Synthesis and Reactivity of Bis(alkoxysilylamido)yttrium η^2-Pyridyl and η^2-α-Picolyl Compounds

Robbert Duchateau, Edward A. C. Brussee, Auke Meetsma, and Jan H. Teuben*

Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

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The synthesis and reactivity of bis(alkoxysilylamido)yttrium pyridyl and α-picolyl complexes $[Me_2Si(NCMe_3)(OCMe_3)]_2YR$ (R = η^2-(*C,N*)-2-NC_5H_4 (**1**); R = η^2-(*C,N*)-CH_2-2-NC_5H_4 (**2**); R = η^2-(*C,N*)-C(H)Me-2-NC_5H_4 (**3**); R = η^2-(*C,N*)-C(H)Me-2-NC_5H_3-6-Me (**4**)) is reported. **1**−**4** have been prepared by C−H activation of pyridine and the corresponding methyl (ethyl) and dimethyl-substituted pyridines from $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ and by salt metathesis with the appropriate lithium salts from $[Me_2Si(NCMe_3)(OCMe_3)]_2YCl\cdot THF$. The molecular structure of **2** shows that the picolyl group is bonded to yttrium in an η^3-aza−allylic fashion. With dihydrogen, stepwise hydrogenation of the pyridyl fragment of **1** has been observed, finally yielding the 2,3-dihydropyridyl complex $[Me_2Si(NCMe_3)(OCMe_3)]_2Y-NC_5H_8$ (**7**). Compound **1** inserts ethene to form the α-methylpicolyl derivative **4**. Polymerization of ethene was not observed. The pyridyl compound **1** reacts with PhC≡CH to yield the corresponding acetylide pyridine complex $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh\cdot Py$ (**8**). The complexed pyridine can be substituted by THF to give $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh\cdot THF$ (**9**), which easily loses THF and forms the base-free acetylide $[Me_2Si(NCMe_3)(OCMe_3)]_2$-YC≡CPh (**10**). Compounds **1** and **2** readily insert nitriles yielding imido−pyridine complexes. The imido−pyridine complexes that contain α-hydrogen readily undergo a 1,3-H shift affording the corresponding enamido−pyridine compounds. With CO, the pyridyl compound **1** gives a dipyridylketone complex $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y\}\{\mu,\eta^2,\eta^2$-(*N,N′*,O)-OC(2-$NC_5H_4)_2\}$ (**15**).

Introduction

Although metallocene derivatives are still the most extensively studied compounds of group 3 metals and lanthanides,[1] there is rapidly growing interest in organometallic compounds of these elements stabilized by other ligands.[2] As part of a study to assess the effect of the ancillary ligand system on the reactivity of yttrium alkyl and hydrido bonds, we recently reported bis(*N,N′*-bis(trimethylsilyl)benzamidinato)yttrium, $[PhC(NSiMe_3)_2]_2YR$,[3] and bis(*N,O*-bis(*tert*-butyl)alkoxy(dimethylsilyl)amido)yttrium complexes, $[Me_2Si(NCMe_3)(OCMe_3)]_2YR$[4] (R = alkyl, hydrido). It was found that the ligand environment has a pronounced influence on the stability and reactivity of the complexes. Whereas benzamidinates form a robust ancillary ligand system, the alkoxysilylamidos are not inert but reactive ligands. For instance, active hydrogen on substrate molecules leads to spectator ligand protonation and loss of alkoxysilylamine $Me_2Si(N(H)CMe_3)(OCMe_3)$. Other typical reactivity features are facile exchange of alkoxysilylamido ligands between metal centers (leading to disproportionation) and limited thermal stability (leading to degradation of the alkoxysilylamido ligands).

In the alkyl compound $[Me_2Si(NCMe_3)(OCMe_3)]_2Y-CH(SiMe_3)_2$, the reactions of the Y−C bond and of the Y−N and N−C bonds of the alkoxysilylamido ligand have about the same activation barrier and it is difficult to study them independently. The possibility of separating these two reactivities is much better for bis(alkoxysilylamido)yttrium pyridyl and picolyl complexes. The reduced steric hindrance (relative to the bis(trimethylsilyl)methyl ligand) and the Y−C-N ring strain of the pyridyl (picolyl) group is expected to increase the reactivity of the Y−C bond, while the bidentate bonding of the pyridyl/picolyl fragment is expected to increase the thermal stability of the complexes.[5]

This paper reports the synthesis and characterization of bis(*N,O*-bis(*tert*-butyl)alkoxy(dimethylsilyl)amido)-yttrium pyridyl and (substituted) α-picolyl complexes.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

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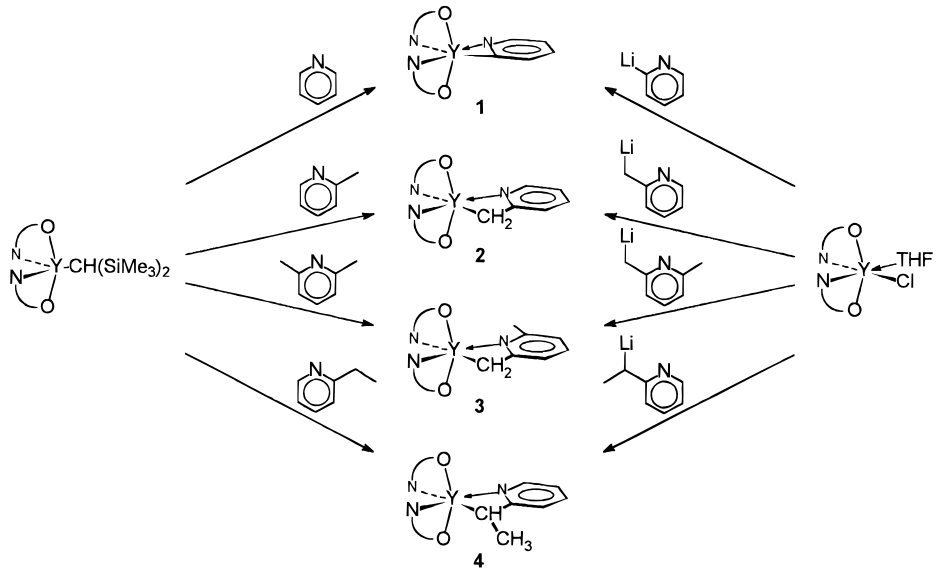
Scheme 1. Synthesis of Bis(alkoxysilylamido)yttrium Pyridyl and α-Picolyl Complexes



Their reactivity has been investigated and compared with the chemistry of $Cp^*_2Ln(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$ (Ln = Sc, Y, Lu),[5,6] $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)]^+$,[7,8] and $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)]^+$.[7,9]

Results and Discussion

Synthesis of Bis(Alkoxysilylamido) Yttrium Pyridyl and α-Picolyl Complexes. (a) Through C−H Bond Activation. Group 3 metal and lanthanide alkyl and hydride complexes easily activate aromatic C−H bonds by σ-bond metathesis.[5−6] This reaction forms an attractive route to new M−C bond containing complexes and appears to be useful for the synthesis of the pyridyl and picolyl complexes reported in this paper. Treatment of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ with (*ortho*-substituted) pyridines (NC_5H_5, 2-Me-NC_5H_4, 2,6-Me_2-NC_5H_3, 2-Et-NC_5H_4) gave the corresponding metalation products **1**−**4** (Scheme 1). However, the reactions had to be carried out at elevated temperatures, and competitive thermal decomposition of the starting compound and the products kept yields (as determined by ^{1}H NMR) low to moderate (**1**, 9%; **2**, 72%; **3**, 65%, **4**, 65%). Interestingly, with α-picoline and 2-ethylpyridine, the α-alkyl group and not the aryl is metalated exclusively to give **2** and **4**, respectively. This is similar to the reaction of $[PhC(NSiMe_3)_2]_2YR$ (R = CH_2Ph·THF, $CH(SiMe_3)_2$) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ with α-picoline[3c] but is in marked contrast with bis(pentamethylcyclopentadienyl) derivatives like Cp^*_2YMe·THF[6c] or $[Cp_2ZrMe$·$THF]^+$,[7] which selectively afford the pyridyl compounds $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)$ and $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)$·$(THF)]^+$, respectively.

(b) Chloride Metathesis of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCl$·THF. Chloride metathesis of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCl$·THF with pyridyl and (substituted) α-picolyl lithium reagents[10] appears to be a much better synthetic method (Scheme 1). Exploratory NMR-tube experiments showed that the reactions are essentially quantitative within hours at room temperature. On a preparative scale, the compounds $[Me_2Si(NCMe_3)(OCMe_3)]_2YR$ (R = η^2-(*C*,*N*)-2-NC_5H_4 (**1**), η^2-(*C*,*N*)-CH_2-2-NC_5H_4 (**2**), η^2-(*C*,*N*)-CH_2-2-NC_5H_3-6-Me (**3**), η^2-(*C*,*N*)-C(H)Me-2-NC_5H_4 (**4**)) could be isolated in moderate to high yields as red-brown or yellow crystals. The success of this method is surprising since earlier attempts to synthesize bis(alkoxysilylamido)yttrium alkyl complexes with alkyl ligands less bulky than the bis(trimethylsilyl)methyl ligand by chloride metathesis invariably failed.[4] Probably, the bidentate bonding of the pyridyl and picolyl groups efficiently blocks coordination of the salt (LiCl) or solvent molecules which often hampers purification.

(c) Characterization of 1−4. All compounds are very air sensitive and are extremely soluble in common organic solvents (pentane, toluene, THF). They are stable at room temperature, but like $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$,[4] they thermolyze rapidly above about 60 °C with degradation of the ancillary ligands to give isobutene, the alkoxysilyamine ($Me_2Si(N(H)CMe_3)(OCMe_3)$), the corresponding (substituted) pyridine, and other, so far not identified products. The NMR data of the pyridine-derived parts of **1**−**4** correspond well with those of $Cp^*_2Ln(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$ (Ln = Sc,[6b,d] Y,[5,6c] Lu[6a]), $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4\text{-}6\text{-}R)]^+$ (R = H, Me),[7] $[PhC(NSiMe_3)_2]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$,[3c] and $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)]^+$,[7] respectively. Due to coupling to Y, the resonance of the *ipso*-carbon of the pyridyl group in **1** appears as a doublet (δ = 226.0 ppm, $^1J_{Y-C}$ = 26 Hz) in the ^{13}C NMR spectrum. For the picolyl complex **2**, the α-CH_2 group also emerges

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(10) Lithiation of pyridine, α-picoline, lutidine, and 2-ethylpyridine were carried out in either pentane, ether, or THF at −80 °C using *n*-BuLi. See also: Colgan, D.; Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1708.

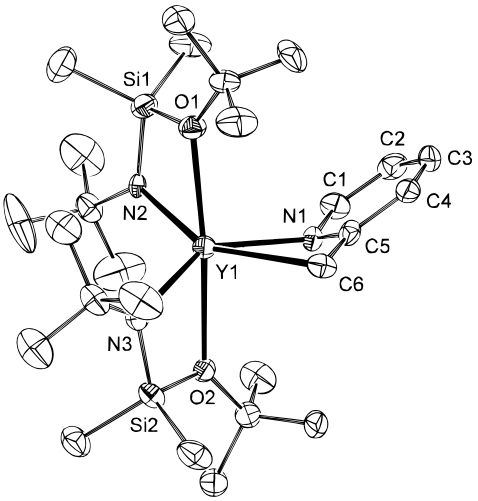

Figure 1. ORTEP drawing of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$-($\eta^2$-(*C,N*)-$CH_2$-2-$NC_5H_4$) (**2**) at the 50% probability level. Hydrogen atoms are omitted for clarity. Relevant carbon atoms are labeled only.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Me_2Si(NCMe_3)(OCMe_3)]_2$-$Y(\eta^2$-(*C,N*)-$CH_2$-2-$NC_5H_4)$ (2)

distances		angles	
Y(1)−O(1)	2.427(4)	Si(1)−Y(1)−Si(2)	138.46(4)
Y(1)−O(2)	2.498(4)	O(1)−Y(1)−N(2)	64.83(12)
Y(1)−N(2)	2.269(4)	O(2)−Y(1)−N(3)	63.53(12)
Y(1)−N(3)	2.243(3)	O(1)−Y(1)−O(2)	174.21(11)
Y(1)−N(1)	2.389(3)	N(2)−Y(1)−N(3)	108.63(13)
Y(1)−C(6)	2.632(5)	O(1)−Y(1)−C(5)	89.62(12)
N(1)−C(1)	1.349(6)	O(2)−Y(1)−C(5)	95.77(12)
N(1)−C(5)	1.386(6)	Y(1)−C(6)−C(5)	84.4(3)
C(1)−C(2)	1.361(7)	N(2)−Y(1)−C(5)	122.59(13)
C(2)−C(3)	1.402(8)	N(3)−Y(1)−C(5)	128.79(13)
C(3)−C(4)	1.359(7)	N(1)−Y(1)−C(6)	56.30(14)
C(4)−C(5)	1.406(7)	N(1)−C(5)−C(6)	115.9(4)
C(5)−C(6)	1.420(7)		

as a doublet (δ = 2.73 ppm, $^2J_{Y-H}$ = 0.9 Hz) in the ^{1}H NMR and as a double-triplet (δ = 52.3 ppm, $^1J_{C-H}$ = 143 Hz, $^1J_{Y-C}$ = 6 Hz) in the ^{13}C NMR spectrum. The observed $^1J_{Y-C}$ in **2** is very small compared with other yttrium carbyl species (bridging carbyls, $^1J_{Y-C}$ = 18−21 Hz; terminal carbyls, $^1J_{Y-C}$ = 23−74 Hz)[3,4,5] and suggests a relatively weak interaction between the methylene fragment and yttrium (*vide infra*). Since the NMR spectra of **1**−**4** are so closely analogous with those of the corresponding $Cp^*_2Ln(\eta^2$-(*C,N*)-$NC_5H_4)$ (Ln = Sc, Y, Lu),[6a,d] $[Cp_2Zr(\eta^2$-(*C,N*)-2-NC_5H_3-6-Me)·$(PMe_3)]^+$,[8c] and $[Cp_2Zr(\eta^2$-(*C,N*)-C(H)Me-2-NC_5H_3-6-Et)$]^+$ [9b] systems, we assume that the pyridyl and picolyl fragments are also η^2-bonded in complexes **1**−**4**. The data of **3** and **4** show no remarkable features, and with chemical shifts and $^1J_{Y-C}$ values strictly comparable to **2**, they are assumed to be structurally very similar to **2**.

To verify the assigned bonding of the α-picolyl fragment, an X-ray structure determination of **2** was carried out. An ORTEP drawing of the molecular structure is shown in Figure 1, and selected bond distances and angles are listed in Table 1. Details concerning the data collection and refinement are given in Table 3. The α-picolyl fragment can be assumed to occupy one coordination vertex and the yttrium regarded in distorted trigonal-pyramidal coordination, with the alkoxysilylamido nitrogens (N(2), N(3)) and the picolyl carbon C(5) in a tilted equatorial plane and the oxygen atoms of the alkoxysilylamido ligands in axial positions. The bonding of the alkoxysilylamido ligands in **2** is similar to that found in other crystallographically characterized bis(*N,O*-bis(*tert*-butyl)alkoxysilylamido) yttrium[4] and -lanthanide[11] derivatives: The alkoxysilylamido ligands form almost planar four-membered rings with yttrium. The short Y−N and long Y−O bonds indicate that the ligands are mainly bonded through the Y−N bonds.[4] Of particular interest is the bonding of the (planar) α-picolyl fragment to yttrium. The Y(1)−C(6) bond (2.632(5) Å) is notably longer than other nonbridging Y−C bonds (ranging from 2.38(2) to 2.558(19) Å),[4,12] whereas Y(1)−N(1) (2.389(3) Å) is very short for a Y←:N(sp^2) dative bond.[13] The weak Y(1)−C(6) interaction is confirmed by the small coupling constant ($^1J_{Y-C}$ = 6 Hz) as compared with other yttrium carbyl species (*vide supra*). The four-membered (Y(1)−N(1)−C(5)−C(6)) ring is folded over an angle of 32.2(5)° along the N(1)−C(6) vector. As a result, the yttrium atom is located 1.55 Å out of the pyridine plane. The exo C(5)−C(6) bond length (1.420(7) Å) is intermediate to that of a regular C−C and C=C bonds. The high value of $^1J_{C-H}$ (143 Hz) found for the methylene group of the picolyl fragment indicates a considerable sp^2 hybridization of this carbon atom. Hence, the bonding of the α-picolyl fragment can be described as a distorted η^3-(*C,C,N*)-aza−allylic interaction. This type of bonding is common in alkali metal and early transition metal α-picolyl complexes and is intermediate between an η^2-alkyl−amine and an η^1-amido−olefin.[10,14]

Reactivity of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(*C,N*)-2-$NC_5H_4)$ (1) and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(*C,N*)-$CH_2$-2-$NC_5H_4)$ (2). Yttrocene and cationic zirconocene pyridyl and picolyl complexes, $Cp^*_2Y(\eta^2$-(*C,N*)-2-$NC_5H_4)$,[5] $[Cp_2Zr(\eta^2$-(*C,N*)-2-NC_5H_3-6-R$]^+$ (R = H, Me),[7,8] and $[Cp_2Zr(\eta^2$-(*C,N*)-C(H)Me-2-NC_5H_3-6-Et$)]^+$,[7,9] have a diverse chemistry which ranges from simple complexation of Lewis bases to catalytic alkylation of pyridine. With **1** and **2** available, we decided to explore their reactivity toward dihydrogen and unsaturated substrates. In order to make a realistic comparison, the reactions selected to be investigated were those reported for the yttrocene and zirconocene pyridyl and α-picolyl derivatives.[7−9]

Dihydrogen. Under dihydrogen (NMR tube experiment, 4 atm, 65 °C), compound **1** was rapidly hydrogenated (96%, 85 min) to yield $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$−$NC_5H_6$ (**5**).[15] This reaction is comparable to the Ziegler alkylation of pyridines by alkyllithium reagents, for

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(12) 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.; Drummond, D. K.; Hanusa, T. P.; Olofson, J. M. *J. Organomet. Chem.* **1989**, *376*, 311.

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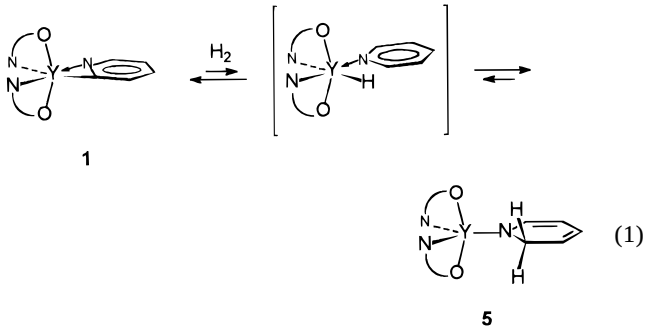
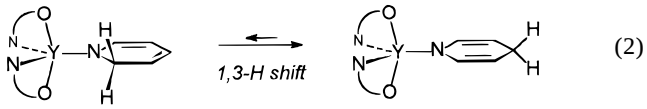
(15) The reaction of **2** and **3** with hydrogen is similar to that observed for **1**, although the reaction rate decreases dramatically with increasing steric bulk. Hence, thermolysis of the complexes becomes substantial. Duchateau, R.; Brussee, E. A. C.; Teuben, J. H. Unpublished results.

which 1,2-addition products of pyridine have been observed as intermediates.[16] Similar 1,2-addition products were obtained when hydrides $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$[3c] and $\{[C_5H_4R]_2Y(\mu\text{-}H)\cdot THF\}_2$ (R = H, Me)[13b] were treated with pyridine, which strongly suggests that **1** is first hydrogenolyzed to the corresponding hydride which subsequently inserts the pyridine (eq 1).[17]



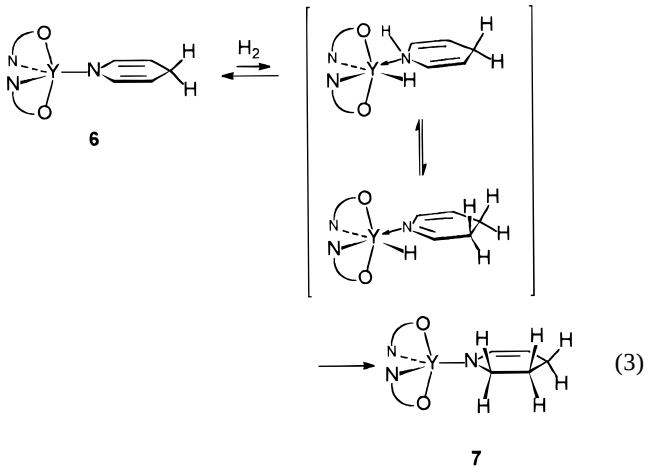
1 **5** (1)

Upon heating (hours, 65 °C), **5** rearranged, presumably by a 1,3-H-shift, to the 1,4-isomer (**6**, eq 2).



5 **6** (2)

Similarly, the hydrides $\{[C_5H_4Me]_2Y(\mu\text{-}H)\cdot THF\}_2$[13b] and $\{Cp^*_2Y(\mu\text{-}H)\}_2$[5,18] reacted with pyridine to form the corresponding 1,4-insertion products. Direct formation of the 1,4-insertion product has not been observed, and this seems to exclude nucleophilic attack at the *para*-position of pyridine (*vide infra*). When **1** was treated with deuterium, incorporation of deuterium was mainly observed at the *ortho* and *para* positions of the pyridyl ligand, indicating that hydrogenolysis of **1** and isomerization of **5** to **6** are reversible (eqs 1 and 2). With excess dihydrogen, **6** was not the final product. Subsequent hydrogenation of one of the double bonds in **6** was observed, affording the 2,3-dihydropyridyl complex **7** (24 h at 65 °C, 50% yield, eq 3). Most likely, formation of **7** follows hydrogenolysis of **6** (eq 3). Although hydrogenolysis of a Ln−N bond (Ln = Sc, Y, lanthanide) is not expected to be facile, it has been proposed as one of the key steps in the scandium-catalyzed hydrogenation of nitriles.[19] Hydrogenolysis of **6** will give an intermediate hydride enamine adduct (eq 3). Subsequent enamine−imine tautomerism affords the N=C double bond, necessary for 1,2-insertion of the intermediate hydride to yield **7** (eq 3).[20]

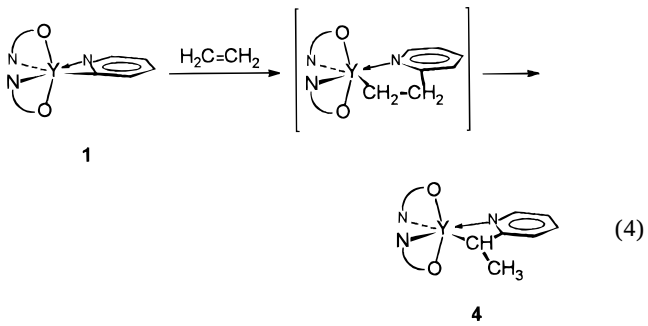


6 **7** (3)

Although feasible within the proposed mechanism, hydrogenation of the final double bond in **7** was not observed. Heating of mixtures containing **7** under dihydrogen (4 atm) for prolonged periods of time (days, 65 °C) resulted exclusively in the thermolysis of **7** (^{1}H NMR). A vanadium-mediated, partial reduction of pyridine, similar to the reaction described here, has been reported by Gambarotta *et al.*[21] Reaction of $[(Me_3Si)_2N]V[\eta^2\text{-}(C,N)\text{-}N(SiMe_3)Si(Me_2)CH_2]$ with pyridine under dihydrogen, resulted in partial hydrogenation, giving the vanadium analog of **7**, $[(Me_3Si)_2N]_2V{-}NC_5H_8$.

Ethene. When **1** reacted with excess ethene, the insertion product $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}C(H)Me\text{-}2\text{-}NC_5H_4)$ (**4**) formed in 36% yield (65 h, 50 °C).

The reaction is not clean, and the formation of substantial amounts of $Me_2Si(N(H)CMe_3)(OCMe_3)$, 2-ethylpyridine, and isobutene illustrates concurrent degradation of the ancillary ligand system. Nevertheless, **4** could unequivocally be identified by NMR spectroscopy. The expected 1,2-insertion product $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2CH_2\text{-}2\text{-}NC_5H_4)$ (eq 4) was not observed. Probably, it had been formed as an intermediate which rapidly rearranged into **4** under the conditions applied. A comparable isomerization has been observed for the reaction of $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$ with ethene.[5] Initially, the 1,2-insertion product $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}CH_2CH_2\text{-}2\text{-}NC_5H_4)$ was formed, which upon heating, rearranged into a mixture of $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Et)$ and $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}(C(H)Me\text{-}2\text{-}NC_5H_4)$.



1 **4** (4)

In analogy with the catalytic conversion of pyridine into 2-ethylpyridine by $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$[5] re-

(16) (a) March, J. *Advanced Organic Chemistry, Reactions, Mechansims and Structure*, 3rd ed.; John Wiley and Sons: New York, 1985; p 598. (b) Joule, J. A.; Smith, G. F. *Heterocyclic Chemistry*; Van Nostrand Reinhold Company: London, 1972; Chapter 4 and references cited therein.

(17) The existence of the hydride $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}H)\}_2$, formed during hydrogenolysis of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ was proven with NMR, see ref 4.

(18) The 1,4-insertion product $Cp^*_2Y{-}NC_5H_6$ was formed only in the presence of additional hydrogen. In the absence of hydrogen, the pyridyl compound, $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$, was obtained.

(19) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

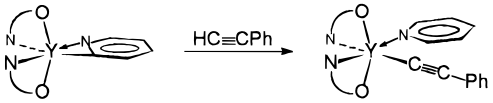
(20) If **7** is formed by hydrogenolysis of the Y−N bond in **6**, competitive hydrogenolysis of the alkoxysilylamido ligands should be taken into account. It is not clear whether the $Me_2Si(N(H)CMe_3)(OCMe_3)$ present (15%) after 21 h at 65 °C is formed by thermolysis or by hydrogenolysis.

(21) Berno, P.; Gambarotta, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2419.

ported earlier, **1** was treated with excess ethene and pyridine (65 °C). However, catalytic pyridine alkylation was not observed, and the reaction stops after the formation of **4**, leaving the excess of ethene and pyridine unreacted. Heating (70 °C) the reaction mixture for prolonged periods of time resulted exclusively in the thermal decomposition of **4**.

As expected on the basis of these results, the picolyl complex **2** did not react with ethene. Heating (days, 65 °C) a benzene-d_6 solution of **2** under ethene (4 atm) only gave thermal decomposition of **2**; no ethene consumption could be observed.

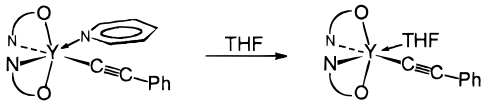
Phenylacetylene. Whereas the yttrium alkyl $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ reacts completely in a nonselective fashion with HC≡CR (R = Ph, $SiMe_3$, CMe_3), liberating $H_2C(SiMe_3)_2$ and $Me_2Si(N(H)CMe_3)(OCMe_3)$ (1:2 ratio),[4] reaction of **1** with PhC≡CH (1 equiv) selectively gave the alkynyl complex $[Me_2Si(NCMe_3)(OCMe_3)]_2Y{-}C{\equiv}CPh{\cdot}Py$ (**8**, eq 5) in 51% yield (^{1}H NMR).[22]



1 **8** (5)

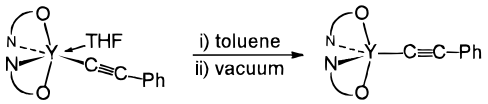
The reaction of **1** with PhC≡CH resembles that of $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$, which affords $Cp^*_2Y{-}C{\equiv}CR{\cdot}Py$.[5] In contrast, $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)]^+$ and $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)]^+$ insert terminal alkynes,[8c] which clearly indicates the difference in the character of the Y−C and Zr−C bonds.

The extreme solubility of $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh{\cdot}Py$ (**8**) hampered its purification and isolation. While attempts to remove the coordinated pyridine (stripping with toluene, sublimation) failed, the pyridine could be replaced by THF yielding the adduct $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh{\cdot}THF$ (**9**, eq 6).[23] Complex



8 **9** (6)

9 could also be synthesized directly by chloride metathesis of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCl{\cdot}THF$ with NaC≡CPh. Surprisingly, stripping **9** with toluene resulted in the loss of the coordinated THF (eq 7) and produced the base-free alkynyl $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh$, **10**. Interestingly, the ^{13}C NMR spectrum of **10** is identical to that of **9**, with the only exception being that the resonances are slightly shifted. The doublet resonance for the α-C of **10** (δ = 144.2 ppm, $^1J_{Y-C}$ = 60 Hz; cf. **9**(α-C) δ = 145.3 ppm, $^1J_{Y-C}$ = 53 Hz) excludes a dimeric structure with bridging alkynyl fragments, as normally found in organoyttrium and lanthanide chemistry. For such complexes, the resonances of the



9 **10** (7)

α-carbons appear as triplets ($^1J_{Y-C} \approx 20$ Hz),[3] due to the coupling of two (time-averaged) identical yttrium atoms. Probably, the alkoxysilylamido ligands (larger than two Cp* ligands[4]) hamper coordination of THF and even block dimerization of unsolvated **10**. Similarly, the steric congestion in $\{Cp^*_2Sm{-}C{\equiv}CCMe_3\}_2$ precluded bridging of the alkynyl fragments, and the monomeric units are stabilized by a peculiar agostic interaction of a Cp*-methyl group of an adjacent molecule.[24c] Unfortunately, compound **10** crystallizes as thin needles unsuitable for X-ray analysis so that verification of the assigned structure was not possible.

Compared to other bis(alkoxysilylamido)yttrium carbyl complexes (*vide supra*), the acetylides **8**−**10** are thermally remarkably stable and show no decomposition in benzene after several days at 100 °C. For **10**, no C−C coupling to μ-trienediyl species was observed, in contrast to the reaction found upon heating of $\{Cp^*_2Ln{-}C{\equiv}CR\}_n$ (Ln = La, R = Ph, CMe_3; Ln = Ce, R = Me, CMe_3; Ln = Sm, R = Ph, CH_2CH_2Ph, $CH_2CH_2CHMe_2$).[24] Probably, the steric bulk of the alkoxysilylamido ligands in **10**, which prevents dimerization, also blocks C−C coupling of the acetylide fragments.

The molecular structure of **9** is shown in Figure 2. Selected bond distances and angles listed in Table 2 (details of the data collection and refinement are listed in Table 3). The *n*-pentane in the crystal lattice is not shown. The center of the monomeric molecule is a distorted octahedral yttrium atom coordinated by two alkoxysilylamido ligands, one acetylide fragment, and one THF molecule.

In *pseudo*-trigonal-pyramidal-coordinated complexes $[Me_2Si(NCMe_3)(OCMe_3)]_2Y{-}CH(SiMe_3)_2$[4] and **2**, the alkoxysilylamido nitrogens are in the equatorial plane. In **9**, one of the nitrogen atoms is equatorial, *trans* to the acetylide group, whereas the other is axial. Since the same orientation of the alkoxysilylamido ligands was observed in $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}(N,N')\text{-}N(H){-}C(Me){=}C(H){-}C{\equiv}N)\}_2$[4] and $[Me_2Si(NCMe_3)(OCMe_3)]_2Yb(\mu\text{-}Cl)_2Li{\cdot}THF_2$,[11] this seems to be the most favorable conformation in octahedral bis(alkoxysilylamido) complexes. With torsion angles of −3.63(10)° (N(1)−Y(1)−O(1)−Si(1)) and −5.67(11)° (N(2)−Y(1)−O(2)−Si(2)), respectively, both alkoxysilylamido ligands form almost planar rings with yttrium. The Y(1)−N(1) (2.279(3) Å) and Y(1)−N(2) (2.266(3) Å) bonds are within the normal range for Y−N σ-bonds in bis(*N*,*O*-bis(*tert*-butyl)alkoxy(dimethylsilyl)amido)yttrium derivatives.[4] Whereas the Y(1)−O(2) (2.375(2) Å) and Y(1)−O(3) (2.378(2) Å) bond distances are normal Y←:O dative bonds,[4] O(1) seems only weakly bonded to yttrium with Y(1)−O(1) = 2.571(2) Å. The Y(1)−C(1) (2.448(4) Å) distance is very similar to the yttrium−carbon bonds in $[p\text{-}MeO\text{-}C_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (2.431(5) Å),[3b]

(22) Partial protolysis of the alkoxysilylamido was also observed and indicates that this reaction still competes with the protolysis of the pyridyl fragment. With 3 equiv of PhC≡CH, complete protolysis of both the pyridyl and alkoxysilylamido ligands was observed.

(23) The solubility of **9** was sufficiently low to allow recrystallization and isolation from *n*-pentane. Unfortunately, crystals of **9** readily lost *n*-pentane from the crystal lattice. While stable enough to obtain a low-temperature X-ray structure determination (*vide infra*), the *n*-pentane had to be removed to obtain a satisfactory elemental analysis.

(24) (a) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628. (b) Heeres, H. J.; Nijhof, J.; Teuben, J. H. *Organometallics* **1993**, *12*, 2609. (c) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1994**, *12*, 2618. (d) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J. *Organometallics* **1993**, *12*, 3618.

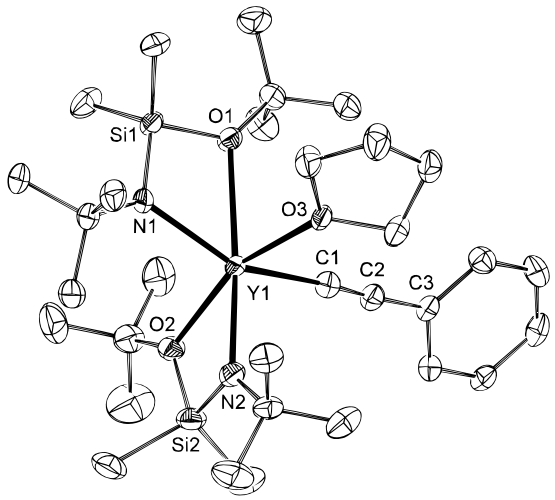


Figure 2. ORTEP drawing of $[Me_2Si(NCMe_3)(OCMe_3)]_2$-YC≡CPh·THF (**9**) at the 50% probability level. Hydrogen atoms are omitted for clarity. Relevant carbon atoms are labeled only.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh{\cdot}THF$ (9)

distances		angles	
Y(1)−N(1)	2.279(3)	N(1)−Y(1)−O(1)	62.22(9)
Y(1)−N(2)	2.266(3)	N(2)−Y(2)−O(2)	65.36(9)
Y(1)−O(1)	2.571(2)	N(2)−Y(1)−O(1)	173.47(9)
Y(1)−O(2)	2.375(2)	N(1)−Y(1)−O(2)	97.25(9)
Y(1)−O(3)	2.378(2)	C(1)−Y(1)−O(3)	87.67(10)
Y(1)−C(1)	2.448(4)	O(1)−Y(1)−C(1)	87.78(10)
C(1)−C(2)	1.217(5)	O(2)−Y(1)−C(1)	85.15(11)
C(2)−C(3)	1.444(5)	O(1)−Y(1)−O(3)	80.85(8)
		N(2)−Y(1)−O(3)	98.37(10)
		N(1)−Y(1)−C(1)	147.69(11)
		N(1)−Y(1)−O(3)	98.28(9)
		O(2)−Y(1)−O(3)	160.87(8)
		Si(1)−Y(1)−Si(2)	133.00(3)
		N(1)−Y(1)−N(2)	111.66(10)

$Cp^*_2YMe{\cdot}THF$ (2.44(2) Å),[25a] and $Cp^*_2YCH(SiMe_3)_2$ (2.446(7) Å),[25b] respectively. This is unusual since metal−alkynyl bonds are generally shorter than the corresponding metal−alkyl bonds.[12c] Interestingly, a comparable long metal−alkynyl bond has been observed in the closely related $Cp^*_2Sm-C{\equiv}CPh{\cdot}THF$ complex.[26] Whereas the long Sm−C bond is accompanied by a short C≡C bond ($C{\equiv}C_{av}$, 1.12(2) Å), the C≡C bond (1.217(5) Å) in **9** is normal for nonbridging alkynyl groups.[27]

Nitriles. Group 3 metal and lanthanide alkyl and hydrido complexes $(\{[C_5H_4R]_2Y(\mu\text{-}H){\cdot}THF\}_2$ (R = H, Me),[28] Cp^*_2LnR (Ln = Sc, R = C_6H_4-4-Me, H; Ln = Y, La, Ce, R = $CH(SiMe_3)_2$),[19,28b] $[PhC(NSiMe_3)_2]_2YR$ (R = CH_2Ph,THF, $CH(SiMe_3)_2$), $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$)[3c] react smoothly with nitriles, either giving insertion or C−H bond activation.

The reactions of **1** and **2** with benzonitrile and acetonitrile are summarized in Scheme 2. The reactivity of both complexes is dominated by insertion and, when possible, subsequent 1,3-H shift. Generally, the reactions are fast at room temperature and the products are formed in high yield. The extremely high solubility of the complexes hampered their purification. Only **13b** and **14b** could be isolated as analytically pure crystals. However, all compounds could unequivocally be identified by ^1H and ^{13}C NMR spectroscopy.

With benzonitrile, **1** gave insertion affording $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N{=}C(Ph)\text{-}2\text{-}NC_5H_4)$ (**11**). Similarly, **2** inserted benzonitrile, but the initially formed $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N{=}C(Ph)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$ (**12a**) rearranged by a 1,3-H shift to the corresponding enamide−pyridine complex, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N(H){-}C(Ph){=}C(H)\text{-}2\text{-}NC_5H_4)$ (**12b**). With acetonitrile, either C−H bond activation or insertion may occur. Which reaction will take place depends strongly on the character of the M−C bond. Compound **1** reacted instantaneously with MeC≡N, initially yielding $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N{=}C(Me)\text{-}2\text{-}NC_5H_4)$ (**13a**). This complex is not stable and rearranged (room temperature) by a 1,3-H shift into $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N(H){-}C(=CH_2)\text{-}2\text{-}NC_5H_4)$ (**13b**). Similar to the reaction with benzonitrile, **2** reacted with acetonitrile to form $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N(H){-}C(Me){=}C(H)\text{-}2\text{-}NC_5H_4)$ (**14b**). The reaction is fast at room temperature. Although $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N{=}C(Me)CH_2\text{-}2\text{-}NC_5H_4)$ (**14a**) was not observed in the ^1H NMR spectra recorded during the reaction, it is likely that it was formed as an intermediate that rearranges rapidly into **14b** (Scheme 2). With the CH_3 resonance located at δ 1.94 ppm, the vinylic proton as a doublet at δ 5.02 ppm ($^4J_{HH}$ = 2.1 Hz), and the N*H* as a broad singlet at δ 6.23 ppm, the ^1H NMR spectrum of **14b** corresponds well with that of $[Cp_2Zr(\eta^2\text{-}(N,N')\text{-}N(H){-}C(Me){=}C(H)\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)]^+$, formed by reaction of $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)]^+$ with acetonitrile.[9]

The observation that both **1** and **2** insert acetonitrile demonstrates that the pyridyl and picolyl groups are not as strong a Brønsted base as the bulky $CH(SiMe_3)_2$ group in $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce),[28b] $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$,[3] and $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$[4] for which C−H bond activation is observed.

Carbon Monoxide. Group 3 and lanthanide carbyl complexes are known to react with CO with the formation of unstable η^2-acyl compounds which either rearrange to enolates or form dinuclear enedione diolate derivatives.[2e,29] Deelman *et al.*[5] reported the formation of a novel μ,η^2,η^2-dipyridylketone derivative upon treatment of $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$ with CO. This reaction clearly demonstrates the ability of pyridyl fragments to stabilize otherwise unstable functionalities. In order to compare the pyridyl group in **1** with that in $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$, reaction with CO was carried out.

Treatment of **1** with excess CO resulted in the intensely blue compound $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y\}$-

(25) (a) Den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *323*, 181. (b) Den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.

(26) Evans, W. J.; Ulibarry, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124.

(27) (a) Atwood, J. L.; Hains, C. F., Jr.; Tsutsui, M.; Gebala, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 452. (b) Atwood, J. L.; Tsutsui, M.; Ely, N.; Gebala, A. E. *J. Coord. Chem.* **1976**, *5*, 209. (c) Evans, W. J.; Bloom, I.; Doedens, R. J. *J. Organomet. Chem.* **1984**, *265*, 249.

(28) (a) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008. (b) Heeres, H. J. Ph.D. Thesis, University of Groningen, Groningen, The Netherlands, 1990.

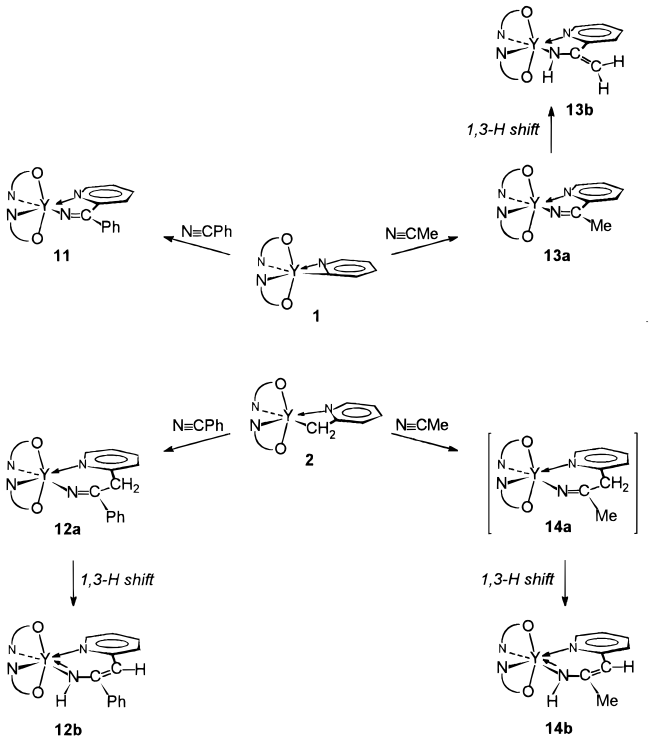
(29) (a) Evans, W. J.; Wayda, A. D.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706. (b) Jeske, G.; Schock, L. E.; Swepton, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

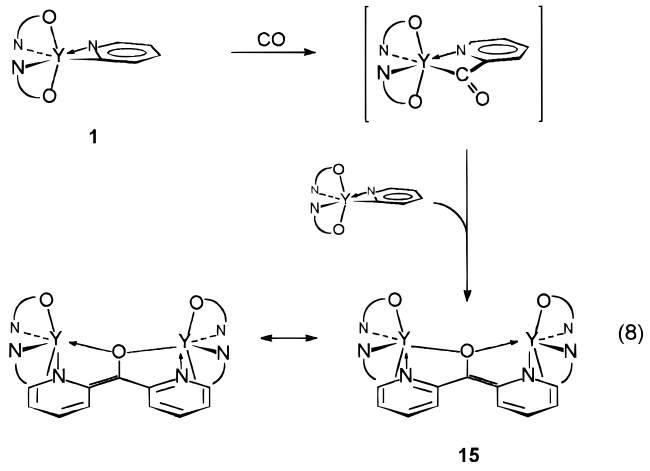
Table 3. Details of the X-ray Structure Determination of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$ (2) and $\{Me_2Si(NCMe_3)(OCMe_3]_2YC{\equiv}CPh{\cdot}THF$ (9)

	2	9
formula	$C_{26}H_{54}N_3O_2Si_2Y$	$C_{32}H_{61}N_2O_3Si_2Y{\cdot}(C_5H_{12})_{0.5}$
mol wt	585.81	703.00
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a, Å	16.757(1)	21.041(1)
b, Å	12.170(1)	19.321(1)
c, Å	17.454(1)	21.437(1)
β, deg	112.401(8)	107.946(6)
V, Å^3	3290.8(4)	8290.9(8)
D_{calc}, g mol^{-3}	1.182	1.126
Z	4	8
$F(000)$	1256	3032
μ (Mo Kα), cm^{-1}	18.77	15.0
cryst size, mm	0.30 × 0.35 × 0.40	0.20 × 0.27 × 0.37
T, K	130	130
θ range; min, max, deg.	1.26, 27.0	1.00, 27.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.85 + 0.34$ tan q	$\Delta\omega = 0.80 + 0.34$ tan θ
data set	h, −21 to 19; k, −1 to 15, l, 0 to 22	h, −26 to 25; k, 0 to 24; l, 0 to 27
total no. of data	8933	9603
no. of unique data	7166	8998
no. of obsd data ($I \geq 2.5\ \sigma(I)$)	4741	5735
no. of refined params	497	628
final agreement factors:		
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.060	0.045
$wR = [\Sigma(w(\|F_o\| - \|F_c\|^2)/\Sigma w\|F_o\|^2]^{1/2}$	0.056	0.041
weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$ [a]	2.30(2)	1.549(15)
residual electron density in final diff Fourier map, e/Å^3	−0.86, 1.25	−0.48, 0.51

[a] m = No. of observations; n = No. of variables.

Scheme 2. Reaction of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$ (1) and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$ (2) with Benzonitrile and Acetonitrile





$\{\mu,\eta^2,\eta^2\text{-}(N,N',O)\text{-}OC(2\text{-}NC_5H_4)_2\}$ (**15**, eq 8). This reaction proceeds analogously to that of the permethylated yttrocene derivative which gives $\{Cp^*_2Y\}_2\{\mu,\eta^2,\eta^2\text{-}(N,N',O)\text{-}OC(2\text{-}NC_5H_4)_2\}$.[5] The spectral data ($^{13}C$ NMR, δ = 147.3 ppm ($C(=O)$-*ipso*); IR, $\nu_{C=O}$ = 1404 cm^{-1}) of **15** are nearly identical to those of $\{Cp^*_2Y\}_2\{\mu,\eta^2,\eta^2\text{-}(N,N',O)\text{-}OC(2\text{-}NC_5H_4)_2\}$[5] and indicate a considerable reduction of the carbonyl functionality.[29b,30] As proposed by Deelman *et al.*, the formation of **15** is thought to proceed by CO insertion followed by nucleophilic attack of an other equivalent of **1** and is schematically presented in eq 8. A more detailed discussion concerning the bonding of the μ,η^2,η^2-dipyridylketone fragment is given elsewhere.[5]

Concluding Remarks. Even though the intrinsic reactivity of the alkoxysilylamido ligands of the bis(alkoxysilylamido)yttrium complexes may make this system unsuitable for catalytic applications, the bis(alkoxysilylamido)yttrium pyridyl (**1**) and picolyl (**2**) derivatives show interesting stoichiometric reactions. Whereas the bulky bis(trimethylsilyl)methyl ligand in $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ reacts as a classical Brønsted base, the pyridyl and picolyl ligands in **1** and **2** are much better nucleophiles, as illustrated by their diverse insertion chemistry. Reduction of the

(30) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522.

steric saturation at yttrium and introduction of reactivity promoting ring strain by replacing the bulky CH(SiMe$_3$)$_2$ by a pyridyl group clearly leads to an increased reactivity of the Y−C bond, e.g., with dihydrogen and phenylacetylene. When substrates containing acidic protons and high reaction temperatures are avoided, the bis(alkoxysilylamido)yttrium pyridyl and picolyl complexes **1** and **2** react comparably to the corresponding permethylated yttrocene and cationic zirconocene pyridyl and α-picolyl complexes.

The fact that the bis(*N*,*O*-bis(*tert*-butyl)alkoxy(dimethylsilyl)amido) ligand environment is sterically more demanding than the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato) and bis(pentamethylcyclopentadienyl) ligand systems is clearly illustrated by the isolation of a monomeric, unsolvated acetylide complex [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YC≡CPh (**10**). This is in strong contrast with the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)yttrium analogs [{PhC(NSiMe$_3$)$_2$}$_2$YC≡CR]$_2$ that exclusively form stable dimers. The electronic differences induced by the auxiliary ligand systems that have been compared are illustrated by the difference in reactivity between [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YC≡CPh and the unsolvated compounds Cp*$_2$YC≡CR. The latter undergo further insertion and catalytically dimerize terminal alkynes to enynes, while [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YC≡CPh does not react.

Experimental Section

General Comments. For general aspects and methods and techniques used, see ref 3b. Hydrogen (Hoekloos 99.9995%), deuterium (Matheson, C.P.), and ethylene (DSM Research B.V.) were used as purchased. PhC≡CH, MeC≡N, PhC≡N, pyridine, α-picoline, and 2,6-dimethylpyridine (Janssen) were dried over 4 Å molecular sieves and distilled prior to use. [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YCl·THF and [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y−CH(SiMe$_3$)$_2$ were prepared following literature procedures.[4]

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*C*,*N*)-NC$_5$H$_4$) (1). 2-bromopyridine (0.63 mL, 6.61 mmol) was dissolved in ether (40 mL) and cooled to −80 °C. Then *n*-BuLi (2.67 mL, 2.5 M solution in hexanes, 6.67 mmol) was added. After the mixture was stirred for 30 min, [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YCl·THF (3.97 g, 6.60 mmol) was added to the resulting red solution. The reaction mixture was allowed to warm slowly to room temperature and stirred for 20 h. The volatiles were removed *in vacuo*, and the resulting sticky residue was stripped with *n*-pentane (3 × 7 mL). Extraction with *n*-pentane (15 mL), concentration, and cooling to −80 °C yielded **1** (1.10 g, 1.92 mmol, 29%) as red-brown crystals. Further concentration of the mother liquor yielded a second crop of **1** (0.65 g, 1.13 mmol, 17%) as a microcrystalline powder after cooling to −80 °C. ^{1}H NMR (benzene-d_6, δ): 8.41 (dd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 0.9 Hz), 7.96 (dd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.07 (td, 1H, NC$_5H_4$, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.3 Hz), 6.70 (ddd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 1.3 Hz), 1.53 (s, 18H, C(CH_3)$_3$), 1.08 (s, 18H, C(CH_3)$_3$), 0.39 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 226.0 (d, N*C*$_5$H$_4$(*ipso-C*), $^1J_{Y-C}$ = 26 Hz), 145.8 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 174 Hz), 132.9 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 162 Hz), 132.3 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 157 Hz), 121.0 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 158 Hz), 76.3 (s, *C*(CH$_3$)$_3$), 51.9 (s, *C*(CH$_3$)$_3$), 37.2 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 31.4 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 8.0 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd for C$_{25}$H$_{52}$N$_3$O$_2$Si$_2$Y: C, 52.52; H, 9.17; N, 7.35; Y, 15.55. Found: C, 52.19; H, 9.04; N, 6.97; Y, 15.43.

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*C*,*N*)-CH$_2$-2-NC$_5$H$_4$) (2). A THF (40 mL) solution of α-picoline (0.7 mL, 7.0 mmol) was treated with *n*-BuLi (2.8 mL, 2.5 M in hexanes, 7.0 mmol) at −40 °C. The red solution obtained was allowed to warm to room temperature and then stirred for 90 min. The volatiles were removed *in vacuo*, and the residue was dissolved in toluene (80 mL). After the mixture was cooled to −80 °C, [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YCl·THF (4.2 g, 7.0 mmol) was added and the reaction mixture was allowed to warm to room temperature. After the mixture was stirred for 20 min, the solvent was evaporated and the crude product stripped with *n*-pentane (3 × 15 mL). Then the product was redissolved in *n*-pentane (30 mL). Filtration, concentration, and slow cooling to −30 °C yielded **2** (2.05 g, 3.5 mmol, 50%) as rod-shaped orange crystals. ^{1}H NMR (benzene-d_6, δ): 7.75 (d, 1H, NC$_5H_4$, $^3J_{H-H}$ = 5.6 Hz), 6.73 (ddd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.52 (d, 1H, NC$_5H_4$, $^3J_{H-H}$ = 8.6 Hz), 5.90 (ddd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 6.8 Hz, $^3J_{H-H}$ = 5.6 Hz, $^4J_{H-H}$ = 1.3 Hz), 2.73 (d, 2H, Y−CH_2, $^2J_{Y-H}$ = 0.9 Hz), 1.51 (s, 9H, C(CH_3)$_3$), 1.49 (s, 9H, C(CH_3)$_3$), 1.31 (s, 18H, C(CH_3)$_3$), 0.43 (s, 6H, Si(CH_3)$_2$), 0.36 (s, 3H, Si(CH_3)$_2$), 0.32 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 166.9 (s, N*C*$_5$H$_4$(*ipso-C*)), 146.2 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 169 Hz), 135.5 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 158 Hz), 120.8 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 163 Hz), 106.7 (d, N*C*$_5$H$_4$, $^1J_{C-H}$ = 164 Hz), 77.1 (s, *C*(CH$_3$)$_3$), 52.3 (td, Y−*C*H$_2$, $^1J_{C-H}$ = 143 Hz, $^1J_{Y-C}$ = 6 Hz), 52.1 (s, *C*(CH$_3$)$_3$), 37.0 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 125 Hz), 32.0 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 128 Hz), 8.2 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd for C$_{26}$H$_{54}$N$_3$O$_2$Si$_2$Y: C, 53.31; H, 9.29; Y, 15.18. Found: C, 53.35; H, 9.24; Y, 15.21.

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*C*,*N*)-CH$_2$-2-NC$_5$H$_3$-6-CH$_3$) (3). To a *n*-pentane solution (20 mL) of 2,6-dimethylpyridine (0.39 mL, 3.3 mmol), *n*-BuLi (1.3 mL, 2.5 M in hexanes, 3.3 mmol) was added at −30 °C. The resulting yellow suspension was allowed to warm to room temperature and then stirred for 20 min. Subsequently, [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YCl·THF (2.0 g, 3.3 mmol) was added at −80 °C. After the mixture was warmed to room temperature, it was stirred for 2 h. The volatiles were removed *in vacuo*, and the residue was stripped with *n*-pentane (3 × 10 mL). Subsequently, the crude product was extracted with *n*-pentane (25 mL). Concentration and cooling to −80 °C afforded **3** (0.61 g, 1.0 mmol, 31%) as yellow crystals. ^{1}H NMR (benzene-d_6, δ): 6.74 (dd, 1H, NC$_5H_3$, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 6.8 Hz), 6.44 (d, 1H, NC$_5H_3$, $^3J_{H-H}$ = 8.6 Hz), 5.81 (d, 1H, NC$_5H_3$, $^3J_{H-H}$ = 6.8 Hz), 2.75 (d, 2H, Y−CH_2, $^2J_{Y-H}$ = 1.3 Hz), 2.43 (s, 3H, CH_3), 1.50 (s, 18H, C(CH_3)$_3$), 1.28 (s, 18H, C(CH_3)$_3$), 0.45 (s, 3H, Si(CH_3)$_2$), 0.40 (s, 3H, Si(CH_3)$_2$), 0.36 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 168.2 (s, N*C*$_5$H$_3$(*ipso-C*)), 154.5 (s, N*C*$_5$H$_3$(*ipso-C*)), 136.4 (d, N*C*$_5$H$_3$, $^1J_{C-H}$ = 156 Hz), 118.1 (d, N*C*$_5$H$_3$, $^1J_{C-H}$ = 163 Hz), 106.6 (d, N*C*$_5$H$_3$, $^1J_{C-H}$ = 163 Hz), 76.9 (s, *C*(CH$_3$)$_3$), 52.3 (s, *C*(CH$_3$)$_3$), 50.6 (td, Y−*C*H$_2$, $^1J_{C-H}$ = 142 Hz, $^1J_{Y-C}$ = 8 Hz), 37.2 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 123 Hz), 36.7 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 128 Hz), 32.0 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 24.9 (q, *C*H$_3$, $^1J_{C-H}$ = 126 Hz), 8.0 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd for C$_{27}$H$_{56}$N$_3$O$_2$Si$_2$Y: C, 54.06; H, 9.41; N, 7.01; Y, 14.82. Found: C, 54.28; H, 9.48; N, 6.73; Y, 14.72.

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*C*,*N*)-CH(CH$_3$)-2-NC$_5$H$_4$) (4). To a THF solution (40 mL) of 2-ethylpyridine (0.38 mL, 3.5 mmol), *n*-BuLi (1.4 mL, 2.5 M in hexanes, 3.5 mmol) was added at −80 °C to give an orange suspension. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. After the THF was evaporated, the remaining sticky solid was stripped with *n*-pentane (3 × 5 mL) and subsequently dissolved in toluene (40 mL). The orange-red solution was cooled to −80 °C, and [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YCl·THF (2.0 g, 3.5 mmol) was added. After the mixture was warmed to room temperature, the dark-orange solution formed was stirred for 20 h. After filtration, the volatiles were removed *in vacuo*. The oily residue was stripped with *n*-pentane (3 × 15 mL), leaving an oily residue which did not solidify (1.3 g, 2.1 mmol, 60%). The extreme solubility of **4** precluded further purification. ^{1}H NMR (benzene-d_6, δ): 7.64 (dd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 5.6 Hz, $^4J_{H-H}$ = 1.3 Hz), 6.78 (ddd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 7.7 Hz, $^3J_{H-H}$ = 5.6 Hz, $^4J_{H-H}$ = 0.9 Hz), 6.36 (d, 1H, NC$_5H_4$, $^3J_{H-H}$ = 9.0 Hz), 5.74 (t, 1H,

NC_5H_4, $^3J_{H-H}$ = 6.0 Hz), 3.00 (qd, 1H, Y−C(*H*)CH_3, $^3J_{H-H}$ = 5.6 Hz, $^2J_{Y-H}$ = 2.1 Hz), 1.78 (d, 3H, YC(H)CH_3, $^3J_{H-H}$ = 5.6 Hz), 1.52 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 1.32 (s, 9H, C(CH_3)$_3$), 1.22 (s, 9H, C(CH_3)$_3$), 0.43 (s, 6H, Si(CH_3)$_2$), 0.39 (s, 3H, Si(CH_3)$_2$), 0.34 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 162.2 (s, NC_5H_4(*ipso-C*)), 146.2 (d, NC_5H_4, $^1J_{C-H}$ = 175 Hz), 135.5 (d, NC_5H_4, $^1J_{C-H}$ = 155 Hz), 114.3 (d, NC_5H_4, $^1J_{C-H}$ = 163 Hz), 103.4 (d, NC_5H_4, $^1J_{C-H}$ = 165 Hz), 77.4 (s, *C*(CH$_3$)$_3$), 60.9 (td, Y−*C*(H)CH_3, $^1J_{C-H}$ = 162 Hz, $^1J_{Y-C}$ = 5 Hz), 52.1 (s, *C*(CH$_3$)$_3$), 37.7 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 37.2 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 36.9 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 33.0 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 31.8 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 12.8 (q, Y−C(H)*C*H$_3$, $^1J_{C-H}$ = 124 Hz), 8.2 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz), 7.9 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz).

Hydrogenation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*C,N*)-NC$_5$H$_4$) (1). An NMR tube containing a solution of **1** (17 mg, 0.030 mmol) in benzene-d_6 (0.5 mL) was charged with hydrogen (ca. 4.0 atm). For 21 h, the reaction was followed by ^{1}H NMR spectroscopy at 65 °C. ^{1}H NMR spectra, recorded at fixed time intervals, showed the gradual conversion of **1** into the 1,2-inserted product [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y−NC$_5$H$_6$ (**5**, 96% after 85 min). While the intensity of resonances attributable to the 1,4-inserted product [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y−NC$_5$H$_6$ (**6**, 10% after 20 h) and the hydrogenated product [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y−NC$_5$H$_8$ (**7**, 46% after 20 h) increased, the resonances of **1** and **5** subsided. Some Me$_2$Si(N(H)CMe$_3$)(OCMe$_3$) (15% after 21 h) was also formed during the reaction.[20] Separation and purification of the various reaction products proved to be impossible due to their high solubility. **5**: ^{1}H NMR (benzene-d_6, δ) 7.01 (d, 1H, NC$_5H_6$, $^3J_{H-H}$ = 6.4 Hz), 6.24 (ddd, 1H, NC$_5H_6$, $^3J_{H-H}$ = 5.6 Hz, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 0.9 Hz), 5.20 (td, 1H, NC$_5H_6$, $^3J_{H-H}$ = 6.4 Hz, $^4J_{H-H}$ = 0.9 Hz), 4.87 (m, 1H, NC$_5H_6$), 4.29 (m, 2H, NC$_5H_6$), 1.39 (s, 18H, C(CH_3)$_3$), 1.36 (s, 18H, C(CH_3)$_3$), 0.37 (s, 12H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 144.3 (s, NC_5H$_6$), 127.5 (s, NC_5H$_6$), 101.9 (s, NC_5H$_6$), 94.8 (s, NC_5H$_6$), 78.8 (s, *C*(CH$_3$)$_3$), 52.0 (s, *C*(CH$_3$)$_3$), 47.5 (s, NC_5H$_6$(*C2*)), 37.1 (s, C(*C*H$_3$)$_3$), 31.6 (s, C(*C*H$_3$)$_3$), 7.8 (s, Si(*C*H$_3$)$_2$). **6**: ^{1}H NMR (benzene-d_6, δ) 6.45 (dd, 2H, NC$_5H_6$, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.3 Hz), 4.48 (dt, 2H, NC$_5H_6$, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 3.0 Hz), 3.54 (td, 2H, NC$_5H_6$, $^3J_{H-H}$ = 3.0 Hz, $^4J_{H-H}$ = 1.7 Hz), 1.47 (s, 18H, C(CH_3)$_3$), 1.34 (s, 18H, C(CH_3)$_3$), 0.35 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 135.8 (d, NC_5H$_6$(*C2*, *C6*), $^1J_{C-H}$ = 162 Hz), 94.7 (d, NC_5H$_6$(*C3*, *C5*), $^1J_{C-H}$ = 158 Hz), 79.1 (s, *C*(CH$_3$)$_3$), 52.0 (s, *C*(CH$_3$)$_3$), 37.1 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 129 Hz), 31.5 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 23.7 (t, NC$_5$H$_6$(*C4*), $^1J_{C-H}$ = 126 Hz), 7.7 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). **7**: ^{1}H NMR (benzene-d_6, δ) 6.87 (d, 1H, NC$_5H_8$, $^3J_{H-H}$ = 7.3 Hz), 4.51 (m, 1H, NC$_5H_8$), 3.61 (m, 2H, NC$_5H_8$), 2.42 (m, 2H, NC$_5H_8$), 1.94 (m, 2H, NC$_5H_8$), 1.40 (s, 18H, C(CH_3)$_3$), 1.37 (s, 18H, C(CH_3)$_3$), 0.38 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 139.2 (d, NC_5H$_8$, $^1J_{C-H}$ = 153 Hz), 87.8 (d, NC_5H$_8$(*C5*), $^1J_{C-H}$ = 159 Hz), 78.5 (s, *C*(CH$_3$)$_3$), 51.9 (s, *C*(CH$_3$)$_3$), 47.0 (t, NC_5H$_8$(*C2*), $^1J_{C-H}$ = 133 Hz), 37.1 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 128 Hz), 31.5 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 25.0 (t, NC_5H$_6$(*C3*), $^1J_{C-H}$ = 126 Hz), 23.8 (t, NC_5H$_8$(*C4*), $^1J_{C-H}$ = 126 Hz), 7.8 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz).

NMR Tube Reaction of 1 with Ethene. An NMR tube containing a solution of **1** (56 mg, 0.10 mmol) in benzene-d_6 (0.5 mL) was charged with ethene (4.7 atm, 0.27 mmol) and heated to 50 °C. The ^{1}H NMR spectra collected at fixed intervals during the reaction showed the slow formation of **4**. The reaction was not clean and considerable amounts of thermolysis products were formed. After 65 h at 50 °C, 95% of **1** had been consumed to give a mixture (^{1}H NMR) of **4** (36%), Me$_2$Si(N(H)CMe$_3$)(OCMe$_3$) (15%), 2-ethylpyridine (15%), and isobutene (19%).

NMR Tube Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YC≡CPh·Py (8). PhC≡CH (7.8 μL, 0.071 mmol) was added to an NMR tube charged with a solution of **1** (40 mg, 0.070 mmol) in benzene-d_6 (0.5 mL). After 1 h at room temperature, nearly all of **1** had reacted, yielding a mixture of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y−C≡CPh·Py (**8**, 51%) and Me$_2$Si(N(H)CMe$_3$)(OCMe$_3$) (37%). Subsequent addition of 16 μL (0.15 mmol) of PhC≡CH resulted in fast protolysis of the alkoxysilylamido ligands (^{1}H NMR). ^{1}H NMR (benzene-d_6, δ): 9.62 (s (br), 2H, NC$_5H_5$), 7.68 (dd, 2H, *o*-C$_6H_5$, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.13 (t, 2H, *m*-C$_6H_5$, $^3J_{H-H}$ = 7.7 Hz), 6.99 (t, 1H, *p*-C$_6H_5$, $^3J_{H-H}$ = 7.3 Hz), 6.85 (t (br), 1H, NC$_5H_5$, $^3J_{H-H}$ = 6.8 Hz), 6.59 (t (br), 2H, NC$_5H_5$, $^3J_{H-H}$ = 6.4 Hz), 1.53 (s, 18H, C(CH_3)$_3$), 1.48 (s, 18H, C(CH_3)$_3$), 0.59 (s, 6H, Si(CH_3)$_2$), 0.45 (s, 6H, Si(CH_3)$_2$).

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YC≡CPh·THF·(pentane)$_{0.5}$ (9). To a toluene solution (20 mL) of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YCl·THF (1.50 g, 2.5 mmol), NaC≡CPh (0.31 g, 2.5 mmol) was added at −80 °C. The initially white suspension turned light orange within 10 min. After the mixture was stirred for 30 min at room temperature, the solvent was removed *in vacuo* and the resulting brown oil was stripped with *n*-pentane (3 × 7 mL). Extraction with *n*-pentane (10 mL), concentration of the extracts, and cooling to −30 °C gave **9** (0.77 g, 1.1 mmol, 44%) as a white microcrystalline powder. Repeated recrystallization from *n*-pentane yielded colorless bar-shaped crystals of **9** suitable for an X-ray structure analysis. Since the crystals rapidly lost solvent (*n*-pentane) from the crystal lattice, satisfactory elemental analyses could not be obtained. ^{1}H NMR (benzene-d_6, δ): 7.59 (d, 2H, *o*-*C*$_6H_5$, $^3J_{H-H}$ = 8.3 Hz), 7.09 (t, 2H, *m*-C$_6H_5$, $^3J_{H-H}$ = 7.7 Hz), 6.96 (t, 1H, *p*-C$_6H_5$, $^3J_{H-H}$ = 6.8 Hz), 4.05 (m, 4H, THF-α-CH_2), 1.61 (s, 18H, C(CH_3)$_3$), 1.47 (s, 18H, C(CH_3)$_3$), 1.38 (m, 4H, THF-*β*-CH_2), 1.23 (m, 3H, *n*-pentane-CH_2), 0.88 (t, 3H, *n*-pentane-CH_3, $^3J_{H-H}$ = 6.7 Hz), 0.49 (s, 6H, Si(CH_3)$_2$), 0.39 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 145.3 (d, Y−*C*≡C−Ph, $^1J_{Y-C}$ = 53 Hz), 131.3 (d, Ar, $^1J_{C-H}$ = 159 Hz), 128.1 (d, Ar, $^1J_{C-H}$ = 159 Hz), 125.5 (d, Ar, $^1J_{C-H}$ = 161 Hz), 108.1 (dt, Y−C≡*C*−Ph, $^2J_{Y-C}$ = 5 Hz, $^3J_{C-H}$ = 11 Hz), 77.6 (s, *C*(CH$_3$)$_3$), 70.5 (t, THF-α-*C*H$_2$, $^1J_{C-H}$ = 149 Hz), 52.0 (s, *C*(CH$_3$)$_3$), 37.1 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 123 Hz), 31.8 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 125 Hz), 25.1 (t, THF-*β*-*C*H$_2$, $^1J_{C-H}$ = 133 Hz), 22.9 (t, *n*-pentane-*C*H$_2$, $^1J_{C-H}$ = 126 Hz), 14.2 (q, *n*-pentane-*C*H$_3$, $^1J_{C-H}$ = 124 Hz), 8.1 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz), 7.8 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 117 Hz).

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$YC≡CPh (10). Compound **9** (0.50 g, 0.7 mmol) was stripped with toluene (3 × 5 mL) and subsequently dried *in vacuo* until all the THF resonances in the ^{1}H NMR spectrum of the product had disappeared. Then the product was dissolved in *n*-pentane (7 mL). Crystallization at −80 °C yielded **10** (0.39 g, 0.64 mmol, 91%) as white needles. ^{1}H NMR (benzene-d_6, δ): 7.57 (d, 2H, *o*-C$_6H_5$, $^3J_{H-H}$ = 8.2 Hz), 7.09 (t, 2H, *m*-C$_6H_5$, $^3J_{H-H}$ = 7.3 Hz), 6.98 (t, 1H, *p*-C$_6H_5$, $^3J_{H-H}$ = 7.3 Hz), 1.62 (s, 18H, C(CH_3)$_3$), 1.40 (s, 18H, C(CH_3)$_3$), 0.42 (s, 6H, Si(CH_3)$_2$), 0.38 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 144.2 (d, Y−*C*≡C−Ph, $^1J_{Y-C}$ = 60 Hz), 131.5 (d, Ar, $^1J_{C-H}$ = 160 Hz), 128.3 (d, Ar, $^1J_{C-H}$ = 159 Hz), 126.0 (d, Ar, $^1J_{C-H}$ = 157 Hz), 108.9 (dt, Y−C≡*C*−Ph, $^2J_{Y-C}$ = 5 Hz, $^2J_{C-H}$ = 12 Hz), 79.1 (s, *C*(CH$_3$)$_3$), 52.2 (s, *C*(CH$_3$)$_3$), 37.1 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 121 Hz), 31.5 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 8.0 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz), 7.6 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 117 Hz). Anal. Calcd for $C_{28}H_{53}N_2O_2Si_2Y$: C, 56.54; H, 8.98; Y, 14.95. Found: C, 56.67; H, 8.96; Y, 15.03.

NMR Tube Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*N,N′*)-N=C(Ph)-2-NC$_5$H$_4$) (11). PhC≡N (11.0 μL, 0.108 mmol) was added to an NMR tube containing a benzene-d_6 (0.4 mL) solution of **1** (59 mg, 0.103 mmol). Upon addition, the red solution turned intense purple. The ^{1}H NMR spectrum recorded after 10 min at room temperature showed full conversion of **1** to **11**. ^{1}H NMR (benzene-d_6, δ): 9.04 (d, 1H, NC$_5H_4$, $^3J_{H-H}$ = 4.6 Hz), 7.74 (d, 2H, *o*-C$_6H_5$, $^3J_{H-H}$ = 6.8 Hz), 7.25 (t, 2H, *m*-C$_6H_5$, $^3J_{H-H}$ = 7.3 Hz), 7.17 (m, 2H, NC$_5H_4$, *p*-C$_6H_5$), 7.05 (td, 1H, NC$_5H_4$, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.61 (ddd, 1H, NC$_5H_4$, $^3J_{H-H}$ = 6.4 Hz, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 1.2 Hz), 1.41 (s br, 36H, C(CH_3)$_3$), 0.44 (s, 6H, Si(CH_3)$_2$), 0.39 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6): 161.3 (s, NC_5H_4-(*ipso-C*)), 156.7 (s, N=*C*), 151.1 (d, Ar, $^1J_{C-H}$ = 179 Hz), 144.0 (s, Ar(*ipso-C*)), 140.0 (d, Ar, $^1J_{C-H}$ = 164 Hz), 128.1 (d, Ar, $^1J_{C-H}$

= 158 Hz), 128.0 (d, Ar, $^1J_{C-H}$ = 158 Hz), 127.4 (d, Ar, $^1J_{C-H}$ = 159 Hz), 122.2 (d, Ar, $^1J_{C-H}$ = 166 Hz), 121.9 (d, Ar, $^1J_{C-H}$ = 166 Hz), 76.4 (s, *C*(CH$_3$)$_3$), 51.8 (s, *C*(CH$_3$)$_3$), 37.4 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 121 Hz), 37.1 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 122 Hz), 31.8 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 127 Hz), 8.1 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 117 Hz), 7.7 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz).

NMR Tube Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y-(η^2-(*N,N′*)-N(H)-C(Ph)=C(H)-2-NC$_5$H$_4$) (12b). To an NMR tube charged with a solution of **2** (39 mg, 0.067 mmol) in benzene-d_6 (0.5 mL), PhC≡N (6.9 μL, 0.068 mmol) was added. Upon addition of the benzonitrile, the solution changed from yellow to orange-red. The ^{1}H NMR spectrum recorded directly after the NMR tube was filled showed resonances characteristic of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*N,N′*)-N=C(Ph)-CH$_2$-2-NC$_5$H$_4$) (**12a**) and [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*N,N′*)-N(H)-C(Ph)=C(H)-2-NC$_5$H$_4$) (**12b**). After 2 h at room temperature, all **12a** had been converted into **12b**. **12a**: ^{1}H NMR (benzene-d_6, δ) 9.41 (dd, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 6.4 Hz, $^4J_{H-H}$ = 2.1 Hz), 8.00 (d, 2H, *o*-C$_6$*H*$_5$, $^3J_{H-H}$ = 6.8 Hz), 7.35 (t, 2H, *m*-C$_6$*H*$_5$, $^3J_{H-H}$ = 6.8 Hz), 7.20 (t, 1H, *p*-C$_6$*H*$_5$, $^3J_{H-H}$ = 6.8 Hz), 6.93 (td, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.63 (m, 2H, NC$_5$*H*$_4$), 4.59 (d, 1H, C*H*$_2$, $^2J_{H-H}$ = 14.3 Hz), 4.18 (d, 1H, C*H*$_2$, $^2J_{H-H}$ = 14.3 Hz), 1.54 (s, 18H, C(C*H*$_3$)$_3$), 1.28 (s, 18H, C(C*H*$_3$)$_3$), 0.50 (s, 6H, Si(C*H*$_3$)$_2$), 0.41 (s, 6H, Si(C*H*$_3$)$_2$). **12b**: ^{1}H NMR (benzene-d_6, δ) 9.18 (s (br), 1H, NC$_5$*H*$_4$), 7.75 (d, 2H, *o*-C$_6$*H*$_5$, $^3J_{H-H}$ = 7.3 Hz), 7.17 (m, 3H, *m,p*-C$_6$*H*$_5$), 6.87 (t, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 7.3 Hz), 6.80 (s (br), 1H, N*H*), 6.72 (d, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 8.1 Hz), 6.27 (t, 1H, NC$_5$*H*$_4$(*C5*), $^3J_{H-H}$ = 6.4 Hz), 5.47 (s (br), 1H, =C*H*), 1.62 (s, 9H, C(C*H*$_3$)$_3$), 1.50 (s, 9H, C(C*H*$_3$)$_3$), 1.31 (s, 9H, C(C*H*$_3$)$_3$), 1.20 (s, 9H, C(C*H*$_3$)$_3$), 0.50 (s, 3H, Si-(C*H*$_3$)$_2$), 0.47 (s, 3H, Si(C*H*$_3$)$_2$), 0.41 (s, 6H, Si(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6): 163.6 (s, N*C*$_5$H$_4$(*ipso-C*)), 159.9 (s, *C*(Ph)=CH), 147.2 (d, Ar, $^1J_{C-H}$ = 170 Hz), 135.7 (d, Ar, $^1J_{C-H}$ = 163 Hz), 128.7 (d, Ar, $^1J_{C-H}$ = 162 Hz), 128.2 (d, Ar, $^1J_{C-H}$ = 160 Hz), 126.1 (d, Ar, $^1J_{C-H}$ = 157 Hz), 124.3 (d, Ar, $^1J_{C-H}$ = 162 Hz), 111.4 (d, Ar, $^1J_{C-H}$ = 165 Hz), 93.4 (d, C(Ph)=*C*H, $^1J_{C-H}$ = 151 Hz), 76.8 (s, *C*(CH$_3$)$_3$), 52.1 (s, *C*(CH$_3$)$_3$), 37.2 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 123 Hz), 32.0 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 125 Hz), 8.0 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 117 Hz).

NMR Tube Reaction of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*C,N*)-2-NC$_5$H$_4$) (1) with MeC≡N. Acetonitrile (5.0 μL, 0.096 mmol) was added to a solution of 52 mg (0.091 mmol) of **1** in benzene-d_6 (0.5 mL). An instantaneous color change from red-brown to brown-yellow occurred. The ^{1}H NMR spectrum taken after 10 min at room temperature showed resonances of [Me$_2$-Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-*N,N′*)-N=C(Me)-2-NC$_5$H$_4$) (**13a**). Within hours at room temperature, **13a** had been rearranged into [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-*N,N′*)-N(H)−C(=CH$_2$)-2-NC$_5$H$_4$) (**13b**). **13a**: ^{1}H NMR (benzene-d_6, δ) 9.00 (d, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 4.7 Hz), 7.10 (dd, 1H, NC$_5$H$_4$, $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.96 (td, 1H, NC$_5$H$_4$, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.58 (ddd, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-H}$ = 4.7 Hz, $^4J_{H-H}$ = 1.3 Hz), 2.45 (s, 3H, C*H*$_3$), 1.47 (s, 18H, C(C*H*$_3$)$_3$), 1.32 (s, 18H, C(C*H*$_3$)$_3$), 0.49 (s, 12H, Si(C*H*$_3$)$_2$).

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*N,N′*)-N-(H)−C(=CH$_2$)-2-NC$_5$H$_4$) (13b). Acetonitrile (120 μL, 2.3 mmol) was added to a solution of **1** (1.3 g, 2.2 mmol) in hexanes (15 mL). After 24 h at room temperature, the volatiles were removed *in vacuo*, leaving a brown sticky solid. After the mixture was stripped (3 × 5 mL) with hexanes, the solid was redissolved in hexanes (5 mL) and cooled to −80 °C for crystallization. Repeated recrystallization from hexanes yielded **13b** (0.9 g, 1.4 mmol, 65%) as a red-brown crystalline material. ^{1}H NMR (benzene-d_6, δ): 9.17 (d, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 4.3 Hz), 7.66 (d, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 8.1 Hz), 6.99 (t, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 7.3 Hz), 6.65 (t, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 6.0 Hz), 4.99 (s (br), 1H, N*H*), 4.50 (s, 1H, =C(*H*)H), 4.20 (s, 1H, =C(*H*)H), 1.56 (s, 9H, C(C*H*$_3$)$_3$), 1.54 (s, 9H, C(C*H*$_3$)$_3$), 1.17 (s, 9H, C(C*H*$_3$)$_3$), 1.11 (s, 9H, C(C*H*$_3$)$_3$), 0.48 (s, 12H, Si(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6): 162.3 (s, NC$_5$H$_4$(*ipso-C*)), 156.9 (s, *C*(=CH$_2$)), 149.8 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 181 Hz), 137.1 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 162 Hz), 121.3 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 164 Hz), 121.1 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 164 Hz), 78.5 (t, =*C*H$_2$, $^1J_{C-H}$ = 155 Hz), 77.1 (s, *C*(CH$_3$)$_3$), 76.6 (s, *C*(CH$_3$)$_3$), 51.9 (s, *C*(CH$_3$)$_3$), 37.1 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 31.9 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 29.3 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 125 Hz), 7.9 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd for C$_{27}$H$_{55}$N$_4$O$_2$Si$_2$Y: C, 52.92; H, 9.05; N, 9.14; Y, 14.51. Found: C, 52.14; H, 8.75; N, 9.05; Y, 14.35.

Preparation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(*N,N′*)-N-(H)−C(Me)=C(H)-2-NC$_5$H$_4$) (14b). To a toluene solution (20 mL) of **2** (0.52 g, 0.89 mmol), acetonitrile (48 μL, 0.92 mmol) was added at −80 °C. The solution was allowed to warm to room temperature and stirred for 4 h, after which the solvent was evaporated. Extraction of the yellow residue with pentane (10 mL), followed by concentration and cooling to −80 °C, afforded **14b** (0.43 g, 0.69 mmol, 77%) as yellow crystals. ^{1}H NMR (benzene-d_6, δ): 9.10 (s (br), 1H, NC$_5$*H*$_4$), 6.84 (ddd, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.61 (d, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 8.6 Hz), 6.22 (s (br), 1H, N*H*), 6.20 (td, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 1.3 Hz), 5.02 (d (br), 1H, =C*H*, $^4J_{H-H}$ = 2.1 Hz), 1.93 (s, 3H, C*H*$_3$), 1.55 (s, 18H, C(C*H*$_3$)$_3$), 1.23 (s, 18H, C(C*H*$_3$)$_3$), 0.50 (s, 6H, Si(C*H*$_3$)$_2$), 0.44 (s, 3H, Si(C*H*$_3$)$_2$), 0.41 (s, 3H, Si(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 162.0 (s, N*C*$_5$H$_4$(*ipso-C*)), 159.5 (s, *C*(Ph)=CH), 147.3 (d (br), NC$_5$H$_4$, $^1J_{C-H}$ = 173 Hz), 135.5 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 160 Hz), 123.2 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 162 Hz), 110.5 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 166 Hz), 92.7 (d, C(Ph)=*C*H, $^1J_{C-H}$ = 154 Hz), 76.6 (s, *C*(CH$_3$)$_3$), 52.0 (s, *C*(CH$_3$)$_3$), 37.1 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 125 Hz), 31.9 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 29.3 (q, *C*H$_3$, $^1J_{C-H}$ = 124 Hz), 7.9 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for C$_{28}$H$_{57}$N$_4$O$_2$Si$_2$Y: C, 53.65; H, 9.17; N, 8.94; Y, 14.18. Found: C, 53.44; H, 8.97; N, 9.00; Y, 14.08.

Preparation of {[Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y}$_2${μ,η^2,η^2-(*N,N′*,O)-OC-(2-NC$_5$H$_4$)$_2$} (15). A Schlenk flask (200 mL) containing a red-brown solution of **1** (0.50 g, 0.87 mmol) in *n*-pentane (20 mL) was degassed and charged with CO (1 atm). The color of the solution instantaneously turned purple. After 20 h at room temperature, the color of the solution had changed to deep blue. Evaporation of the volatiles gave **15** (0.72 g, 0.61 mmol, 70%) as a microcrystalline powder. ^{1}H NMR (benzene-d_6, δ): 9.04 (s (br), 1H, NC$_5$*H*$_4$), 7.65 (d, NC$_5$*H*$_4$, $^3J_{H-H}$ = 8.8 Hz), 7.04 (t, 1H, NC$_5$*H*$_4$, $^3J_{H-H}$ = 6.5 Hz), 5.93 (m, 1H, NC$_5$*H*$_4$), 1.52 (s, 9H, C(C*H*$_3$)$_3$), 1.48 (s, 9H, C(C*H*$_3$)$_3$), 1.34 (s, 9H, C(C*H*$_3$)$_3$), 1.30 (s, 9H, C(C*H*$_3$)$_3$), 0.54 (s, 3H, Si(C*H*$_3$)$_2$), 0.52 (s, 3H, Si(C*H*$_3$)$_2$), 0.47 (s, 3H, Si(C*H*$_3$)$_2$), 0.45 (s, 3H, Si-(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 149.2 (s, *ipso-C*), 147.3 (s, *ipso-C*), 146.9 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 166 Hz), 133.5 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 158 Hz), 120.1 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 159 Hz), 104.7 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 164 Hz), 78.0 (s, *C*(CH$_3$)$_3$), 77.1 (s, *C*(CH$_3$)$_3$), 52.5 (s, *C*(CH$_3$)$_3$), 51.9 (s, *C*(CH$_3$)$_3$), 37.4 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 37.0 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 32.4 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 31.7 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 8.2 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz), 7.9 (q, Si(*C*H$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd for C$_{51}$H$_{104}$N$_6$O$_5$Si$_4$Y$_2$: C, 52.28; H, 8.95; N, 7.17; Y, 15.18. Found: C, 52.04; H: 9.01; N, 7.07; Y, 15.08.

X-ray Structure Determination of [Me$_2$Si(NCMe$_3$)-(OCMe$_3$)]$_2$Y(η^2-(*C,N*)-CH$_2$-2-NC$_5$H$_4$) (2) and [Me$_2$Si(NCMe$_3$)-(OCMe$_3$)]$_2$YC≡CPh·THF·(pentane)$_{0.5}$ (9). Suitable crystals were measured at 130 K with graphite-monochromated Mo Kα radiation on an Enraf-Nonius CAD-4F diffractometer equipped with a low-temperature unit.[31] Precise lattice parameters and their standard deviation and orientation matrix were derived from the angular settings of 22 reflections (**2**, 14.93° < θ < 19.90°; **9**, 16.55 < θ < 20.33°) in four alternative settings.[32] The unit cell was identified as monoclinic, space group $P2_1/n$ for **2** and space group $C2/c$ for **9**.[33] Intensity data were corrected for Lorentz and polarization effects and scale

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variation and reduced to F_o.[34] The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[35] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms refined with block-diagonal least-squares procedures (CRYLSQ)[36] minimizing the function $Q = \sum_{\mathbf{h}} [w(|F_o| - k|F_c|)^2]$. After completion of the isotropic refinement of **2**, empirical absorption corrections based on $(F_o - F_c)$ difference were applied with the program DIFABS.[37] Final refinement on F_o was by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms. The crystals of **2** exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter ($g = 0.27(4) \times 10^{-4}$).[38] Scattering factors were taken from Cromer and Mann.[39] Anomalous dispersion factors were taken from Cromer and Liberman.[40] All calculations were carried out on a HP9000/735 computer at the University of Groningen with the program packages Xtal,[41] PLATON[42] and ORTEP.[43]

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Supporting Information Available: Text giving the IR spectral data for complexes **1**−**4**, **9**, **10**, **13b**, **14b**, and **15** and tables of anisotropic thermal displacement parameters, atomic coordinates, bond lengths, bond angles, and torsion angles for $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$ (**2**) and $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh{\cdot}THF{\cdot}(pentane)_{0.5}$ (**9**) (30 pages). Ordering information is given on any current masthead page.

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