Insertion and C−H Bond Activation of Unsaturated Substrates by Bis(benzamidinato)yttrium Alkyl, $[PhC(NSiMe_3)_2]_2YR$ (R = $CH_2Ph\cdot THF$, $CH(SiMe_3)_2$), and Hydrido, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$, Compounds

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The reactivity of benzamidinate-stabilized yttrium complexes $[PhC(NSiMe_3)_2]_2YR$ (R = $CH_2Ph\cdot THF$, $CH(SiMe_3)_2$) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ has been investigated. The complexes are thermally stable showing no sign of decomposition, ligand or solvent metalation, or H/D exchange after hours at 100 °C in cyclohexane-d_{12} or benzene-d_6. The alkyls are also stable in ethereal solvents. However, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ induces C−O cleavage in THF solutions. The complexes $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ are modestly active in ethylene polymerization but are inactive toward propylene and 1-hexene. Terminal alkynes react stoichiometrically with $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ to give μ-acetylide dimers, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CR)\}_2$ (**1**, R = H; **2**, R = Me; **3**, R = *n*-Pr; **4**, R = $SiMe_3$; **5**, R = Ph; **6**, R = CMe_3). Treatment with THF leads to cleavage of these dimers, yielding $[PhC(NSiMe_3)_2]_2YC{\equiv}CR\cdot THF$ (**7**, R = H; **8**, R = CMe_3). $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}Me)_2Li\cdot TMEDA$ reacts with $HC{\equiv}CCMe_3$ to afford $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li\cdot TMEDA$. $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ catalyzes the regioselective dimerization of bulky 1-alkynes. With small 1-alkynes, HC≡CR (R = H, Me, *n*-Pr), no dimerization was observed and the reaction stops with the formation of the alkynyl dimers $\{PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CR)\}_2$ (**1**−**3**). Treatment of $[PhC(NSiMe_3)_2]_2YR$ with acetonitrile gives either C−H bond activation or insertion. For R = $CH(SiMe_3)_2$, C−H bond activation occurs, yielding $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}(N,N')\text{-}N(H)C(Me){=}C(H)C{\equiv}N)\}_2$ (**10**). For R = $CH_2Ph\cdot THF$ a mixture of C−H bond activation (**10**, 10%) and insertion products, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}N{=}C(Me)CH_2Ph)\}_2$ (**11a**, 50%) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}N(H)C(Me){=}C(H)Ph)\}_2$ (**11b**, 40%), was obtained. The hydride $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ exclusively gives insertion of acetonitrile, affording $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}N{=}C(H)Me)\}_2$ (**12**). With pyridine, $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ gives C−H bond activation, whereas $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ undergo insertion yielding $[PhC(NSiMe_3)_2]_2Y(NC_5H_5R)$ (**13**, R = H; **14**, R = CH_2Ph). In contrast, with α-picoline, $[PhC(NSiMe_3)_2]_2YR$ (R = $CH(SiMe_3)_2$, $CH_2Ph\cdot THF$) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ afford the α-picolyl derivative, $[PhC(NSiMe_3)_2]_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}CH_2NC_5H_4$ (**15**). The difference in reactivity of the bis(benzamidinate)-stabilized complexes compared to the corresponding Cp^*_2YR systems, e.g. the low tendency to catalyze C−C bond formation, the reduced or even the absence of C−H/C−O activation properties, and the enhanced nucleophilic and Brønsted base reactivities, is interpreted in terms of the high ionicity of the benzamidinate-stabilized yttrium complexes. The contracted yttrium orbitals are less exposed than in the dicyclopentadienyl derivatives and therefore not suited to establish the first initiating interaction with substrate molecules.

Introduction

In a previous article[1] we have reported a new class of yttrium complexes $[PhC(NSiMe_3)_2]_2YX$ in which Y−H, Y−C, and Y−X (X = heteroatom) bonds are stabilized by two *N*,*N*′-bis(trimethylsilyl)benzamidinato ligands. These new ancillary ligands may function as attractive alternatives for pentamethylcyclopentadienyls. Molecular modeling studies indicate that the steric aspects of the two ligand systems do not differ dramatically. Theoretical considerations on the other hand suggest that benzamidinate ligands accumulate negative charge more strongly than cyclopentadienyls and therefore the bis(benzamidinato)yttrium complexes are more ionic. This increased ionicity is expected to have a notable effect on the reactivity of Y−C and Y−H (and Y−X) bonds. To probe this, an exploratory study of the reactivity of bis(benzamidinato)yttrium complexes, $[PhC(NSiMe_3)_2]_2YR$ (R = $CH(SiMe_3)_2$, CH_2Ph) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$, was carried out. For (pentamethyl)cyclopentadienyl ligand-stabilized yttrium systems, the dominant reaction pathways are insertion of unsaturated substrates into Ln−X (X = C, H, N) bonds and X−H (X = C, H, N, O) bond activation.[2] In the latter

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case, the activation of saturated hydrocarbons like methane is among the most intriguing.[2a,d,f] Although some modifications of the ligand system have been introduced,[3,4] the most extensively studied system is Cp^*_2LnR (Ln = Sc, Y, lanthanides; R = alkyl, hydride).[2]

This contribution reports the results of an extensive study on the potential of bis(benzamidinato)-stabilized Y−C and Y−H bonds in (catalytic) insertion and activation chemistry (e.g. with alkenes, alkynes, nitriles, C−O, and aromatic C−H bonds). In order to make a realistic comparison, the substrates and reactions selected to be investigated were those studied earlier for the well-known yttrocene and analogous systems.[2,3] Parts of this work have been published in communication form.[5]

Results and Discussion

Thermolysis and Behavior of $[PhC(NSiMe_3)_2]_2YR$ (R = $CH_2Ph\cdot THF$, $CH(SiMe_3)_2$) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ in Common Solvents. Before the reactivity of these compounds toward unsaturated substrates was tested, their thermolysis in, and behavior toward, common solvents was investigated.

(a) Aromatic and Aliphatic Solvents. The alkyl and hydrido complexes are stable in aromatic (benzene-d_6) and aliphatic solvents (cyclohexane-d_{12}) for prolonged periods of time at 100 °C. This stability is quite surprising when compared with the Cp^*_2LnR analogues (R = alkyl, H; Ln = Sc, Y, lanthanides) which undergo metalation of the Cp* ligands upon thermolysis, yielding fulvene species.[2,6] Another interesting feature of the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)yttrium alkyls and hydride is their complete lack of C−H bond activation of solvent molecules, i.e. H/D scrambling and metalation of deuterated aromatic solvents, which is a prominent and well-investigated feature of Cp^*_2LnR systems.[2]

(b) Ether Solvents. The alkyls $[PhC(NSiMe_3)_2]_2YR$ (R = $CH_2Ph\cdot THF$, $CH(SiMe_3)_2$) are stable in ethers (Et_2O, THF; reflux, days). Whereas $\{Cp^*_2Y(\mu\text{-}H)\}_2$ reacts instantaneously with Et_2O at room temperature, the hydride $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ is stable (2 weeks, 25 °C) in ether.[2f] In benzene, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ does not react with THF (2 equiv, room temperature, days), but in neat THF (hours, room temperature), ethane and minor amounts (±15%) of ethylene (Töpler pump determination, GC−MS) are formed. Olefinic resonances in the ^1H NMR spectrum of the product mixture suggest the formation of yttrium enolate species as a result of C−O bond activation.

Group 3 metal and lanthanide complexes can cleave THF in a variety of ways. Which route is followed seems to depend on many variables like metal, ancillary ligand system, and the nature of the carbyl or hydrido ligand. For $[C_5H_4Me]_2YR\cdot THF$ (R = Me, CH_2SiMe_3),[7] *ortho*-metalation followed by extrusion of ethylene has been proposed (Scheme 1A). The hydrides $\{Cp^*_2Ln(\mu\text{-}H)\}_2$ (Ln = Y, Sm) activate the C−O bond yielding *n*-butoxo derivatives $Cp^*_2LnO\text{-}n\text{-}Bu$[2o,8] In an analogous reaction, $[Cp^*_2Sm\cdot 2THF]^+[BPh_4]^-$ reacts with Cp*K to form $Cp^*_2SmO(CH_2)_4C_5Me_5\cdot THF$ (Scheme 1B).[9] In contrast, the closely related $\{Cp^*_2Ce(\mu\text{-}H)\}_2$ yields a μ-oxo species with elimination of ethane (0.5 mol/mol Ce; Scheme 1C).[8] The almost quantitative formation of ethane in combination with the ^1H NMR spectrum of the product mixture, which indicates that an enolate fragment, $[Y]-OCH{=}CH_2$, has been formed, suggests that the reaction of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ with THF proceeds by the same mechanism as proposed for $\{Cp^*_2Ce(\mu\text{-}H)\}_2$. The presence of minor amounts of ethylene, also formed during the reaction of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ with THF, suggests that subsequent C−O bond activation of the enolate, yielding a μ-oxo species, also occurs (Scheme 1C).

Reactivity toward Alkenes. (a) Olefin Polymerization. When heated to 65 °C, in benzene-d_6, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ polymerizes ethylene (4 atm). ^1H NMR spectra collected during the reaction showed the gradual consumption of ethylene and, more importantly, no other yttrium compounds other than $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$. Resonances attributable to ethylene oligomers and mixed hydrido−alkyl species, $[Y](\mu\text{-}H)(\mu\text{-}R)[Y]$ ([Y] = $[PhC(NSiMe_3)_2]_2Y$), as observed by Marks *et al.* for $[Y] = [\mu,\eta^5,\eta^5\text{-}(C_5Me_4)SiR_2(C_5H_4)]_2Y$[3e] and by Schaverien for [Y] = Cp*[ArO]Y,[4d] were absent. Under more drastic conditions (55 °C, 70 atm of ethylene) a

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(5) The reaction of $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ with ethyne, leading to the ethynyl-bridged dimer $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH)\}_2$ and the molecular structure of this acetylide complex have been published: Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931.

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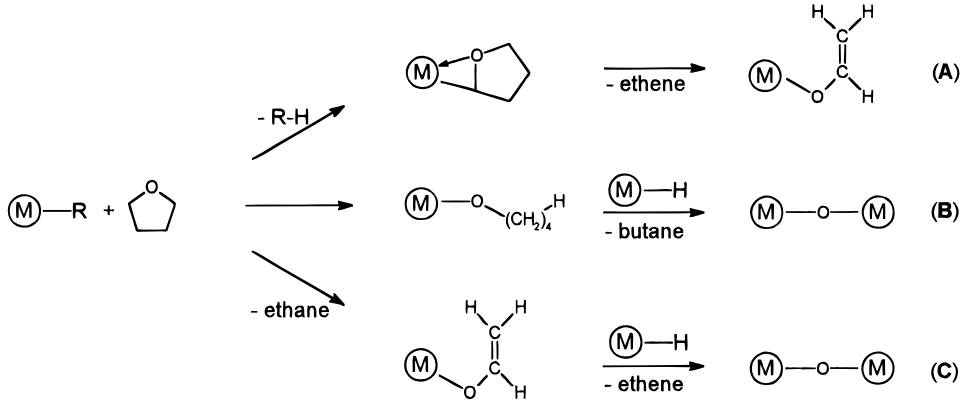
Scheme 1. Examples of C−O Bond Activation and Metalation of THF by Group 3 Metal and Lanthanide Alkyls and Hydrides[a]



[a] Key: (**A**) M = $[C_5H_4Me]_2Y$, R = CH_3·THF, CH_2SiMe_3·THF; (**B**) M = Cp^*_2Ln (Ln = Y, Sm), R = μ-H; (**C**) M = Cp^*_2Ce, $[C_6H_5C(NSiMe_3)_2]_2Y$, R = μ-H.

somewhat higher activity was found (4 g of PE/mmol of [Y]·h), but the total yield of polyethylene remained low. The benzyl THF adduct, $[PhC(NSiMe_3)_2]_2YCH_2Ph$·THF, also polymerizes ethylene (65 °C, 4 atm of ethylene), but the rate appears to be even lower than for $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ under the same conditions. Again, the ^{1}H NMR spectra collected during and after the reaction showed the gradual consumption of ethylene and $[PhC(NSiMe_3)_2]_2YCH_2Ph$·THF as the only detectable organoyttrium derivative present. With propylene (4 atm) and 1-hexene (neat), the precursors $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ and $[PhC(NSiMe_3)_2]_2YCH_2Ph$·THF were found unreacted. Neither oligo/polymerization nor indication for the formation of an η^3-allyl species, as found for $\{Cp^*_2Ln(\mu\text{-H})\}_2$ (Ln = Y, lanthanides),[2dg,10] could be observed under the conditions employed (days, 80 °C).

Clearly, activation of the precatalysts by dissociation and/or precomplexation of ethylene is unfavorable in these complexes. This can be explained as a consequence of the high ionic character of these bis(benzamidinato)yttrium compounds, which causes the yttrium orbitals to contract strongly, making them less available to interact with an incoming olefin. The fact that the precursors are the only organoyttrium complexes present in detectable amounts during NMR tube polymerization experiments indicates that dissociation of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ into the corresponding monomeric hydride, and dissociation of THF from $[PhC(NSiMe_3)_2]_2YCH_2Ph$·THF, is slow which will also reduce the activity. The polyethylene obtained (M_w = 239 900, M_n = 46 300) has a broad molecular weight distribution (M_w/M_n = 5.2). In this it strongly resembles the polyethylene obtained by Schaverien *et al.*,[4d] who used a cyclopentadienyl aryloxy stabilized yttrium hydride, $\{Cp^*[2,6\text{-}(CMe_3)_2C_6H_3O]Y(\mu\text{-H})\}_2$, as a catalyst. Several possibilities were discussed (slow initiation and rapid propagation, heterogenization, β-H elimination, chain transfer) to explain the observed broad dispersity.[4d,11] For the system reported here, these explanations may hold too but there may be another reason as well, e.g. the generation of several active species by ligand loss or redistribution. The GPC chromatogram indicates a multimodality of the polyethylene obtained. However, in view of the low catalytic activity of the system studied this aspect has not been analyzed further.

(b) Olefin Hydroboration. As part of a more general study on the hydroboration of alkenes catalyzed by group 3 and 4 metals and lanthanides, the catalytic activity of the bis(benzamidinato)yttrium alkyl, $[PhC(NSiMe_3)_2]_2YR$ (R = CH_2Ph, $CH(SiMe_3)_2$), and hydrido, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$, compounds in the hydroboration of 1-hexene with catecholborane was investigated. Although published elsewhere,[12] a short account of the results for the compounds under discussion here seems appropriate. The bis(benzamidinato)yttrium complexes proved to be catalytically active, but the activity is about 5−10% of that of the lanthanum complex, $Cp^*_2LaCH(SiMe_3)_2$, for which the highest activity has been reported.[2q] In all cases, fast catalyst deactivation occurs, probably due to the reaction of catecholborane with the benzamidinato ligands. Nevertheless, $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ showed catalytic activities substantially higher than that for $Cp^*_2YCH(SiMe_3)_2$.[12] This is surprising, because, in the absence of catecholborane, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ does not react at all with 1-hexene. Possibly, catecholborane activates the yttrium catalyst by forming intermediates such as $[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})_2B(O_2C_6H_4)$. It could also be that activation is due to partial transfer of benzamidinate ligands from yttrium to boron, comparable to the observed ligand exchange reaction of $[PhC(NSiMe_3)_2]_2YCl$·THF with $LiAlH_4$ yielding $[PhC(NSiMe_3)_2]_2AlH$.[1] Probably, reaction of the precursors with catecholborane yields initially an active, though unstable, catalyst which rapidly decomposes.

Reactivity toward 1-Alkynes. Both $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ react quickly (1 h, room temperature) with 1-alkynes (stoichiometric amounts or excess) affording dimeric alkynyl complexes, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-C}{\equiv}CR)\}_2$. With respect to the formation of these alkynyls, the catalytic dimerization of 1-alkynes is very slow and the rate strongly depends on the steric bulk of the alkyne substituents. Whereas bulky alkynes are dimerized, sterically unhindered 1-alkynes are not and the reaction stops with the formation of the dimeric alkynyl com-

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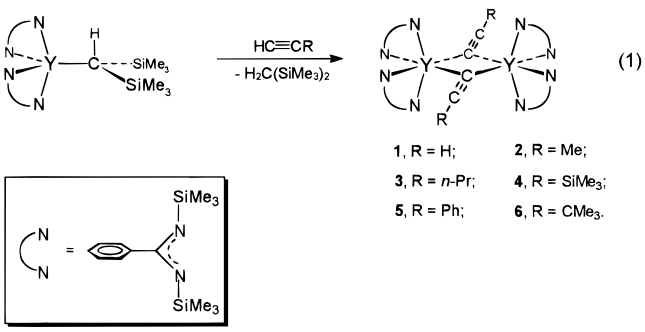
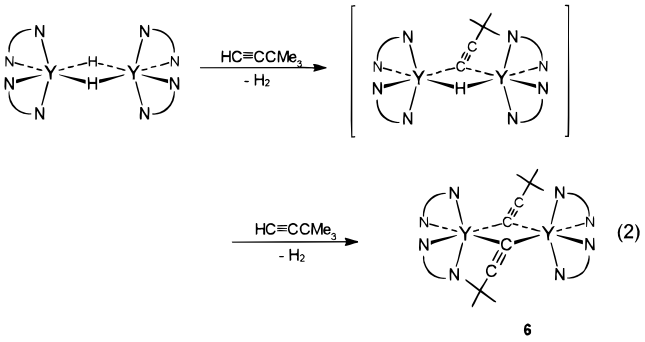
plexes. Clearly, the dimeric alkynyls play a decisive role, stabilizing the catalytically active monomeric alkynyl species. First the synthesis and characterization of some well-defined alkynyl derivatives will be described. A study concerning the dimerization of 1-alkynes catalyzed by bis(benzamidinato)yttrium complexes will be discussed further on.

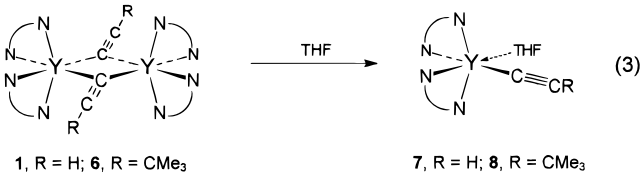
(a) Synthesis of Bis(*N*,*N*-bis(trimethylsilyl)benzamidinato)yttrium Alkynyls. $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ reacts with 1 equiv of 1-alkyne, HC≡CR, to form the corresponding dimeric alkynyls, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CR)\}_2$ (R = H (**1**), Me (**2**), *n*-Pr (**3**), $SiMe_3$ (**4**), Ph (**5**), CMe_3 (**6**); eq 1).[5] With the hydride $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ as starting material for **6**, minor amounts of the intermediate $[\{[PhC(NSiMe_3)_2]_2Y\}_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CCMe_3)]$ (^{1}H NMR: δ 8.0, t, μ-H, $^1J_{YH}$ = 28 Hz) and traces of H_2 and $H_2C{=}C(H)CMe_3$ could be identified by ^{1}H NMR spectroscopy. The presence of the intermediate suggests a stepwise reaction with HC≡$CCMe_3$ (eq 2), similar to the reaction of $\{Cp^*[ArO]Y(\mu\text{-}H)\}_2$ with HC≡$CSiMe_3$.[4d]





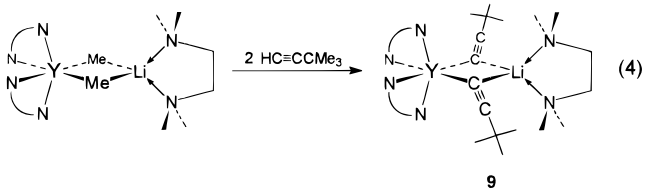
The traces of $H_2C{=}C(H)CMe_3$ indicate insertion of the alkyne into the Y−H bond and subsequent protonation by another alkyne. This could even take place in the dimeric hydride and form the first step to the mixed hydride−alkynyl intermediate. It is not due to straightforward hydrogenation of the alkyne by $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ since in a reaction with excess H_2 and HC≡$CCMe_3$ no $H_2C{=}C(H)CMe_3$ was formed. Clearly, the insertion of an alkyne into an Y−H bond cannot compete with protonolysis by the acidic hydrogen of the alkyne and formation of the alkynyls. The insertion/protonation competition is very similar to the reaction of $[PhC(NSiMe_3)_2]_2AlH$ with HC≡$CCMe_3$, but here the insertion is much easier and considerable amounts of the olefin are formed.[13]

The ^{13}C NMR spectra (benzene-d_6) of the yttrium acetylides (**1**−**6**) at elevated temperatures (70−80 °C) did not show any sign of dissociation, suggesting stable dimeric structures. However, the dimers can be cleaved by a Lewis base. Addition of THF to solutions of **1** or **6** resulted in instantaneous formation of the corresponding monomeric THF adducts, $[PhC(NSiMe_3)_2]_2YC{\equiv}CR{\cdot}$THF (R = H (**7**); R = CMe_3 (**8**), eq 3). This corresponds



with the reaction of $\{Cp^*_2Ce(\mu\text{-}C{\equiv}CCMe_3)\}_n$ with THF, affording $Cp^*_2CeC{\equiv}CCMe_3{\cdot}$THF.[2l,17b] In contrast, the compounds $[C_5H_4R]_2Y(\mu\text{-}C{\equiv}CCMe_3)\}_2$ (R = H, Me) do not react with THF.[2d]

When $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}Me)_2Li{\cdot}$TMEDA was treated with HC≡$CCMe_3$, the corresponding $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li{\cdot}$TMEDA (**9**, eq 4) could be isolated. This



compound is analogous with $Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}C{\equiv}CCMe_3)_2Li{\cdot}$TMEDA[13] and $Cp^*_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li{\cdot}$THF and $[Cp^*_2Sm(\mu\text{-}C{\equiv}CPh)K]_n$, prepared by Evans *et al.*[14]

(b) Characterization. The IR spectra of the acetylides (**1**−**9**) show ν(C≡C) frequencies ranging from 1914 to 2060 cm^{-1}, comparable to those of other dimeric group 3 and lanthanide acetylide compounds[2e,f,l,4d,14,15] and notably lower than for the corresponding free acetylenes.[16] The ^{1}H NMR spectra (25 °C) of **1**−**9** show sharp singlets for the benzamidinato trimethylsilyl groups, indicating fast fluxional behavior in solution. The ^{13}C NMR spectra of **1**−**6** display a triplet ($^1J_{Y-C}$ = 20−21 Hz) for the α-carbon of the acetylide. The splitting is due to ^{89}Y−^{13}C coupling and indicates that each alkynyl ligand interacts with two (time-averaged) identical yttrium centers. It is remarkable that the α-C resonance of **4** (δ = 172.3 ppm, $^1J_{Y-C}$ = 19 Hz) is considerably shifted to low field compared to **1**−**3** and **5** and **6** (these range from 136.0 to 146.6 ppm); why this should be so is, as yet, unclear. The ^{13}C NMR spectra of **7**−**9** show a doublet (**7**, δ = 111.6 ppm, $^1J_{Y-C}$ = 11 Hz; **8**, δ = 89.3 ppm, $^1J_{Y-C}$ = 12 Hz; **9**, δ = 121.1, $^1J_{Y-C}$ = 15 Hz) for the α-carbon of the acetylide, in agreement with a monomeric structure. Worth mentioning is that, due to the coupling with yttrium, the β-H of the ethynyl

(13) Duchateau, R.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.*, submitted for publication.

(14) (a) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Olofson, J. M. *J. Organomet. Chem.* **1989**, *376*, 311. (b) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618.

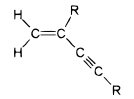
(15) For example see: (a) Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.* **1980**, *202*, C6. (b) Evans, W. J.; Engerer, W. J.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672. (c) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115. (d) Boncella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710. (e) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709. (f) Shen, Q.; Zheng, D.; Lin, L.; Lin, Y. *J. Organomet. Chem.* **1990**, *391*, 307.

(16) HC≡CH, ν(C≡C)(Raman) = 1947 cm^{-1}; HC≡CMe, ν(C≡C) = 2140 cm^{-1}; HC≡CPh, ν(C≡C) = 2110 cm^{-1}; HC≡$CCMe_3$, ν(C≡C) = 2110 cm^{-1}; HC≡$CSiMe_3$, ν(C≡C) = 2037 cm^{-1}.

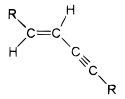
Table 1. Product Distribution of the Oligomerization of Terminal Alkynes, HC≡CR, Catalyzed by Group 3- and Lanthanide-Based Complexes

compd	R[a]	2,4-dimer[b,d]	1,4-dimer[c,d]	higher oligomers	ref
$[C_6H_5C(NSiMe_3)_2]_2YR'$	Me	100			this work
(R′ = $CH(SiMe_3)_2$, μ-H)	CMe_3	100			
	Ph	100			
	$SiMe_3$		100		
Cp^*_2ScMe	H			100	1e
	Me	100			
$Cp^*_2YCH(SiMe_3)_2$	CMe_3	100			1k
	Ph	89	11		
	$SiMe_3$	20	80		
$Cp^*_2LaCH(SiMe_3)_2$	Me	78		21	1k
	CMe_3	100			
	Ph		86	14	
	$SiMe_3$	4	45	51	
$Cp^*_2CeCH(SiMe_3)_2$	Me	74		25	1k
	CMe_3	100			
	Ph		82	18	
	$SiMe_3$	7	61	32	
$Cp^*_2Ce[CH(SiMe_3)_2]_2$	CMe_3	100			22
$Cp^*[ArO]YCH(SiMe_3)_2$	$SiMe_3$		100		4d

[a] Alkyne substituent. [b] 2,4-Disubstituted 1-buten-3-yne. [c] 1,4-Disubstituted 1-buten-3-yne. [d] Structures:



2,4-substituted 1-buten-3-yne



1,4-substituted 1-buten-3-yne

ligand of **7** appears as a doublet in the ^{1}H NMR spectrum (δ = 1.99 ppm, $^3J_{Y-H}$ = 1.3 Hz). This suggests a stronger interaction of yttrium with the ethynyl fragment in the monomeric **7** than in the dimeric **1**, for which no yttrium coupling is observed. However, the yttrium−carbon coupling constants in these compounds (**7**, $^1J_{Y-C}$ = 11 Hz; **1**, $^1J_{Y-C}$ = 20 Hz) suggest the opposite.

(c) Thermolysis of {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-C≡CR)}$_2$. Thermolysis (24−72 h, 100 °C) of the dimeric alkynyls (**1**−**6**) resulted in the formation of several unidentified products. The rate of the thermolysis strongly depends on the alkynyl substituent. Complex **1** decomposes within hours at 100 °C, while for **4** the characteristic triplet signal for the alkynyl α-carbon is still present after 2 days at 100 °C. Unequivocal assignment of resonances in the NMR spectra arising from C−C-coupled μ-trienediyl compounds, as formed upon thermolysis of {$Cp^*_2LnC{\equiv}CR$}$_n$ (Ln = La, Ce, Sm),[17] was not possible. Although the β-H signal in the ^{1}H NMR of **1** disappeared upon thermolysis (100 °C, 24h), formation of an acetylenediyl species, similar to $Cp^*_2LnC{\equiv}CLnCp^*_2$ (Ln = Sc,[18a] Sm[18b]), could not be established for our system. Since a complicated mixture of very soluble thermolysis products was formed, isolation and characterization of the individual products proved to be not possible.

(d) Catalytic Dimerization of Terminal Alkynes. To probe the catalytic activity of bis(benzamidinato)-yttrium compounds in 1-alkyne dimerization, a variety of different 1-alkynes were examined and the results compared with those obtained from Cp^*_2LnR (Ln = Sc,[2f,18a] Y,[2e,l] La,[2l,17b] Ce,[2l,17b] Sm;[14b] R = alkyl, alkynyl, H), $Cp^*Ce[CH(SiMe_3)_2]_2$,[19] and Cp*[ArO]YR (R = alkyl, alkynyl)[4d] systems.

(d.1) Scope of the Dimerization. The dimerization of 1-alkynes catalyzed by $[PhC(NSiMe_3)_2]_2YR$ (R = $CH(SiMe_3)_2$, $CH_2Ph{\cdot}THF$) and {$[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})$}$_2$ strongly depends on the alkyne substituent. For small 1-alkynes, HC≡CR (R = H, Me, *n*-Pr), no dimerization is observed (days, 80 °C) and the reaction stops with the formation of the dimeric acetylides (**1**−**3**). It is only for acetylenes HC≡CR with bulky substituents (R = Ph, $SiMe_3$, CMe_3) that catalytic dimerization takes place at all (*vide infra*). This observation strongly contrasts with the Cp^*_2LnR-catalyzed dimerization of 1-alkynes, for which high activity was observed for all alkynes regardless the size of the substituent. The assumption that the first step in the dimerization is formation of the acetylide is supported by the fact that the reaction rate is independent from whether $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$, {$[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})$}$_2$, or the acetylides **4**−**6** are used as precursor.

Compared to the $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce) catalyzed dimerization of 1-alkynes (N_t(25 °C) ≥ 1900 mol of substrate·mol of catalyst$^{-1}{\cdot}h^{-1}$),[2l,17b] the observed catalytic activity of $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ or {$[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})$}$_2$ is much lower (N_t(80 °C) = 20−40 mol·mol$^{-1}{\cdot}h^{-1}$). Although the coordinated THF retards the reaction considerably, the THF adduct **8** still does catalyze the dimerization of $HC{\equiv}CCMe_3$ (N_t(50 °C) ≈ 1 mol·mol$^{-1}{\cdot}h^{-1}$), which implies that coordinated THF can be replaced by an incoming acetylene.

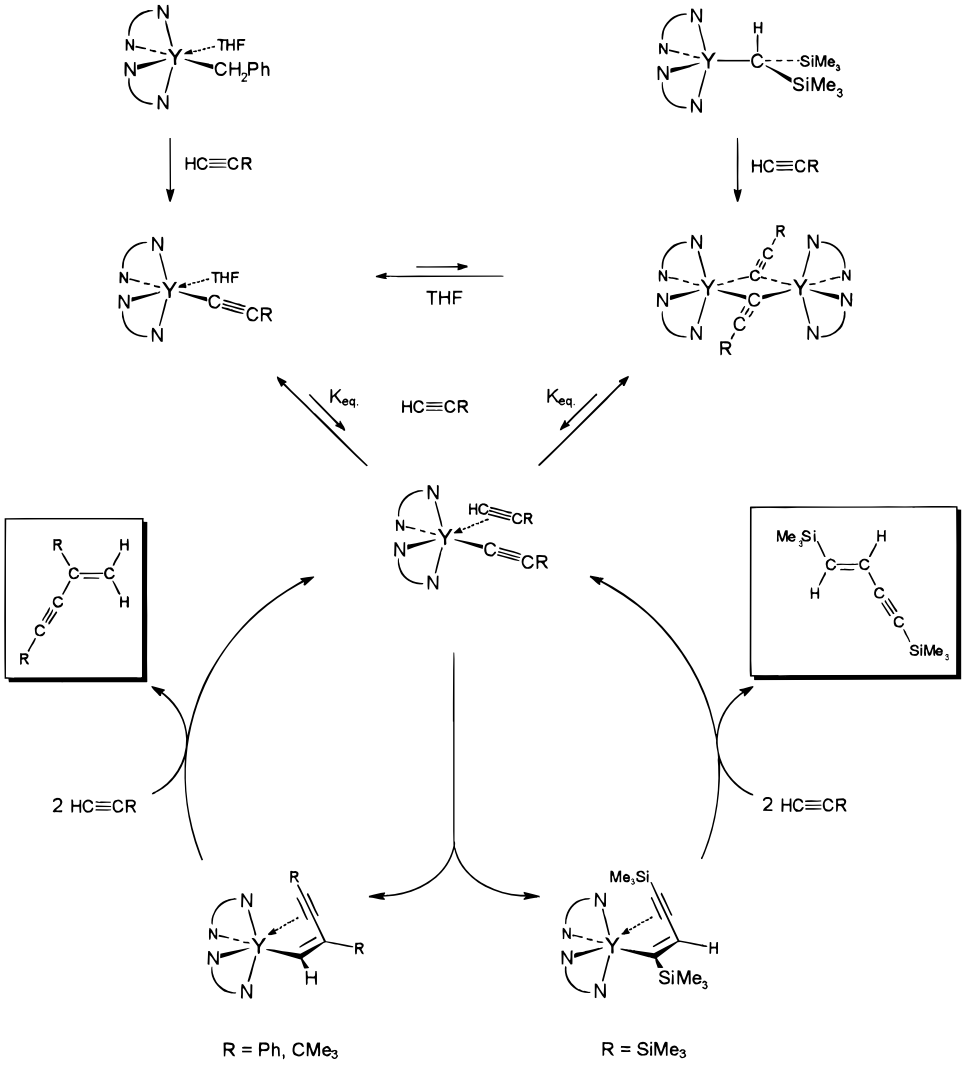
The regio- and stereoselectivity of the reaction depends strongly on the acetylene substituent and catalyst applied. For $Cp^*_2LnCH(SiMe_3)_2$, the only other group 3 metal and lanthanide complexes for which the dimerization of a variety of 1-alkynes has been investigated,

(17) (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) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J.; Reingold, A. L. *Organometallics* **1993**, *12*, 3618.

(18) (a) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525. (b) Evans, W. J.; Rabe, G. W.; Ziller, J. W. *J. Organomet. Chem.* **1994**, *483*, 21.

(19) Heeres, H. J. Ph.D. Thesis, University of Groningen, 1990.

Scheme 2



$HC{\equiv}CCMe_3$ is selectively coupled to the head-to-tail $H_2C{=}C(CMe_3)C{\equiv}CCMe_3$. For all other 1-alkynes tested, $HC{\equiv}CR$ (R = Me, Ph, $SiMe_3$), the selectivity was lower, yielding either mixtures of head-to-tail and head-to-head isomers (Ln = Y, La, Ce) or the additional formation of higher oligomers (Ln = La, Ce; Table 1).

In our system, $HC{\equiv}CPh$ and $HC{\equiv}CCMe_3$ are selectively coupled to head-to-tail dimers: 2,4-disubstituted 1-buten-3-ynes (Table 1). However, for $HC{\equiv}CSiMe_3$ the regioselectivity is reversed, exclusively yielding the head-to-head coupled product: *trans*-$Me_3SiC(H){=}C(H)C{\equiv}CSiMe_3$ (Table 1). This remarkable change in regioselectivity was also observed by Schaverien and Heeres, who found that $Cp^*[ArO]YCH(SiMe_3)_2$ and $Cp^*_2YCH(SiMe_3)_2$ preferentially couple $HC{\equiv}CSiMe_3$ to *trans*-$Me_3SiC(H){=}C(H)C{\equiv}CSiMe_3$ (Table 1).[2l,4b,17b] The origin of this change in regioselectivity is proposed to be of an electronic nature (*vide infra*).[2l,4b,20] That other factors may also play a decisive role is clearly illustrated by the $[Cp^*_2ZrMe(B(4\text{-}C_6H_4F)_4)]$-catalyzed coupling of $HC{\equiv}CSiMe_3$, which exclusively yields head-to-tail coupled dimers and trimers.[21]

(d.2) Mechanistic Considerations. The same mechanism as generally accepted for the dimerization of 1-alkynes by group 3 metals and lanthanides can also be applied to the system discussed here (Scheme 2).[2e,f,l,4b,14b,17b] Reactions of the precursors $[PhC(NSiMe_3)_2]_2YR$ (R = $CH(SiMe_3)_2$, $CH_2Ph{\cdot}THF$) give the dimers (**4**−**6**) or THF adducts (**7**, **8**) in the presence of 1-alkyne. The essential step, however, is formation of monomeric alkynyl compounds either by dissociation of dimers (**4**−**6**) or by dissociation of THF from adducts like **8**. The monomeric alkynyls $[PhC(NSiMe_3)_2]_2YC{\equiv}CR$ then complex a molecule of 1-alkyne followed by migratory insertion in a selectivity determining step to give enynyl complexes $[PhC(NSiMe_3)_2]_2YC(H){=}C(R)C{\equiv}CR$ (R = CMe_3, Ph) or $[PhC(NSiMe_3)_2]_2YC(R){=}C(H)C{\equiv}CR$ (R = $SiMe_3$), depending on R. The catalytic cycle is closed by hydrogen transfer from an alkyne with formation of the 1-buten-3-ynes, $H_2C{=}C(R)C{\equiv}CR$ (R = CMe_3, Ph) or $RC(H){=}C(H)C{\equiv}CR$ (R = $SiMe_3$) and the alkynyl complex $[PhC(NSiMe_3)_2]_2YC{\equiv}CR$. ^1H NMR studies of the alkyne dimerization show that the only (benzamidinato)yttrium complexes present in sufficiently high concentrations are the dimers, {[PhC-

(20) Stockis and Hoffmann have performed calculations on the polarization of the π^* orbitals of $HC{\equiv}CMe$ and $HC{\equiv}CSiMe_3$. The acetylene substituent appears to have a pronounced influence on the electron density of the alkyne sp-carbon atoms, and distinct differences in polarization were found for both alkynes. These electronic effects are believed to be responsible for the difference in regioselectivity of the catalytic dimerization of 1-alkynes: Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

(21) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185.

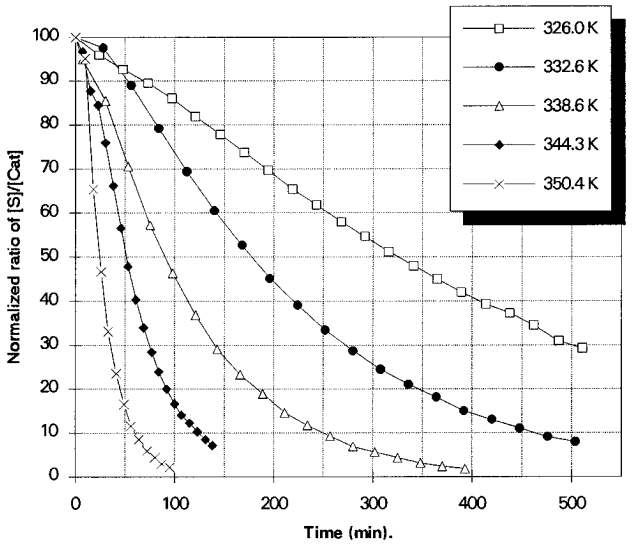


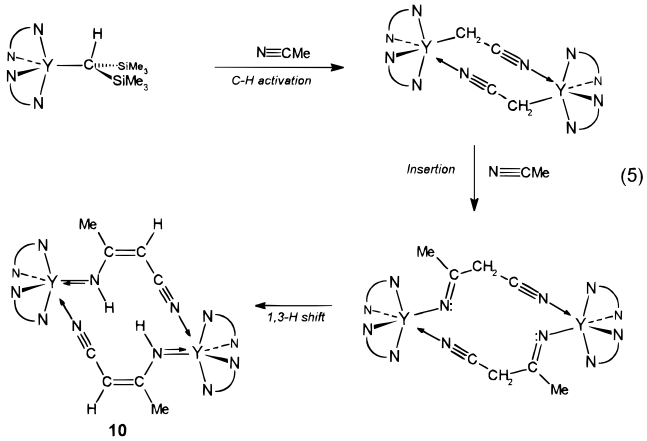
Figure 1. Normalized ratio of substrate to yttrium concentration as a function of time and temperature for the dimerization of $HC{\equiv}CCMe_3$ using $[C_6H_5C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ as precatalyst.

$(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CR)\}_2$, or the THF adducts, $[PhC(NSiMe_3)_2]_2YC{\equiv}CR{\cdot}THF$. This suggests that a very small fraction (<3%) of yttrium is actually involved in the catalytic process as such. An estimate of the catalytic activity based on this 3% participation assumption leads to a turnover frequency N_t = 1300 $mol{\cdot}mol^{-1}{\cdot}h^{-1}$ at 80 °C. Although clearly higher than the observed activity, this intrinsic catalytic activity of the bis(benzamidinato)yttrium complexes is still lower than that of the corresponding Cp^*_2LnR system (Ln = Y, La, Ce; R = CMe_3, at 25 °C; N_t = 1900 $mol{\cdot}mol^{-1}{\cdot}h^{-1}$). The selectivity of the bis(benzamidinato)yttrium system, however, is higher than observed for the corresponding Cp^*_2LnR complexes. It is clear that the decrease of catalytic activity going from Cp^*_2LnR to $[PhC(NSiMe_3)_2]_2YR$ has two reasons. First, presumably very low monomer concentrations refer to low equilibrium concentrations of a monomeric complex (ligated or base free) rather than low substrate (i.e. alkyne) concentrations. The second reason arises from the monomer itself which seems less eager to complex and insert an incoming alkyne. Again this can be explained by the strongly contracted orbitals of the highly positively charged yttrium atom, which reduces the capacity of these orbitals to interact with substrates.[1] This fits the general reactivity pattern observed so far for the highly ionic bis(benzamidinato)yttrium complexes. Why the dimers are so stable is not easy to explain. Steric reasons seem to be important since the smaller the substituent on the alkyne (HC≡CR) is, the more stable the dimer appears to be. The stability increase even results in complete catalytic inactivity for R = H, Me, and *n*-Pr.

Although no build up of intermediates like $[PhC(NSiMe_3)_2]_2YC{\equiv}CR$ (R = CMe_3, Ph, $SiMe_3$), $[PhC(NSiMe_3)_2]_2YC(H){=}C(R)C{\equiv}CR$ (R = CMe_3, Ph), or $[PhC(NSiMe_3)_2]_2YC(R){=}C(H)C{\equiv}CR$ (R = $SiMe_3$,) could be observed, the first-order dependence on 1-alkyne (Figure 1) suggests that the rate-determining step is within the catalytic cycle. If C−H bond activation would be rate-determining, buildup of the yttrium-1-buten-3-ynyl should occur. Since this is not the case, probably insertion of an alkyne into the Y−C≡CR bond is rate-determining. The absence of the expected build up of monomeric $[PhC(NSiMe_3)_2]_2YC{\equiv}CR$ can be explained by fast dimerization of this monomer into the dimeric precursor (or THF adduct).

Reactivity toward Heteroatom-Containing Substrates: Insertion versus C−H Bond Activation. With heteroatom-containing unsaturated substrates such as acetonitrile,[2d,j,22] α,β-unsaturated ketones,[23] or pyridines,[2b,d−f,24] group 3 metal and lanthanide alkyl or hydrido complexes either give insertion or C−H bond activation. Whether insertion or C−H bond activation occurs, strongly depends on the M−C/M−H bond. Therefore, a study of the reactions of $[PhC(NSiMe_3)_2]_2YR$ (R = $CH(SiMe_3)_2$, $CH_2Ph{\cdot}THF$, μ-H) with such substrates will give information about the character of the Y−C and Y−H bond in this system.

(a) Acetonitrile. With acetonitrile, $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ gives C−H bond activation rather than insertion, yielding $H_2C(SiMe_3)_2$ and the novel dimeric crotonitrileamido complex, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}(N,N')\text{-}N(H)C(Me){=}C(H)C{\equiv}N)\}_2$ (**10**, eq 5). This contrasts with



(5)

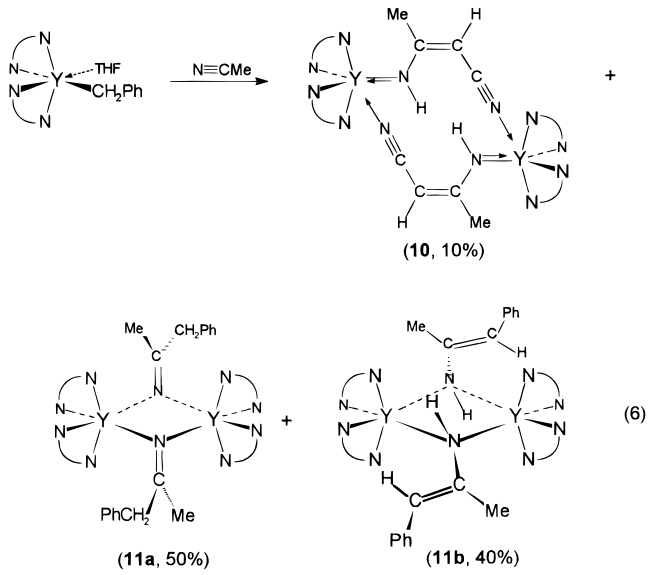
the reactions of $\{[C_5H_4R]_2Y(\mu\text{-}H){\cdot}THF\}_2$ (R = H, Me) and Cp^*_2ScR (R = *p*-Me-C_6H_4, Me) with acetonitrile: both giving clean insertion.[2d,22] Metalation was also observed for $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce) with acetonitrile, resulting in dimeric cyanomethyl complexes, $\{Cp^*_2Ln(\mu\text{-}CH_2C{\equiv}N)\}_2$.[2] For our system, this compound could not be detected. However, it is likely that it is formed as an intermediate which reacts further by insertion of another 1 equiv of acetonitrile, followed by a 1,3-H shift, to give **10** (eq 5).[25]

The reaction is strongly reminiscent of the alkali metal catalyzed dimerization of acetonitrile to crotonitrileamides,[26,27] emphasizing the ionic character of the Y−C bond in the bis(benzamidinato)yttrium system. The IR and NMR data for **10** are in good agreement with those of $Na[N(H)C(Me){=}C(H)C{\equiv}N]$.[26,27] The lowfield shift of the *C*(Me)=C (δ = 131.3 ppm) and the highfield shifts of the *C*(H)=C (δ = 48.1 ppm) and C(*H*)=C (δ = 3.50 ppm) resonances in the ^{13}C and ^1H NMR spectra of **10** clearly demonstrate the extensive charge delocalization within the crotonitrileamido fragment.

(22) Bercaw, J. E.; Davies, D.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.
(23) (a) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908. (b) Deelman, B.-J.; Bijpost, E. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1741.
(24) (a) Deelman, B.-J.; Stevels, W. M.; Lakin, M. T.; Spek, A. L.; Teuben, J. H. *Organometallics* **1994**, *13*, 3881. (b) Deelman, B.-J. Ph.D. Thesis, University of Groningen, 1994.

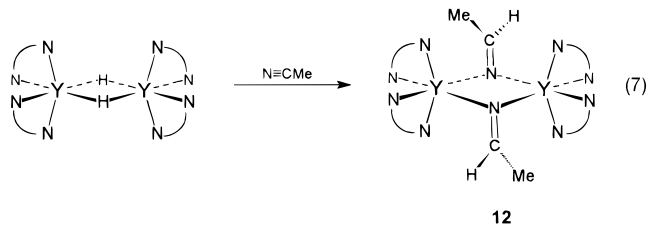
It appears that the bulky carbyl group in $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ acts as a classic Brønsted base, while the sterically less hindered $N{\equiv}CCH_2$ fragment of the intermediate cyanomethyl complex is a better nucleophile which leads to insertion of another acetonitrile. When the reaction of $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ with exactly 1 equiv of acetonitrile was carried out, a 1:1 mixture of $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ and **10** was obtained. Hence, the insertion of the second 1 equiv of $N{\equiv}CMe$ is faster than the preceding metalation. In contrast, for $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce), C−H bond activation is faster as is illustrated by the selective formation of the dimeric cyanomethyl complex.[2j]

The reaction of $[PhC(NSiMe_3)_2]_2YCH_2Ph{\cdot}THF$ with acetonitrile yields a mixture of compounds. Besides insertion products $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}N{=}C(Me)CH_2Ph)\}_2$ (**11a**, 50%) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}NHC(Me){=}C(H)Ph)\}_2$ (**11b**, 40%),[25] competitive deprotonation of acetonitrile is observed yielding the crotonitrileamido complex (**10**, 10%, eq 6). The enamine complex **11b** is formed as a result of imine−enamine tautomerism, similar to that observed for **10**.



(6)

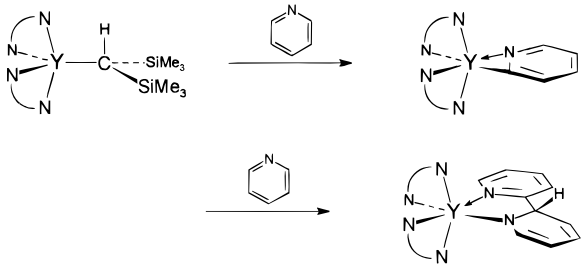
Finally, the hydride $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ reacts instantaneously at room temperature with $N{\equiv}CMe$ (eq 7), exclusively yielding the insertion product $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}N{=}C(H)Me)\}_2$ (**12**). The ^1H NMR spectra of **12** are consistent with those of the corresponding $\{[C_5H_4R]_2Y(\mu\text{-}N{=}C(H)Me)\}_2$ (R = H, Me) species, prepared in a similar fashion by Evans *et al.*[2c] In contrast to its yttrocene analogues, complex **12** is unstable and decomposes rapidly at room temperature, forming an mixture of unidentified products.



(7)

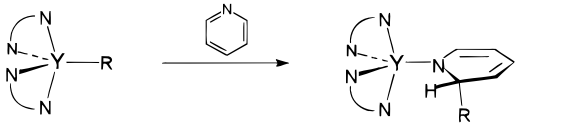
These results show that the competition between nucleophilicity and Brønsted basicity of the R group in $[PhC(NSiMe_3)_2]_2YR$ (R = $CH(SiMe_3)_2$, CH_2Ph, μ-H) has a strong influence on the reaction of these compounds with α-hydrogen-containing nitriles. The bulky bis(trimethylsilyl)methyl substituent tends to react as a classic Brønsted base like M_2−naphthalene (M = Li, Na, K, MgCl)[26] and $NaN(SiMe_3)_2$,[27] deprotonating acetonitrile. With only 10% deprotonation of acetonitrile, the benzyl group in $[PhC(NSiMe_3)_2]_2YCH_2Ph{\cdot}THF$ clearly shows a reduced Brønsted base character and resembles Cp^*_2ScR (R = *p*-Me-C_6H_4, Me),[22] $[Cp'_2MR]^+$ ($Cp' = C_5H_5$, C_5H_4Me; M = Ti, Zr; R = alkyl),[28a−c] and $Al(NEt_2)Et_2$.[29] As a result of its highly nucleophilic character, the hydride, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$, only shows insertion of acetonitrile, analogous to Cp^*_2ScH,[22] $Cp^*_2ZrH_2$,[22a] and $[Cp'_2ZrH]^+$ ($Cp' = C_5H_5$, C_5H_4Me).[28c,d]

(b) Pyridines. When $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ was treated with excess pyridine, a complicated reaction occurred. Quantitative formation of the alkane, $H_2C(SiMe_3)_2$, indicated metalation of pyridine. However, the expected pyridyl species could not be detected by ^1H NMR spectroscopy. Vinylic C−H resonances (δ = 4−6 ppm) suggest partial reduction of pyridine. It is probable that insertion of another 1 equiv of pyridine into the Y−C bond of the initially formed pyridyl derivative occurred, similar to that proposed for the reaction of $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$ with pyridine (eq 8).[24]



(8)

While $\{Cp^*_2Y(\mu\text{-}H)\}_2$ is known to give C−H bond activation with pyridine yielding the pyridyl, $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$,[2e,24] reaction of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ resulted in insertion rather than C−H bond activation, as the 1,2-inserted product $[PhC(NSiMe_3)_2]_2YNC_5H_6$ (**13**, eq 9) was obtained. Hence, the reactivity of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ toward pyridine resembles



13, R = H; **14**, R = CH_2Ph

(9)

(25) The products (**10**, **11a**,**b**) in these reactions and the intermediates proposed in eq 5 all are suggested to be dimeric. The justification for this is the close analogy with strongly related (structurally characterized) complexes, e.g. **10**, $[Me_2Si(CMe_3)(OCMe_3)]_2Y(\mu\text{-}(N,N')\text{-}N(H)C(Me){=}C(H)C{\equiv}N)\}_2$ (Duchateau, R.; Tuinstra, T.; Brussee, E. A.; Meetsma, A.; van Duijnen, P. Th.; Teuben, J. H. Manuscript in preparation), and **11a**,**b**, $\{Cp_2Y(\mu\text{-}N{=}C(H)Me)\}_2$ (ref 2c).

(26) (a) Binev, I. G.; Todorova-Momcheva, R. I.; Juchnovski, I. N. *Dokl. Bolgarskoj Acad. Nauk.* **1976**, *29*, 1301. (b) Juchnovski, I. N.; Binev, I. G. *J. Organomet. Chem.* **1975**, *99*, 1.

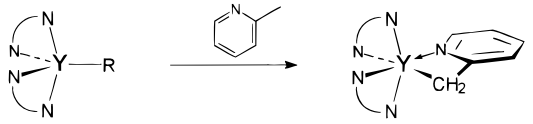
(27) Krüger, C. *J. Organomet. Chem.* **1967**, *9*, 125.

(28) (a) Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833. (b) Borkowsky, S. L.; Baenziger, N. C.; Jordan, R. F. *Organometallics* **1993**, *12*, 486. (c) Alelyunas, Y. W.; Guo, Z.; LaPointe, R. E.; Jordan, R. F. *Organometallics* **1993**, *12*, 544. (d) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546.

(29) Hirabayashi, T.; Itoh, K.; Sakai, S.; Ishii, Y. *J. Organomet. Chem.* **1970**, *21*, 273.

that of $\{[C_5H_4R]_2Y(\mu\text{-H})\cdot THF\}_2$ (R = H, Me).[2c] Subsequent thermal isomerization into the 1,4-addition product, as observed for the latter, did not occur in our system (days, 100 °C), however. Since the reactivity of the benzyl derivative, $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ toward acetonitrile was found to be intermediate between that of the bulky alkyl, $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (C−H bond activation), and the hydride, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ (insertion), we were interested to see how it would react with excess pyridine. Compound $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ reacts instantaneously with pyridine (2.5 equiv) by insertion to form exclusively the 1,2-insertion product, $[PhC(NSiMe_3)_2]_2YNC_5H_5\text{-}2\text{-}CH_2Ph$ (**14**, eq 9). Unfortunately, its extremely high solubility precluded purification, although it could conclusively be identified (^1H, ^{13}C NMR). Hence, the reactivity of $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ toward pyridine is very similar to that of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ and alkyllithium reagents. The Ziegler alkylation of pyridines by alkyllithium reagents involves intermediate 1,2-insertion products which subsequently undergo elimination of LiH.[30] However, analogous formation of the yttrium hydride $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ and release of 2-benzylpyridine, or formation of $[PhC(NSiMe_3)_2]_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}C(H)PhNC_5H_4)$ (*vide infra*), was not observed in this system.

Since its methyl protons are rather acidic, metalation at the methyl position of picoline was expected to compete with insertion. NMR tube reactions of $[PhC(NSiMe_3)_2]_2YR$ (R = $CH(SiMe_3)_2$, $CH_2Ph\cdot THF$) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ with α-picoline indeed showed the formation of $H_2C(SiMe_3)_2$, toluene, and H_2, respectively, together with the α-picolyl derivative, $[PhC(NSiMe_3)_2]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$ (**15**, eq 10).[31] While



(10)

R = $CH(SiMe_3)_2$, $CH_2Ph.THF$, μ-H

15

this reaction is strictly analogous to that of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$[31] and alkyllithium reagents with α-picoline,[32] it fully contrasts that of the corresponding Cp^*_2YR (R = Me·THF, $CH(SiMe_3)_2$) systems, which metalated the pyridyl ring to give $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Me)$.[2e]

Conclusions

It is clear that the chemistry of bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)yttrium alkyl and hydrido compounds is significantly different from that of the corresponding Cp^*_2YR complexes. Most outstanding is the low tendency of bis(benzamidinato)yttrium complexes to induce C−O activation with ethers and their complete inactivity in aromatic/aliphatic C−H bond activation upon thermolysis. Furthermore, the bis(benzamidinato)yttrium complexes are clearly less suited to catalyze C−C bond formation, e.g. with unsaturated hydrocarbons like olefins and 1-alkynes. Although this may be due to several factors like the high stability of the (dimeric) precursors, the low ability of the potential catalytic site to complex substrates is thought to be the main reason. During ethylene polymerization, 1-hexene hydroboration, and 1-alkyne dimerization, activation of the (dimeric or ether complexed) precursors appears to be difficult as the dimeric complexes, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-R})\}_2$ (R = H, C≡CR), are very stable. The absence of notable amounts of monomeric bis(benzamidinato)yttrium complexes (with or without substrates complexed to them) during these reactions clearly emphasizes the relative difference in stability between the dimeric precursors and the monomeric active catalysts. The highly ionic character of the bis(benzamidinato)yttrium complexes is indicated by their strong nucleophilic and Brønsted base behavior which is observed in the reactions with acetonitrile and pyridines and which is very similar to that of alkali-metal compounds. Treatment of $[PhC(NSiMe_3)_2]_2YR$ with acetonitrile gives, dependent on R, either C−H bond activation or insertion and reflects the different character of the R (R = $CH(SiMe_3)_2$, $CH_2Ph\cdot THF$, μ-H) group. Replacing the bulky alkyl group by a benzyl or an hydrido group results in an increased tendency of the compounds, $[PhC(NSiMe_3)_2]_2YR$ (R = $CH_2Ph\cdot THF$, μ-H), to undergo insertion rather than C−H bond activation. These observations are as expected for strongly ionic complexes in which the contracted metal orbitals are too small and unsuited to start initial complexation and activation of the substrate prior to reaction. The view of too high ionicity is supported by theoretical calculations.[1]

Experimental Section

General Comments. All compounds are extremely oxygen- and moisture-sensitive. Manipulations were therefore carried out under nitrogen by using glovebox (Braun MB-200) and Schlenk techniques. Hydrogen (Hoek-Loos 99.9995%), ethylene, propylene (DSM Research B.V.), acetylene (Ucar, C.P.), and propyne (Matheson, C.P.) were used as purchased. 1-Hexene, alkynes, nitriles, pyridine, and picoline (Janssen) were dried over 4 Å molecular sieves and distilled prior to use. Benzene-d_6 and cyclohexane-d_{12} were degassed and dried over Na/K alloy. All solvents were distilled from Na (toluene), K (THF), or Na/K alloy (ether, pentane) and stored under nitrogen. $[PhC(NSiMe_3)_2]_2YR$ (R = $(\mu\text{-Me})_2\cdot TMEDA$, $CH_2Ph\cdot THF$, $CH(SiMe_3)_2$) and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ were prepared according to literature procedures.[1] NMR spectra were recorded on a Varian VXR 300 (^1H NMR at 300 MHz, ^{13}C NMR at 75.4 MHz) spectrometer. ^1H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrophotometer. Elemental analyses were carried out at the Analytical Department of this laboratory; quoted data are the average of at least two independent determinations.

NMR Tube Reaction of $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ with Ethylene. NMR tubes containing benzene-d_6 (0.5 mL) solutions of $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ or $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ (0.01−0.02 mmol) were charged with ethylene (4 atm) and monitored at fixed time intervals. Heating was required for the reaction to proceed. At 65 °C the ethylene was gradually consumed with

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(31) Complex **15** is formulated as a monomer on the basis of the close spectroscopic analogy with the structurally characterized $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$: Duchateau, R.; Brussee, E. A.; Meetsma, A.; Teuben, J. H. Manuscript in preparation.

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formation of polyethylene. For $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$, the ethylene was consumed after several hours. For $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ the reaction is complete within 30 min (^1H NMR). The contents of the NMR tubes were quenched with methanol. The polyethylene was filtered off, dried, and characterized by IR.

Ethylene Polymerization Experiment. A 200 mL autoclave was charged with 100 mg (0.16 mmol) of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ dissolved in 75 mL of toluene. The autoclave was closed, pressurized with ethylene (70 atm), and heated to 50 °C. After 1.5 h, the autoclave was cooled to room temperature and the pressure released. After quenching of the reaction mixture (methanol), the polyethylene was filtered off and washed with methanol and pentane. After drying, 1.0 g of polyethylene was obtained. The product was characterized by IR spectroscopy and high temperature GPC: $M_n = 46\,300$, $M_w = 239\,900$, $M_w/M_n = 5.2$.

NMR Tube Reaction of $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ with Propylene and 1-Hexene. Propylene. NMR tubes containing benzene-d_6 (0.5 mL) solutions of $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ or $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ (0.01−0.02 mmol) were charged with propylene (4 atm) and monitored at fixed time intervals. Heating at 80 °C for several days only resulted in partial thermolysis of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$. No propylene polymers/oligomers were formed. The ^1H NMR spectrum of the reaction mixture showed no evidence for the presence of η^3-allyl species.

1-Hexene. In the drybox, a 5 mL vessel was charged with 1-hexene (2 mL) solutions of $[PhC(NSiMe_3)_2]_2YCH_2Ph\cdot THF$ or $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ (0.02−0.04 mmol). The vessel was then heated to 80 °C for several days. The volatiles were removed *in vacuo* and checked by GC and ^1H NMR: Exclusively 1-hexene was detected. The ^1H NMR spectrum of the remaining powder exclusively showed resonances attributable to $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ and traces of thermolysis products but no 1-hexene oligomers.

Preparation of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CR)\}_2$ (1, R = H; 2, R = Me). 1. Method a. A 100 mL Schlenk flask charged with a solution of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ (1.4 g, 1.1 mmol) in benzene (10 mL) was treated with acetylene (1.5 mmol) and allowed to stand for 3 days at room temperature, upon which large colorless crystals of **1** were formed (1.1 g, 0.86 mmol, 78%).

Method b. A 100 mL Schlenk flask charged with a solution of $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (1.95 g, 2.52 mmol) in benzene (10 mL) was treated with acetylene (2.6 mmol). The flask was allowed to stand for 3 days at room temperature, upon which large colorless crystals of **1** were formed (1.3 g, 1.0 mmol, 80%). IR (KBr/Nujol, cm^{-1}): 3262 (w), 2926 (vs), 2855 (s), 1914 (w), 1445 (vs), 1387 (vs), 1242 (s), 1003 (m), 982 (s), 841 (vs), 785 (w), 760 (s), 725 (w), 700 (w), 679 (w), 482 (w). ^1H NMR (benzene-d_6, δ): 7.33 (m, 4H, Ar), 7.10 (m, 6H, Ar), 3.22 (s, 1H, C≡C*H*), 0.19 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 184.5 (s, Ph*C*(NSiMe$_3$)$_2$), 146.7 (dt, Y−*C*(≡CH)−Y, $^1J_{Y-C}$ = 20 Hz, $^2J_{C-H}$ = 27 Hz), 143.2 (s, Ar), 128.1 (d, Ar, $^1J_{C-H}$ = 218 Hz), 126.5 (d, Ar, $^1J_{C-H}$ = 160 Hz), 115.4 (d, C≡*C*H, $^1J_{C-H}$ = 218 Hz), 3.19 (q, PhC(NSi(*C*H$_3$)$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{56}H_{94}N_8Si_8Y_2$: C, 52.47 (52.83); H, 7.39 (7.52); Y, 13.87 (13.91).

2. Compound **2** was prepared by a similar procedure from $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (1.00 g, 1.29 mmol) and propyne; it was isolated as microcrystalline material (0.60 g, 0.46 mmol, 71%). IR (KBr/Nujol, cm^{-1}): 2924 (vs), 2855 (s), 2060 (w), 1445 (vs), 1429 (vs), 1402 (vs), 1246 (s), 1005 (m), 982 (s), 843 (vs), 785 (w), 760 (s), 727 (w), 702 (w), 480 (w). ^1H NMR (benzene-d_6, δ): 7.37 (m, 4H, Ar), 7.10 (m, 6H, Ar), 2.01 (s, 3H, C≡CCH_3), 0.21 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, δ): 184.8 (s, Ph*C*(NSiMe$_3$)$_2$), 143.3 (s, Ar), 136.0 (t, Y−*C*(≡CMe)−Y, $^1J_{Y-C}$ = 21 Hz), 128.1 (s, Ar), 126.8 (s, Ar), 8.0 (s, C≡C*C*H$_3$), 3.9 (s, PhC(NSi(*C*H$_3$)$_3$)$_2$). Anal. Calcd (found) for $C_{58}H_{98}N_8Si_8Y_2$: C, 53.18 (53.85); H, 7.54 (7.56); Y, 13.57 (13.48).

NMR Tube Preparation of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}C\text{-}n\text{-}Pr)\}_2$ (3). To an NMR tube charged with a benzene-d_6 (0.7 mL) of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ (32 mg, 0.052 mmol), 1-pentyne (5.5 μL, 0.056 mmol) was added. After 24 h at room temperature, all 1-pentyne had been consumed to give $\{(PhC(NSiMe_3)_2)_2Y(\mu\text{-}C{\equiv}C\text{-}n\text{-}Pr\}_2$ (**3**) as the only product. ^1H NMR (benzene-d_6, δ): 7.40 (m, 4H, Ar), 7.07 (m, 6H, Ar), 2.60 (t, 2H, C≡CCH_2), 1.91 (dt, 2H, $CH_2CH_2CH_3$), 1.03 (t, 3H, CH_2CH_3), 0.26 (s, 36H, Ph(NSi(CH_3)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 185.1 (s, Ph*C*(NSiMe$_3$)$_2$), 143.3 (s, Ar), 136.5 (t, Y−*C*(≡C(CH$_2$)$_2$CH$_3$)Y, $^1J_{Y-C}$ = 21 Hz), 132.4 (s, Y−C≡*C*), 128.4 (d, Ar, $^1J_{C-H}$ = 155 Hz), 127.7 (d, Ar, $^1J_{C-H}$ = 159 Hz), 126.5 (d, Ar, $^1J_{C-H}$ = 173 Hz), 25.1 (t, C≡C*C*H$_2$CH$_2$, $^1J_{C-H}$ = 129 Hz), 22.8 (m, $CH_2CH_2CH_3$), 14.4 (q, CH_2CH_3, $^1J_{C-H}$ = 117 Hz), 4.1 (q, PhC(NSi(CH$_3$)$_3$)$_2$, $^1J_{C-H}$ = 117 Hz).

Preparation of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CR)\}_2$ (4, R = $SiMe_3$; 5, R = Ph; 6, R = CMe_3). 4. At room temperature, HC≡C$SiMe_3$ (0.34 mL, 2.47 mmol) was made to diffuse slowly into a pentane (5 mL) solution of $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (1.65 g, 2.13 mmol). After 24 h, the colorless microcrystalline material formed was washed with pentane (5 mL) and dried *in vacuo*, yielding **4** (1.00 g, 1.4 mmol, 66%) as colorless crystals. IR (KBr/Nujol, cm^{-1}): 2957 (vs), 2926 (vs), 2855 (s), 1983 (w), 1952 (w), 1904 (w), 1447 (vs), 1435 (vs), 1389 (vs), 1246 (s), 1005 (m), 986 (s), 922 (w), 843 (vs), 783 (w), 760 (s), 729 (w), 702 (w), 677 (w), 650 (w), 567 (w), 480 (w), 438 (w). ^1H NMR (benzene-d_6, δ): 7.49 (m, 4H, Ar), 7.10 (m, 6H, Ar), 0.54 (s, 9H, C≡CSi(CH_3)$_3$), 0.28 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, δ): 185.6 (s, Ph*C*(NSiMe$_3$)$_2$), 172.3 (t, Y−C(≡CSiMe$_3$)−Y, $^1J_{Y-C}$ = 20 Hz), 143.1 (s, Ar), 140.3 (s, C≡*C*SiMe$_3$), 128.3 (s, Ar), 127.9 (s, Ar), 125.6 (s, Ar), 4.8 (s, PhC(NSi(*C*H$_3$)$_3$)$_2$), 2.8 (s, C≡CSi(*C*H$_3$)$_3$). Anal. Calcd (found) for $C_{62}H_{110}N_8Si_{10}Y_2$: C, 52.21 (52.35); H, 7.77 (7.81); Y, 12.47 (12.57). Compounds **5** and **6** were prepared by a similar procedure (1−2 g scale) and isolated as colorless crystals in 70% (**5**) and 77% (**6**) yield.

5. NMR data and elemental analysis showed that **5** contained 0.25 equiv of pentane/dimer in the crystal lattice. IR (KBr/Nujol, cm^{-1}): 3040 (w), 2912 (vs), 2857 (vs), 2049 (m), 1883 (w), 1769 (w), 1597 (w), 1576 (w), 1441 (vs), 1414 (vs), 1381 (vs), 1072 (m), 982 (m), 843 (vs), 785 (s), 756 (vs), 721 (vs), 702 (s), 689 (s), 544 (m), 482 (s), 438 (m). ^1H NMR (benzene-d_6, δ): 7.92 (d, 2H, Ar), 7.48 (m, 4H, Ar), 7.07 (m, 9H, Ar), 1.23 (m, 1.5H, pentane), 0.88 (m, 1.5H, pentane), 0.16 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 184.8 (s, Ph*C*(NSiMe$_3$)$_2$, 143.0 (s, Ar), 141.8 (t, Y−*C*(≡CPh)−Y, $^1J_{Y-C}$ = 21 Hz), 133.7 (dt, Ar, $^1J_{C-H}$ = 162 Hz, $^2J_{C-H}$ = 7 Hz), 131.1 (s, C≡*C*Ph), 129.3 (dt, Ar, $^1J_{C-H}$ = 158 Hz, $^2J_{C-H}$ = 7 Hz), 124.6 (t, Ar, $^2J_{C-H}$ = 9 Hz), 22.7 (t, pentane, $^1J_{C-H}$ = 124 Hz), 14.2 (q, pentane, $^1J_{C-H}$ = 124 Hz), 4.0 (q, PhC(NSi(*C*H$_3$)$_3$)$_2$, $^1J_{C-H}$ = 119 Hz). Anal. Calcd (found) for $C_{68}H_{112}N_8Si_8Y_2(C_5H_{12})_{0.25}$: C, 57.60 (57.44); H, 7.40 (43); Y, 12.09 (12.25).

6. IR (KBr/Nujol, cm^{-1}): 3057 (w), 2957 (vs), 2926 (vs), 2870 (s), 2855 (s), 2037 (m), 1443 (s), 1429 (vs), 1414 (vs), 1397 (vs), 1248 (vs), 1003 (w), 980 (s), 839 (vs), 785 (m), 758 (s), 748 (s), 721 (s), 704 (s), 480 (s), 438 (m), 415 (m). ^1H NMR (benzene-d_6, δ): 7.39 (4H, *Ar*), 7.04 (m, 6H, *Ar*), 1.52 (s, 9H, C(CH_3)$_3$), 0.19 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 185.7 (s, Ph*C*(NSiMe$_3$)$_2$), 143.1 (s, Ar), 141.8 (t, Y−*C*(≡C(CMe$_3$))−Y, $^1J_{Y-C}$ = 22 Hz), 140.2 (s, C≡*C*(CMe$_3$)), 128.2 (dt, Ar, $^1J_{C-H}$ = 160 Hz, $^1J_{C-H}$ = 7 Hz), 127.4 (dd, Ar, $^1J_{C-H}$ = 117 Hz, $^1J_{C-H}$ = 7 Hz), 31.8 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 4.8 (q, PhC(NSi(CH$_3$)$_3$)$_2$, $^1J_{C-H}$ = 119 Hz). Anal. Calcd (found) for $C_{64}H_{110}N_8Si_8Y_2$: C, 55.14 (55.23); H, 7.95 (8.01); Y, 12.75 (12.82).

NMR Tube Preparation of $[PhC(NSiMe_3)_2]_2YC{\equiv}CH\cdot THF$ (7). THF (9 μL, 0.1 mmol) was added to an NMR tube charged with **1** (15 mg, 0.023 mmol) in benzene-d_6 (0.5 mL). The ^1H NMR spectrum taken after 5 min at room temperature showed the quantitative formation of **7** and the presence of free THF. ^1H NMR (benzene-d_6, δ): 7.25 (m, 4H, Ar), 7.07 (m, 6H, Ar), 3.70 (m, 17.2 H, THF-α-CH_2), 1.99 (d, 1H, C≡C*H*,

$^3J_{Y-H}$ = 1.3 Hz), 1.45 (m, 17.2H, THF-β-CH_2), 0.16 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 183.5 (s, PhC(NSiMe$_3$)$_2$), 143.4 (s, Ar), 128.2 (s, Ar), 128.0 (s, Ar), 126.2 (s, Ar), 89.2 (d, C≡CH, $^1J_{Y-C}$ = 12 Hz), 68.4 (s, THF-α-CH_2), 25.6 (s, THF-β-CH_2), 2.5 (s, PhC(NSi(CH_3)$_3$)$_2$.

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YC≡CCMe$_3$·THF (8). At room temperature, THF (50 μL, 0.62 mmol) was added to a pentane (20 mL) solution of **6** (0.8 g, 0.57 mmol). After 10 min, the solution was concentrated until crystallization started. Cooling to −30 °C yielded **8** (0.63 g, 0.82 mmol, 72%) as a white microcrystalline solid. IR (KBr/Nujol, cm^{-1}): 3061 (w), 2955 (vs), 2922 (vs), 2854 (s), 2043 (w), 2022 (w), 1446 (vs), 1431 (vs), 1410 (vs), 1366 (s), 1244 (s), 1005 (m), 984 (s), 916 (w), 841 (vs), 787 (m), 758 (s), 723 (m), 700 (m), 480 (m), 457 (w). ^{1}H NMR (benzene-d_6, δ): 7.17 (4H, Ar), 7.02 (m, 6H, Ar), 4.14 (m, 4H, THF-α-CH_2), 1.44 (m, 4H, THF-β-CH_2) 1.41 (s, 9H, C(CH_3)$_3$), 0.13 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 182.8 (s, PhC(NSiMe$_3$)$_2$), 143.7 (s, Ar), 143.1 (s, Y−C(≡CCMe$_3$)), 127.9 (dt, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz), 127.8 (dd, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz), 126.2 (dt, Ar, $^1J_{C-H}$ = 160 Hz; $^2J_{C-H}$ = 7 Hz), 111.1 (d, Y−C(≡CCMe$_3$), $^1J_{Y-C}$ = 11 Hz), 71.1 (t, THF-α-CH_2, $^1J_{C-H}$ = 150 Hz), 32.7 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 126 Hz), 28.1 (s, CMe$_3$), 25.3 (t, THF-β-CH_2, $^1J_{C-H}$ = 133 Hz), 2.56 (q, PhC(NSi(CH_3)$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{36}H_{63}N_4OSi_4Y$: C, 56.22 (56.31); H, 8.26 (8.34); Y, 11.56 (11.65).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$Y(μ-C≡CCMe$_3$)$_2$Li·TMEDA·hexane (9). To a solution of [PhC(NSiMe$_3$)$_2$]$_2$Y(μ-Me)$_2$Li·TMEDA (1.4 g, 1.8 mmol) in ether (40 mL) was added 3,3-dimethyl-1-butyne (0.45 mL, 3.7 mmol). After 16 h at room temperature, the solution was concentrated until crystallization started and cooled to −30 °C. Yield: 1.4 g (1.4 mmol, 75%) of **9** as large colorless crystals. NMR data showed that **9** contains 1 equiv of hexane in the crystal lattice. IR (KBr/Nujol, cm^{-1}): 2956 (vs), 2934 (vs), 2826 (vs), 2047 (m), 1460 (vs), 1454 (vs), 1379 (s), 1290 (m), 1242 (s), 1036 (w), 1022 (w), 1005 (m), 984 (s), 949 (m), 847 (s, br), 785 (s), 756 (s), 735 (s), 702 (s), 683 (m), 602 (m), 478 (m), 421 (m). ^{1}H NMR (benzene-d_6, δ): 7.42 (m, 4H, Ar), 7.14 (m, 6H, Ar), 2.33 (s, 12H, TMEDA-CH_3), 2.02 (s, 4H, TMEDA-CH_2), 1.40 (s, 18H, C(CH_3)$_3$), 0.87 (m broad, 14H, hexane), 0.26 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$. ^{13}C NMR (benzene-d_6, δ): 182.3 (s, PhC(NSiMe$_3$)$_2$), 144.2 (s, Ar), 127.8 (dd, Ar, $^1J_{C-H}$ = 162 Hz, $^2J_{C-H}$ = 6 Hz), 127.4 (d, Ar, $^1J_{C-H}$ = 160 Hz), 126.6 (d, Ar, $^1J_{C-H}$ = 166 Hz), 121.1 (d, Y−C, $^1J_{Y-C}$ = 15 Hz), 57.1 (t, TMEDA-CH_2, $^1J_{C-H}$ = 134 Hz), 46.9 (q, TMEDA-CH_3, $^1J_{C-H}$ = 134 Hz), 32.4 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 126 Hz), 3.3 (q, PhC(NSi(CH_3)$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). The hexane from the crystal lattice could be removed by heating the compound *in vacuo* at 50 °C, leaving an amorphous white solid. Anal. Calcd (found) for $C_{44}H_{85}LiN_6Si_4Y$: C, 58.31 (58.39); H, 9.45 (9.51); Y, 9.81 (9.92).

Catalytic Dimerization of Alkynes HC≡CR (R = Ph, CMe$_3$, SiMe$_3$). Alkynes (100 μL, 0.9−0.7 mmol) were added to NMR tubes charged with benzene-d_6 solutions (0.5 mL) of [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ or {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-R)}$_2$ (R = H, C≡CR′; R′ = Ph, CMe$_3$, SiMe$_3$) (0.015−0.025 mmol). The ^{1}H NMR spectra collected after 1.5 h at 80 °C indicated the nearly quantitative formation of the 1-buten-3-ynes, the presence of some traces of unreacted 1-alkyne and characteristic resonances of {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-C≡CR)}$_2$ (**4**−**6**). N_t(80 °C) = 20−40 mol·mol^{-1}· h^{-1}. For the dimerization of HC≡CMe$_3$, catalyzed by **8** (0.02 mmol of **8**, 100 μL of HC≡CCMe$_3$, 0.5 mL of benzene-d_6), the ^{1}H NMR spectra collected after 1 h at 80 °C showed the presence of H$_2$C=C(CMe$_3$)C≡CCMe$_3$, resonances attributable to **8**, and considerable amounts of unreacted HC≡CCMe$_3$ (N_t(80 °C) ≈ 1 mol·mol^{-1}·h^{-1}).

NMR Kinetic Experiments for the Catalytic Dimerization of HC≡CCMe$_3$ and HC≡CSiMe$_3$. In a typical kinetics experiment, an NMR tube was charged with a standard solution of [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (0.17 mM) in benzene-d_6 (0.7 mL) and 1-alkyne (100 μL, 0.7−0.8 mmol). After the NMR tube was filled and sealed, it was kept at constant temperature (±0.2 °C) and ^{1}H NMR spectra were recorded at regular time intervals until the reaction was complete. The kinetics were monitored by following the difference in integral of the vinylic protons of the 1-butene-3-ynes formed and the 1-alkyne acetylenic proton. The measurements were repeated at different temperatures ranging 53.0−84.0 °C. For both the dimerization of HC≡CCMe$_3$ and HC≡CSiMe$_3$, clean first-order dependence on 1-alkyne was observed.

Preparation of {[PhC(NSiMe$_3$)$_2$]$_2$Y$_2$(μ-(*N*,*N*′)-N(H)C(Me)=C(H)C≡N)}$_2$ (10). To a solution of [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (1.5 g, 1.9 mmol) in pentane (15 mL) was added acetonitrile (200 μL, 3.8 mmol) at room temperature. After being stirred for 16 h at room temperature, the formed yellow solution was concentrated until crystallization started and cooled to −30 °C. After isolation (1.0 g), the crude product was recrystallized from pentane (10 mL). Cooling to −30 °C yielded **10** (0.8 g, 1.1 mmol, 60%) as large colorless crystals. IR (KBr/Nujol, cm^{-1}): 2953 (s), 2924 (vs), 2854 (s), 2152 (s), 1523 (s), 1429 (vs), 1313 (m), 1246 (s), 1180 (m), 1074 (w), 1030 (w), 1004 (m), 986 (s), 920 (m), 839 (vs), 785 (m), 760 (s), 731 (m), 702 (s), 684 (m), 638 (w), 569 (w), 482 (m), 414 (w). ^{1}H NMR (benzene-d_6, δ): 7.22 (m, 4H, Ar), 7.03 (m, 6H, Ar), 6.84 (s, 1H, N*H*), 3.50 (s, 1H, C*H*), 2.16 (s, 3H, CH_3), 0.16 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$. ^{13}C NMR (benzene-d_6, δ): 183.6 (s, PhC(NSiMe$_3$)$_2$), 179.1 (s, C≡N), 143.2 (s, Ar), 131.3 (d, C(CH$_3$)=C, $^2J_{Y-C}$ = 5 Hz), 128.1 (d, Ar, $^1J_{C-H}$ = 161 Hz), 126.3 (d, Ar, $^1J_{C-H}$ = 159 Hz), 48.1 (d, CH, $^1J_{C-H}$ = 175 Hz), 25.1 (qd, CH$_3$, $^1J_{C-H}$ = 127 Hz, $^3J_{Y-C}$ = 10 Hz), 2.5 (q, PhC(NSi(CH_3)$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{60}H_{102}N_{12}Si_8Y_2$: C, 51.70 (51.64); H, 7.38 (7.44); Y, 12.75 (12.78).

NMR Tube Reaction of [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph·THF with N≡CMe. To an NMR tube containing a solution of [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph·THF (21 mg, 0.027 mmol) in benzene-d_6 (0.5 mL) was added acetonitrile (3 μL, 0.05 mmol) at room temperature. The ^{1}H NMR spectrum taken after 10 min at room temperature showed that all [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph·THF had reacted, yielding a mixture of compounds: **10** (10%), {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-N=C(Me)CH$_2$Ph)}$_2$ (**11a**, 50%), {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-NHC(Me)=C(H)Ph)}$_2$ (**11b**, 40%), and uncoordinated THF. A ^{1}H NMR spectrum recorded after 2 days at room temperature showed no changes. ^{1}H NMR (benzene-d_6) for **11a**: 3.47 (s, 2H, CH_2), 1.86 (s, 3H, CH_3), 0.07 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$). ^{1}H NMR (benzene-d_6, δ) for **11b**: 6.60 (s, 1H, N*H*), 4.78 (s, 1H, C*H*), 2.16 (s, 3H, CH_3), 0.16 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$).

NMR Tube Preparation of {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-N=C(H)Me)}$_2$ (12). To an NMR tube containing a benzene-d_6 (0.5 mL) solution of {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (20 mg, 0.032 mmol) was added N≡CMe (1.8 μL, 0.03 mmol). The ^{1}H NMR spectrum monitored directly after the NMR tube was filled showed resonances characteristic for {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-N=C(H)Me)}$_2$ (**12**), δ 9.3 (m, 1H, N=C(*H*)Me), 7.28 (m, 4H, Ar), 7.08 (m, 6H, Ar), 2.40 (d, N=C(H)CH_3, $^3J_{H-H}$ = 3.4 Hz), and 0.11 (s, 36H, PhC(NSi(CH_3)$_3$)$_2$, and uncoordinated THF. Compound **12** is unstable and decomposes within 1 h at room temperature to form a mixture of unidentified products.

NMR Tube Reaction of [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ with Pyridine. Pyridine (6.6 μL, 0.08 mmol) was added to an NMR tube charged with 25 mg (0.032 mmol) of [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ in benzene-d_6 (0.5 mL). The reaction was followed by ^{1}H NMR. At room temperature, no reaction occurred. The NMR tube was warmed to 50 °C, upon which the solution changed from colorless to red. After 1 week at 50 °C, the ^{1}H NMR spectrum showed that all [PhC(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ had reacted. Besides resonances of H$_2$C(SiMe$_3$)$_2$, several resonances in the vinyllic (4−6 ppm) and aromatic (7−9 ppm) regions were present.

NMR Tube Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YNC$_5$H$_6$ (13). Pyridine (2.6 μL, 0.032 mmol) was added at room temperature to a solution of {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (10 mg, 0.016 mmol) in benzene-d_6 (0.5 mL). Upon addition, the solution changed from colorless to yellow. The reaction mixture was transferred into an NMR tube, and a ^{1}H NMR spectrum was recorded. This showed that all {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ had reacted under formation of exclusively the 1,2-insertion product [PhC(NSiMe$_3$)$_2$]$_2$YNC$_5$H$_6$ (**13**). ^{1}H NMR (benzene-d_6, δ): 6.54 (dd, 1H, H4 NC$_5$H$_6$, $^3J_{H-H}$ = 9.0 Hz, $^3J_{H-H}$ = 8.6 Hz), 5.44 (ddd, 1H, H5 NC$_5$H$_6$, $^3J_{H-H}$ = 5.6 Hz, $^3J_{H-H}$ = 6.0 Hz, $^4J_{H-H}$ = 2.4 Hz), 5.22 (dt, 1H, H3 NC$_5$H$_6$, $^3J_{H-H}$ = 9.4 Hz, $^3J_{H-H}$ = 4.3 Hz), 4.52 (d, 2H, H2, H2′, NC$_5$H$_6$, $^2J_{H-H}$ = 4.3 Hz), 0.04 (s, 36H, PhC(NSi(C*H*$_3$)$_3$)$_2$).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YNC$_5$H$_5$-2-CH$_2$Ph (14). Pyridine (0.15 mL, 1.8 mmol) was added at room temperature to a solution of [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph·THF (1.3 g, 1.7 mmol) in toluene (10 mL). The yellow reaction mixtrure formed was stirred for 5 h, after which the solvent was evaporated. The remaining oil was stripped (3 × 5 mL) with pentane. Removal of all volatiles *in vacuo* resulted in a sticky oil. The ^{1}H NMR spectrum of the oil showed that **14** had been formed in 90% yield. Purification by sublimation or vacuum distillation failed and exclusively resulted in decomposition of the product. ^{1}H NMR (benzene-d_6, δ): 7.02 (m, 1H, H6), 6.44 (dd, 1H, H4, $^3J_{H-H}$ = 9.0 Hz, $^3J_{H-H}$ = 8.6 Hz), 5.27 (dd, 1H, H5, $^3J_{H-H}$ = 6.0 Hz, $^3J_{H-H}$ = 4.7 Hz), 5.20 (dt, 1H, H3, $^3J_{H-H}$ = 6.0 Hz, $^4J_{H-H}$ = 2.6 Hz), 4.93 (dt, 1H, H2, $^3J_{H-H}$ = 6.0 Hz, $^3J_{H-H}$ = 5.1 Hz), 3.91 (d, 1H, C(*H*)H, $^2J_{H-H}$ = 11.5 Hz, $^3J_{H-H}$ = 11.0 Hz), 2.74 (dd, 1H C(*H*)H, $^1J_{H-H}$ = 12.0 Hz, $^3J_{H-H}$ = 8.1 Hz), 0.07 (s, 36H, PhC(NSi(C*H*$_3$)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 183.9 (s, Ph*C*(NSiMe$_3$)$_2$), 143.1 (s, *ipso-C*), 140.4 (d, Ar, $^1J_{C-H}$ = 161 Hz), 107.2 (d, CH NC$_5$H$_4$, $^1J_{C-H}$ = 160 Hz), 94.9 (dd, CH NC$_5$H$_4$, $^1J_{C-H}$ = 167 Hz, $^3J_{C-H}$ = 6 Hz), 55.4 (dt, *C*(H)CH$_2$Ph, $^1J_{C-H}$ = 34.7 Hz, $^3J_{C-H}$ = 6 Hz), 41.6 d, *C*H$_2$, $^1J_{C-H}$ = 29 Hz), 2.5 (q, PhC(NS-(*C*H$_3$)$_3$)$_2$, $^1J_{C-H}$ = 119 Hz).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$Y(η^2-(*C*,*N*)-CH$_2$-2-NC$_5$H$_4$) (15). To a solution of [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph·THF (1.4 g, 1.8 mmol) in toluene (20 mL) was added α-picoline (180 μL, 1.8 mmol) at room temperature. After 4 h, the volatiles were removed *in vacuo* and the remaining orange oil was stripped with pentane (3 × 5 mL), but the product did not solidify. The ^{1}H and ^{13}C NMR spectra of the crude product (1.2 g, 1.5 mmol, 84%) showed traces of [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph·THF and α-picoline among the contaminations. Since crystallization, sublimation, and vacuum distillation failed, the product could not be isolated analytically pure. ^{1}H (benzene-d_6, δ): 7.92 (d, 1H, Ar, $^3J_{H-H}$ = 5.6 Hz), 7.30 (m, 4H, Ar), 7.02 (m, 6H, Ar), 6.87 (ddd, 1H, H4 NC$_5$H$_4$, $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-H}$ = 1.2 Hz), 6.68 (d, 1H, H3 NC$_5$*H*$_4$, $^3J_{H-H}$ = 8.3 Hz), 6.07 (dd, 1H, H5 NC$_5$*H*$_4$, $^3J_{H-H}$ = 6.8 Hz, $^3J_{H-H}$ = 5.6 Hz), 2.71 (d, 2H, YC*H*$_2$, $^2J_{Y-H}$ = 0.9 Hz), 0.05 (s, 36H, PhC(NSi(C*H*$_3$)$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 183.8 (s, Ph*C*(NSiMe$_3$)$_2$), 166.3 (s, NC$_5$H$_4$), 146.3 (d, *NC*$_5$*H*$_4$, $^1J_{C-H}$ = 172 Hz), 135.6 (dd, NC$_5$H$_4$, $^1J_{C-H}$ = 158 Hz, $^3J_{C-H}$ = 7 Hz), 127.7 (d, *Ar*, $^1J_{C-H}$ = 161 Hz), 126.3 (d, *Ar*, $^1J_{C-H}$ = 157 Hz), 120.4 (d, Ar, $^1J_{C-H}$ = 163 Hz), 106.9 (d, Ar, $^1J_{C-H}$ = 163 Hz), 52.4 (dt, Y*C*H$_2$, $^1J_{C-H}$ = 143 Hz, $^1J_{Y-H}$ = 6 Hz), 2.6 (q, PhC(NSi(*C*H$_3$)$_3$)$_2$, $^1J_{C-H}$ = 118 Hz).

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