s, 6H, $Si(CH_3)_2$), 0.36 (s, 6H, $Si(CH_3)_2$), 0.32 (s, 18H, $CH(Si(CH_3)_3)_2$). ^{13}C NMR (benzene-d_6, 80 °C, δ, ppm): 77.9 (s, $C(CH_3)_3$), 52.6 (s, $C(CH_3)_3$), 37.3 (q, $C(CH_3)_3$, $^1J_{C-H} = 124$ Hz), 32.8 (q, $C(CH_3)_3$, $^1J_{C-H} = 126$ Hz), 8.5 (q, $Si(CH_3)_2$, $^1J_{C-H} = 119$ Hz), 8.3 (q, $Si(CH_3)_2$, $^1J_{C-H} = 119$ Hz), 6.5 (q, $CH(Si(CH_3)_3)_2$, $^1J_{C-H} = 119$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 80 °C, δ): 33.8 (d, $CH(SiMe_3)_2$, $^1J_{Y-C} = 30$ Hz). ^{89}Y NMR (benzene-d_6, δ, ppm): 645. Anal. Calcd for $C_{27}H_{67}N_2O_2Si_4Y$: C, 49.66; H, 10.34; N, 4.29; Y, 13.61. Found: C, 49.44; H, 10.35; N, 4.42; Y, 13.89.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_3Y$ (8). In a 25 mL flask equipped with a Teflon valve, **6** (0.99 g, 1.5 mmol) was dissolved in cyclohexane (7 mL), cooled to −196 °C, and put under 1 atm of dihydrogen. After a 3 days at 50 °C, the volatiles were removed *in vacuo* and the solid residue was redissolved in hot cyclohexane (7 mL). Slow cooling to room temperature yielded **8** (0.30 g, 0.6 mmol, 60%) as block-shaped, colorless crystals. IR (KBr/Nujol, cm^{-1}): 1252 (s), 1223 (m), 1179 (s), 1042 (s), 1018 (s), 930 (s), 914 (m), 822 (s), 762 (s), 729 (s), 660 (w), 610 (w), 523 (w), 488 (w). ^1H NMR (cyclohexane-d_{12}, δ, ppm): 1.54 (s, 27H, $C(CH_3)_3$), 1.43 (s, 27H, $C(CH_3)_3$), 0.47 (s, 9H, $Si(CH_3)_2$), 0.38 (s, 9H, $Si(CH_3)_2$). ^{13}C NMR (cyclohexane-d_{12}, δ, ppm): 76.2 (s, $C(CH_3)_3$), 53.1 (s, $C(CH_3)_3$), 37.85 (q, $C(CH_3)_3$, $^1J_{C-H} = 124$ Hz), 33.6 (q, $C(CH_3)_3$, $^1J_{C-H} = 125$ Hz), 9.61 (q, $Si(CH_3)_2$, $^1J_{C-H} = 116$ Hz), 9.22 (q, $Si(CH_3)_2$, $^1J_{C-H} = 118$ Hz). Anal. Calcd for $C_{30}H_{72}N_3O_3Si_3Y$: C, 51.77; H, 10.43; Y, 12.77. Found: C, 54.88; H, 10.81; Y, 12.55.

Reaction of 6 with HC≡CR: Formation of $\{Y(\mu\text{-}C{\equiv}CR)_3\}_n$ (R = $SiMe_3$ (9), CMe_3 (10)). In a round-bottomed flask equipped with a Teflon valve, **6** (600 mg, 0.92 mmol) was dissolved in benzene (20 mL). At room temperature, $HC{\equiv}CSiMe_3$ (520 μL, 3.7 mmol) was added and the reaction mixture was kept at 50 °C for 3 days. After the volatiles had been removed *in vacuo*, the remaining solid was washed with pentane (3 × 10 mL), yielding $\{Y[\mu\text{-}C{\equiv}CSiMe_3]_3\}_n$ (**9**, 250 mg, 0.53 mmol, 70%) as a pale yellow solid. IR (KBr/Nujol, cm^{-1}): 2045 (w), 1995 (w), 1412 (w), 1248 (m), 851 (s), 764 (m), 700 (w), 656 (s), 579 (m). Anal. Calcd for $C_{15}H_{27}Si_3Y$: C, 47.34; H, 7.15; Y, 22.36. Found: C, 47.21; H, 7.38; Y, 22.93. An NMR tube study of the reaction showed the formation of $Me_2(N(H)CMe_3)(OCMe_3)$ and $H_2C(SiMe_3)_2$ in a 2:1 ratio. The formation of $Me_2Si(N(H)CMe_3)(OCMe_3)$ and $H_2C(SiMe_3)_2$ was confirmed by GC/MS analysis.

The reaction of **6** with $HC{\equiv}CCMe_3$ was performed analogously, with 528 mg (0.81 mmol) of **6** and 400 μL (3.24 mmol) of $HC{\equiv}CCMe_3$, yielding $\{Y[\mu\text{-}C{\equiv}CCMe_3]_3\}_n$ (**10**, 250 mg, 0.75 mmol, 94%) as a white powder. IR (KBr/Nujol, cm^{-1}): 2047 (s), 1364 (m), 1242 (s), 1204 (m), 714 (m), 422 (m). Anal. Calcd for $C_{18}H_{27}Y$: C, 65.06; H, 8.19; Y, 26.75. Found: C, 63.17; H, 8.27; Y, 25.61. The formation of $Me_2Si(N(H)CMe_3)(OCMe_3)$ and $H_2C(SiMe_3)_2$ (2:1 ratio) was confirmed by ^1H NMR spectroscopy and GC/MS analysis.

Reaction of 6 with HC≡CPh: Formation of Polyphenylacetylene. In a round-bottomed flask equipped with a Teflon valve, **6** (180 mg, 0.28 mmol) was dissolved in phenylacetylene (10 mL, 91 mmol). After 2 days at room temperature, the volatiles were removed *in vacuo*, leaving a black residue (1 g). The solid was redissolved in chloroform (20 mL) and quenched with 1,1-dimethylethanol (2 mL). Filtration yielded about 100 mg of insoluble polymer. IR (KBr/Nujol, cm^{-1}): 1597 (m), 1489 (s), 1443 (s), 1381 (w), 1262 (m), 1094 (w), 1072 (s), 1028 (s), 916 (m), 841 (w), 754 (s), 694 (s). GPC measurements of the chloroform soluble fraction showed two distinct fractions with narrow dispersity: $M_w = 780 \pm 20$ $g{\cdot}mol^{-1}$, $M_w/M_n = 1.2$; $M_w = 21\,750 \pm 350$ $g{\cdot}mol^{-1}$, $M_w/M_n = 1.7$.

Preparation of $\{([Me_2Si(NCMe_3)(OCMe_3)]_2Y)(\mu(N,N')\text{-}NH{-}CMe{=}CH{-}C{\equiv}N)\}_2$ (11). To a solution of **6** (1.1 g, 1.7 mmol) in THF (10 mL), $CH_3C{\equiv}N$ (0.5 mL, 9.6 mmol) was added at room temperature. After 12 h, colorless crystals had precipitated from the yellowish solution. Filtration and washing with pentane yielded **11** (0.30 g, 0.26 mmol, 31%) as bar-shaped crystals. IR (KBr/Nujol, cm^{-1}): 3470 (w), 3351 (w), 3250 (w), 2965 (w), 2184 (s), 1643 (s), 1599 (s), 1425 (s), 1314 (w), 1262 (s), 1202 (w), 1026 (s), 812 (w), 801 (s), 766 (m), 677 (w), 598 (w), 548 (w). ^1H NMR (THF-d_8, δ, ppm): 6.45 (s, 1H, N*H*), 3.32 (s, 1H, C*H*), 2.11 (s, 3H, CH_3), 1.37 (m, 36H, $OC(CH_3)_3$ and $NC(CH_3)_3$), 0.33 (m, 12H, $Si(CH_3)_2$). ^{13}C NMR (THF-d_8, δ, ppm): 179.3 (s, C≡N), 134.5 (s, $C(CH_3){=}CH$), 78.4 (s, $OC(CH_3)_3$), 53.9 (s, $NC(CH_3)_3$), 49.0 (d, *C*H, $^1J_{C-H} = 172$ Hz), 38.76 (q, $OC(CH_3)_3$, $^1J_{C-H} = 128$ Hz), 38.1 (q, $OC(CH_3)_3$, $^1J_{C-H} = 125$ Hz), 33.67 (q, $NC(CH_3)_3$, $^1J_{C-H} = 126$ Hz), 27.95 (q, $C(CH_3){=}C$, $^1J_{C-H}$ 127 Hz), 9.1 (q, $Si(CH_3)_2$, $^1J_{C-H} = 115$ Hz). Anal. Calcd for $(C_{24}H_{53}N_4O_2Si_2Y)_2$: C, 50.15; H, 9.29; Y, 15.47. Found: C, 51.10; H, 9.36; Y, 15.51.

Molecular Orbital Calculations. All molecular orbital calculations were performed with ZINDO94 installed on a HP-750 workstation. The theoretical gamma's, provided by the program, were used.[38] The bond lengths and angles of $[H_2Si(NH)(OH)]^{\bullet}$ and $[H_2Si(NH)(OH)]_2YCH_3$ were taken from X-ray crystal structure data from **6**. The symmetry of the model was restricted to C_2. The Cartesian coordinates of $[H_2Si(NH)(OH)]_2YCH_3$ and Mulliken population analysis can be found in the Supporting Information.

Structure Determination of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(CH(SiMe_3)_2)$ (6). A suitable crystal was measured at 130 K on an Enraf-Nonius CAD-4F diffractometer equipped with a low-temperature unit.[41] The crystals reflected well but showed a high background scattering caused by fluorescence of the Y atoms. Unit cell parameters and orientation matrix were determined from a least-squares treatment of the SET4 setting angles[42] of 22 reflections in the range 11.90° < σ < 18.44°.

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The unit cell was identified as monoclinic, space group $P2_1$.[43] Intensity data were corrected for Lorentz and polarization effects and scale variation but not for absorption. The variance $\sigma^2(I)$ was calculated on the counting statistics plus an instability constant[44] term $(0.0185I)^2$ as derived from the excess variance in the reference reflections. Equivalent reflections were averaged and stated observed if satisfying the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[45] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (*CRYLSQ*),[46] minimizing the function $Q = \sum_h [w(|F_o| - k|F_c|)^2]$. The difference-Fourier map indicated disorder for the methyl groups bonded to C(7) and C(44). Other disorder features were not fully recognized, did not converge in the refinement, or could not have a resolvable disorder stated. All hydrogen atoms (except those bonded to C(21) and C(48)) were included in the refinement. Placed at idealized positions with a fixed isotropic thermal displacement parameter, they were used in the structure factor calculations but were not refined. Refinement on F_o by full-matrix block-diagonal least-squares techniques with anisotropic or isotropic thermal displacement parameters for the non-hydrogen atoms and one common isotropic thermal displacement parameter ($U = 0.05$ Å^2) for the hydrogen atoms converged at $R_F = 0.110$ (wR = 0.096). Disorder in the crystal lattice, a long axis combined with a high mosaic spread, prevented an accurate solution of the structure. Scattering factors were taken from Cromer and Mann.[47] Anomalous dispersion factors were taken from Cromer and Liberman.[48] All calculations were carried out on a CDC-Cyber 962-31 computer at the University of Groningen with the program packages Xtal,[49] PLATON,[50] and ORTEP.[51]

Structure Determination of {[$Me_2Si(NCMe_3)(OCMe_3)]_2$-Y($\eta^2$(*N*,*N*′)-NH−CMe=CH−C≡N)}$_2$ (11). The general procedures for solving the structure were as outlined above. Precise lattice parameters and their standard deviation were derived from the angular settings of 22 reflections in the range 11.67° < σ < 16.84°. The monoclinic unit cell (spacegroup $P2_1/n$) was checked for higher symmetry.[43] A correction for absorption was judged not to be necessary in view of the observed small intensity variation (11%) for a 360° Ψ-scan of the close to axial reflection (2,−2,−1). The structure was solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[45] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ)[46] minimizing the function $Q = \sum_h [w(|F_o| - k|F_c|)^2]$. Final refinement on F_o by full-matrix least-squares techniques. Anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms converged at $R_F = 0.052$ (wR = 0.047). Eight reflections with $w(F_o - 2F_c > 20)$ were excluded from the final cycle: the mismatch is probably due to problems during the data collection and may be due to overlapping scans (a long monoclinic axis).

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Supporting Information Available: Tables of Cartesian coordinates and Mulliken population analysis of $[H_2Si(NH)(OH)]_2YCH_3$ and all atomic coordinates, thermal displacement parameters, bond distances, and bond and torsion angles for **6** and **11** (46 pages). Ordering information is given on any current masthead page.

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(43) No higher metric lattice symmetry or extra metric symmetry elements were found, see: (a) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578. (b) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264. (c) Le Page, Y. *J. Appl. Crystallogr.* **1988**, *21*, 983.

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