Ancillary Ligand Effects in Organoyttrium Chemistry: Synthesis, Characterization, and Electronic Structure of Bis(benzamidinato)yttrium Compounds

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Received October 13, 1995[⊗]

The synthesis of $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}Cl)_2Li\cdot 2THF$ (**1**) from $YCl_3\cdot 3.5THF$ and $[PhC(NSiMe_3)_2]Li$, which is easily transformed into $[PhC(NSiMe_3)_2]_2YCl\cdot THF$ (**2**), provides a useful entry into the chemistry of several bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)yttrium complexes. Those prepared from **2** by chloride metathesis include $[PhC(NSiMe_3)_2]_2YR$ (R = $BH_4\cdot THF$ (**3**), $N(SiMe_3)_2$ (**4**), 2,6-$(CMe_3)_2$-4-$MeOC_6H_2$ (**5**), $(\mu\text{-}Me)_2Li\cdot TMEDA$ (**6**) (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), $CH_2Ph\cdot THF$ (**7**), $CH(SiMe_3)_2$ (**8**)). Similar to **8**, $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**8**$_{\mathbf{OMe}}$) could be prepared starting from $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_2YCl\cdot THF$ (**2**$_{\mathbf{OMe}}$). Hydrogenolysis (4 atm) of **8** and **8**$_{\mathbf{OMe}}$ affords dimeric hydrides $\{[p\text{-}X\text{-}C_6H_4C(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ (X = H (**9**), X = MeO (**9**$_{\mathbf{OMe}}$)). The alkyl **8**$_{\mathbf{OMe}}$ and the hydride **9** have been characterized by an X-ray diffraction structure determination. Sterically the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinate) ligand system resembles more the bis(pentamethylcyclopentadienyl) than the bis(cyclopentadienyl) ligand set. However, INDO/1 semiempirical MO studies indicate that the electronic properties of $[HC(NH)_2]_2YCH_3$ (used as a model for bis(benzamidinato)yttrium alkyl complexes) are rather different from $[C_5H_5]_2YCH_3$. The yttrium atom in $[HC(NH)_2]_2YCH_3$ is considerably more positively charged than in $[C_5H_5]_2YCH_3$. The resulting strong ionic character of the bis(benzamidinate) system is held responsible for the absence of agostic interactions and H/D exchange and the low hydrogenolysis rate observed.

Introduction

Group 3 metal and organolanthanide compounds have been at the center of scientific attention for over a decade.[1] Among the most interesting aspects of this chemistry is that group 3 metal and lanthanide compounds appear to be of great importance in homogeneous catalysis of C−H, C−C, and C−X bond formation.[2−5] Until now most of the work reported was on compounds stabilized by bis(pentamethylcyclopentadienyl) or closely related ligand systems. Alkyl and hydride species, Cp^*_2LnR ($Cp^* = \eta^5\text{-}C_5Me_5$; Ln = Sc, Y, La, Ce, Nd, Sm, Lu; R = $CH(SiMe_3)_2$, Me, H)[2] have been shown to be active, either as catalysts or as stoichiometric reagents, in selective C−C and C−H bond formation and in C−H/C−X bond activation. Typical examples are found in olefin (oligo/polymerization,[2,3] hydrogenation,[4a,b] hydroboration,[4c] hydrosilylation,[4d] amino−olefin hydroamination/cyclization[4e]) and in alkyne (oligomerization,[2,5a−c] hydrogenation,[5c] hydroamination/cyclization[5d]) transformations. Linking the cyclopentadienyl ligands and/or varying the cyclopentadienyl substituents has in most cases led to higher catalytic activity.[6] Recently, there has been an increased attention for other spectator ligands whether as alternatives for, or in addition to, (pentamethyl)cyclopentadienyl groups. Among the systems that have appeared are cyclopentadienyl ligands with a pendant amido or alkoxo functionality,[7] porphyrins,[8] pyrazolylborates,[9] aryloxides,[10] carboranes[11] and amidodiphosphines.[12]

Our exploration of yttrium complexes with alternative spectator ligand systems is aimed at comparing the reactivity of these compounds with that of bis(penta-

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) (a) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (b) Evans, W. J. *Polyhedron* **1987**, *6*, 803. (c) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 289.

(2) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (d) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495. (e) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423. (f) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (g) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

(3) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

(4) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (b) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266. (c) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220. (d) Sakakura, T.; Lautenschlager, H.-J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40. (e) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275.

(5) (a) Heeres, H. J.; Heeres, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 1508. (b) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980. (c) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525. (d) Li, Y.; Fu, P.-F.; Marks, T. J. *Organometallics* **1994**, *13*, 439.

(6) (a) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (b) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (c) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. (d) Gagné, M. R.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003. (e) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606. (f) Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y.; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761. (g) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.

S0276-7333(95)00813-2 CCC: $12.00

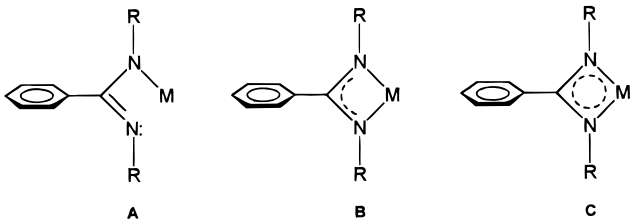


Figure 1. Possible bonding modes of the benzamidinate ligands: A, σ-bonded; B, σ,σ'-bonded; C, $\sigma,\sigma + \pi$-bonded.

methylcyclopentadienyl) and related systems. When deciding which direction to go, we argued that replacing cyclopentadienyls by hard Lewis basic ligands such as alkoxides or amides would render the metal center more electron deficient. This is expected to increase the polymerization activity for α-olefins. Chain termination by β-hydrogen transfer will be suppressed, since the alkyl compound will be thermodynamically prefered relative to the hydride olefin complex.[13] Furthermore, decreasing electron density at the metal center in cationic ethylene-bridged bis(indenyl)zirconium systems has been found to increase the stereoselectivity of propylene insertion.[14]

We decided to focus on hard basic benzamidinate anions as alternatives for (pentamethyl)cyclopentadienyl ligands. The pioneering work of Dehnicke,[15] Roesky,[16] and Edelmann[17] with *N*,*N*′-bis(trimethylsilyl)-benzamidinate has shown that this ligand can coordinate to a large variety of metal centers in different bonding modes (Figure 1). So far, however, no reports have been made of the use of benzamidinates as stabilizing ligands in catalysis.

Apart from a few exceptions (Figure 1A),[18] the negative charge of the benzamidinate ligand appears fullly delocalized within the NCN fragment through π-bonding of the C-pπ and N-pπ orbitals, giving a very stable diazaallylic ligand which is normally σ,σ'-bonded to the metal (4 e^- donor, Figure 1B).[15−17] This charge delocalization makes the ligand essentially insensitive for nucleophilic attack. Furthermore, partial electron donation from the benzamidinate π-system to the metal center may occur (Figure 1C), as is often observed for amido and alkoxo complexes.[19] In general, the ligand is bonded to one metal center, although a few examples of binuclear complexes with bridging *N*,*N*′-bis(trimethylsilyl)benzamidinate ligands are known as well.[20]

In this paper the synthesis and characterization of a range of bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)-yttrium derivatives is described, together with the molecular structures of $[p\text{-MeOC}_6\text{H}_4\text{C(NSiMe}_3)_2]_2\text{YCH(SiMe}_3)_2$ and $\{[\text{PhC(NSiMe}_3)_2]_2\text{Y}(\mu\text{-H})\}_2$. The stabilizing ability of the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinate) ligand system is clearly illustrated by the fact that alkyl and hydrido species are well accessible. In a separate section, the steric and electronic properties of the bis-(benzamidinate) system are compared with those of the extensively investigated bis((pentamethyl)cyclopentadienyl) system.

Results and Discussion

General Considerations. (a) Synthesis. Introduction of *N*,*N*′-bis(trimethylsilyl)benzamidinate ligands is conveniently achieved through salt metathesis. Reaction of $YCl_3\cdot 3.5$THF with 2 equiv of $[\text{PhC(NSiMe}_3)_2]\text{Li}$ in THF results in the monochloride complexed with LiCl·2THF, $[\text{PhC(NSiMe}_3)_2]_2\text{YCl}_2\text{Li}\cdot 2$THF (**1**, Scheme 1). Attempts to remove the LiCl and THF by sublimation of **1** failed due to thermal decomposition. However, the LiCl can easily be cleaved off in refluxing pentane yielding the THF adduct, $[\text{PhC(NSiMe}_3)_2]_2\text{YCl}\cdot$THF (**2**), an excellent precursor to a wide range of derivatives (Scheme 1). Substitution of the chloride proceeds essentially quantitatively on treatment with the indicated reagent in either ether or toluene, affording salt free and pentane soluble products. However, the high solubility of most complexes hampers their purification. Not surprising for small substituents, the coordination sphere of the Lewis acidic metal center is completed either by forming "ate" complexes $[\text{PhC(NSiMe}_3)_2]_2\text{Y}(\mu\text{-X})_2\text{Li}\cdot 2\text{L}$ (**1**, X = Cl, L = THF; **6**, X = Me, L = $^1/_2$ TMEDA) or by complexation of solvent molecules $[\text{PhC(NSiMe}_3)_2]_2\text{YX}\cdot$THF (**2**, X = Cl; **3**, X = BH_4; **7**, X = CH_2-Ph). Solvent-free neutral complexes, $[\text{PhC(NSiMe}_3)_2]_2\text{YX}$ (**4**, X = $N(SiMe_3)_2$; **5**, X = O-2,6-$(CMe_3)_2$-4-MeC_6H_2; **8**, X = $CH(SiMe_3)_2$) can be made only when sterically demanding substituents are employed. Reaction of **2** with small alkylating reagents, RM (M = Li, R = Me, Et, CH_2SiMe_3, CH_2CMe_3; M = K, R = CH_2Ph) is

(7) (a) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4632. (b) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59. (c) Hughes, A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (d) Trouvé, G.; Laske, D.; Meetsma, A.; Teuben, J. H. *J. Organomet. Chem.*, in press.

(8) (a) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968 and references cited therein. (b) Arnold, J.; Hoffman, C. G.; Dawson, D. Y.; Hollander, F. J. *Organometallics* **1993**, *12*, 3645.

(9) For an overview see: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(10) (a) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124. (b) Schaverien, C. J. *Organometallics* **1994**, *13*, 69.

(11) For an overview see: Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081.

(12) (a) Fryzuk, M. D.; Haddad, T. S. *J. Am. Chem. Soc.* **1988**, *110*, 8263. (b) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026. (c) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1992**, *11*, 2967.

(13) (a) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275. (b) Labinger, J. A.; Bercaw, J. E. *Organometallics* **1988**, *7*, 926.

(14) Lee, I.-M.; Gauthier, W. J.; Ball. J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115.

(15) For example see: (a) Dehnicke, K.; Ergezinger, C.; Hartmann, E.; Zinn. A.; Hösler, K. *J. Organomet. Chem.* **1988**, *352*, C1. (b) Fenske, D.; Hartmann, E.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 1611.

(16) Roesky, H. W.; Meller, B.; Noltemeyer, M.; Schmidt, H.-G.; Scholz, U.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1403.

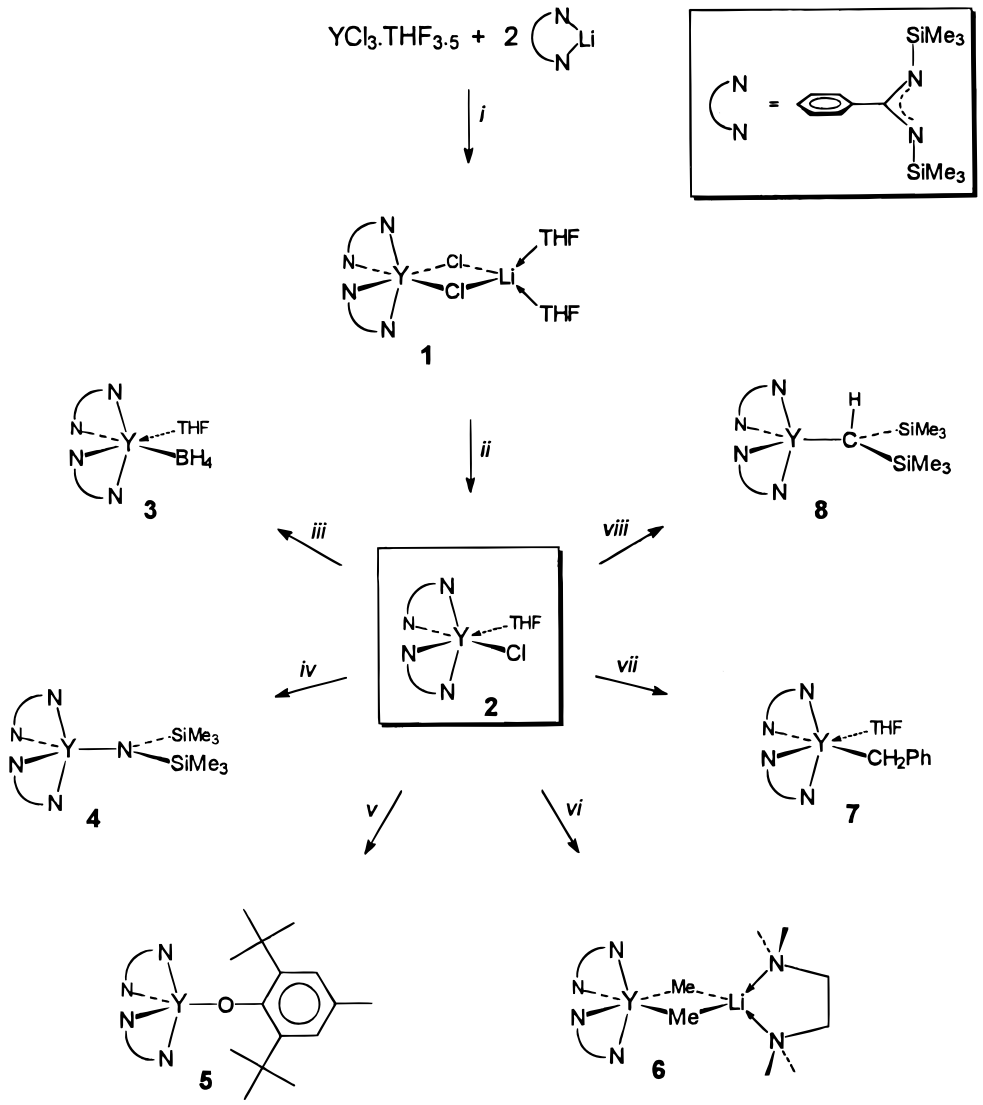
(17) For example see: (a) Recknagel, A.; Knösel, F.; Gornitzka, H.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *417*, 363. (b) Wedler, M.; Recknagel, A.; Gilje, J. W.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1992**, *426*, 295. (c) Wedler, M.; Knösel, F.; Edelmann, F. T.; Behrens, U. *Chem. Ber.* **1992**, *125*, 1313.

(18) The only report of a benzamidinate acting as a 2 electron donor is in bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)mercury, $[\text{PhC(NSiMe}_3)_2]_2\text{Hg}$, where delocalization of the charge within the NCN fragment is negligible as is illustrated by the C-N bond distances which are comparable to those found in *N*,*N*,*N*′-tris(trimethylsilyl)benzamidine, $\text{PhC(NSiMe}_3)\text{N(SiMe}_3)_2$: (a) Zinn, A.; Dehnicke, K.; Fenske, D.; Baum, G. Z. *Z. Anorg. Allg. Chem.* **1991**, *596*, 47. (b) Ergezinger, C.; Weller, F.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 1119.

(19) (a) Schaverien, C. J.; Frijns, J. H. G.; Heeres, H. J.; van den Hende, J. R.; Teuben, J. H.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 642. (b) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1166. (c) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 623. (d) Aspinall, H. C.; Moore, S. R.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 153. (e) Allen, M.; Aspinall, H. C.; Moore, S. R.; Hursthouse, M. B.; Karvalov, A. I. *Polyhedron* **1992**, *11*, 409.

(20) (a) Maier, S.; Hiller, W.; Strähle, J.; Ergezinger, C.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 1628. (b) Fenske, D.; Baum, G.; Zinn, A.; Dehnicke, K. *Z. Naturforsch.* **1990**, *45b*, 1273. (c) Zinn, A.; Weller, F.; Dehnicke, K. *Z. Allg. Anorg. Chem.* **1991**, *594*, 106.

Scheme 1[a]



[a] (*i*) THF; (*ii*) pentane, reflux; (*iii*) $LiBH_4$, toluene; (*iv*) $NaN(SiMe_3)_2$, toluene; (*v*) LiOAr, toluene; (*vi*) MeLi·TMEDA, ether; (*vii*) KCH_2Ph, toluene; (*viii*) $LiCH(SiMe_3)_2$, toluene.

complicated due to both incorporation of solvent molecules and of LiCl, yielding mixtures of products. Among these small alkylating reagents, only MeLi and $PhCH_2K$ gave well-defined products, $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}Me)_2Li\cdot TMEDA$ (**6**) and $[PhC(NSiMe_3)_2]_2YCH_2Ph.THF$ (**7**), respectively.

Attempts to synthesize a neutral methyl complex by reaction of **2** with 1 equiv of MeLi were unsuccessful and so was the attempted removal of the THF molecule in the solvated benzyl complex, **7**.[21] To structurally compare **8** with the analogous $Cp^*_2YCH(SiMe_3)_2$, it was attempted to grow single crystals of **8** for X-ray crystal structure analysis. Due to the extremely high solubility, it appeared to be impossible to recrystallize **8** from pentane. To solve this problem, the less soluble *para*-methoxy-substituted benzamidinate ligand, $p\text{-}MeOC_6H_4C(NSiMe_3)_2$, was introduced. Substitution at the *para*-position does not essentially influence the sterics of the ligand. Moreover, the dihedral angle between the phenyl ring and the NCN plane of the benzamidinate ligand typically ranges from 60 to 90°,[22] precluding effective conjugation between both π-systems. As a result, substitution at the *para*-position of the benzamidinate phenyl group is not expected to have a large electronic influence either. Similar to the syntheses of **2** and **8**, $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_2YCl\cdot THF$ ($\mathbf{2_{OMe}}$) and $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ ($\mathbf{8_{OMe}}$) could be prepared in high yield. Repeated recrystallization of $\mathbf{8_{OMe}}$ yielded single crystals suitable for X-ray analysis (*vide infra*).

(b) Characterization. All complexes (**2**−**8**) are stable at room temperature and show no thermal decomposition in benzene after 24 h at 100 °C, but they are extremely oxygen and moisture sensitive. Spectroscopic and analytical data are presented in the Experimental Section, and only a number of interesting features and general trends will be discussed here. The benzamidinate NMR resonances are not very diagnostic for identification and assignment purposes. The phenyl

(21) (a) In an attempt to prepare a neutral methyl complex, reactions of **2** with 1 equiv of MeLi were carried out in different solvents (pentane, ether, toluene, THF). (b) In attempts to remove the coordinated THF in **7**, the compound was gently warmed (50 °C) *in vacuo*. This did not lead to release of the THF, whereas sublimation exclusively led to decomposition of the compound.

(22) (a) Fenske, D.; Hartmann, E.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 1611. (b) Ergezinger, C.; Weller, F.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 1119.

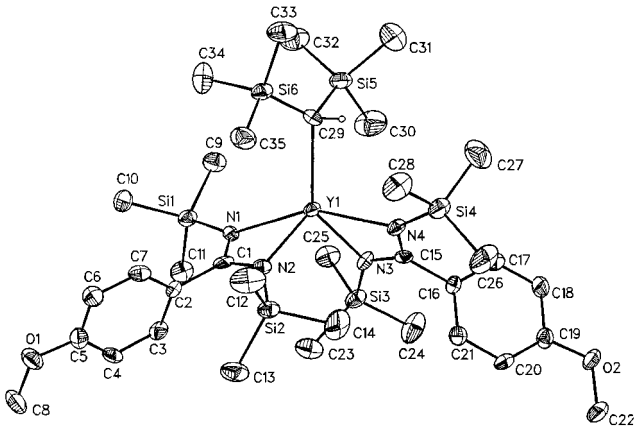


Figure 2. ORTEP drawing of [*p*-$MeOC_6H_4C(NSiMe_3)_2]_2$-$YCH(SiMe_3)_2$ (**8_{OMe}**). Hydrogen atoms (except H(29)) are omitted for clarity.

^1H NMR resonances form a multiplet while the single trimethylsilyl resonance hardly shifts within the range of complexes (^1H: $\delta = 0.03$ (**5**)−0.21 (**6**) ppm). For all compounds, the single resonance in the ^1H and ^{13}C NMR spectra for the benzamidinate trimethysilyl substituents indicates fast fluxional behavior of the ligands around the metal at room temperature. For this equilibration, several mechanisms can be proposed. One possibility, suggested by Edelmann *et al.*, is temporary loss of the bidentate character of the benzamidinate ligands followed by rotation around the Y−N bond.[17c] Another possibility is simultaneous cogwheel type rotation of both benzamidinate ligands around their Y−C axes, i.e. without one of the ligating nitrogen atoms being loosened. Upon cooling, the single benzamidinate−$SiMe_3$ resonance splits into two distinct, equi-intense singlets which can be assigned to equatorial and axial $SiMe_3$ groups (Figure 2). From the coalescence temperatures and the $\Delta\nu_c$ of the two benzamidinate−$SiMe_3$ singlets at the low temperature extreme, the Gibbs energy for rotation for this process in **4** and **6** was calculated (**4**, $\Delta G^{\ddagger}_{Tc} = 57 \pm 1$ kJ·mol^{-1}; **6**, $\Delta G^{\ddagger}_{Tc} = 39 \pm 1$ kJ·mol^{-1}). Assuming that the bonding of the benzamidinate ligands is comparable in both complexes, the different fluxionality ($\Delta G^{\ddagger}_{Tc}$) in these complexes can be attributed to different steric interactions of the various ligands. For the pentacoordinated amido complex **4**, rotation of the benzamidinato ligands is clearly more hindered than for the hexacoordinated alkyl compound **6**. This is in agreement with the larger steric bulk of the $N(SiMe_3)_2$ fragment compared to the (μ-$Me)_2$Li·TMEDA group.

A satisfactory elemental analysis of **1** could not be obtained due to (partial) loss of solvent (THF). The complex was characterized by ^1H and ^{13}C NMR and then converted into **2**. The chloride **2** contains 0.25 equiv of pentane in the crystal lattice (NMR, elemental analysis), which can be removed completely by warming at 50 °C *in vacuo* for 24 h, leaving an amorphous white solid. The B−H vibration bands in the IR spectrum of **3** do not give conclusive information about the bonding mode of the BH_4 group.[23] However, η^2-(μ-H)$_2$$BH_2$ or η^3-(μ-H)$_3$-BH bonding is likely.[23] The single resonance for the borohydrides (δ 1.32 ppm, q, $^1J_{B-H} = 80$ Hz) in the ^1H NMR spectrum indicates fast exchange of terminal and bridging hydrides in solution. In contrast to the analogous $Cp^*_2Y(\mu\text{-}Me)_2Li\cdot(OEt_2)_2$ (δ −1.80, $^2J_{Y-H} = 2.0$ Hz),[24] no yttrium coupling to the methyl groups is observed for **6**. Unlike $Cp^*_2YCH_2Ph$,[25] the absence of highfield resonances for the *ortho*-protons of the benzyl group in the ^1H NMR spectrum of **7**, together with the large coupling constant of the α-carbon ($^1J_{C-H} = 118$ Hz),[26] indicates that γ-agostic interaction of the benzyl group is not important, which is not unexpected for a THF adduct. As observed for all group 3 metal and lanthanide bis(trimethylsilyl)methyl complexes known, the small C−H coupling on the α-carbon in **8** ($^1J_{C-H} = 88$ Hz) and **8_{OMe}** ($^1J_{C-H} = 88$ Hz) suggests an α-agostic interaction of the carbyl C−H bond with yttrium.[26] However, one cannot discard the possibility that the hybridization of the α-C atom in bis(trimethylsilyl)-methyl systems, [Ln]−$CH(SiMe_3)_2$, reflects the steric strain between the large bulk of the $SiMe_3$ substituents and the ancillary ligand system, forcing the α-carbon to adopt a planar geometry.

Another remarkable aspect is the significant downfield shift of the α-carbon resonance in the ^{13}C NMR spectrum (δ 43.5 ppm) and of the yttrium resonance in the ^{89}Y NMR spectrum (δ 721 ppm) of **8**, compared with $Cp^*_2YCH(SiMe_3)_2$ (^{13}C, 25.2 ppm; ^{89}Y, 79 ppm).[19a,27] Replacement of a cyclopentadienyl by more electronegative σ-donor ligands (alkoxide, amide, alkyl) invariably leads to deshielding of the metal and α-carbon nucleus.[10b,19a,28] Although tempting, extreme care should be taken when correlating chemical shifts (^{13}C and ^{89}Y) and the electrophilicity of the metal center, since electrophilicity of the metal center is not the only effect that influences the chemical shift.[28]

To get more insight into the geometry of **8_{OMe}**, a low-temperature X-ray structure determination was carried out. An ORTEP drawing of **8_{OMe}** is shown in Figure 2 and selected bond distances and angles are listed in Table 1. Details concerning the data collection are listed in Table 5. The high quality of the data set allowed solution and refinement of all hydrogen atom positions.

Table 1. Selected Bond Distances and Angles for [*p*-$MeOC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (8_{OMe}**)**

Distances (Å)			
Y(1)−N(1)	2.344(3)	Y(1)−C(15)	2.733(5)
Y(1)−N(2)	2.325(4)	Y(1)−C(29)	2.431(5)
Y(1)−N(3)	2.345(4)	N(1)−C(1)	1.331(6)
Y(1)−N(4)	2.336(3)	N(2)−C(1)	1.342(6)
Y(1)−C(1)	2.718(5)	C (29)−H(29)	1.092(4)
Angles (deg)			
N(1)−Y(1)−N(2)	58.85(12)	C(15)−Y(1)−C(29)	117.76(15)
N(3)−Y(1)−N(4)	58.50(12)	Y(1)−C(29)−Si(5)	115.6(2)
C(1)−Y(1)−C(15)	122.71(13)	Y(1)−C(29)−Si(6)	116.1(2)
C(1)−Y(1)−C(29)	119.23(14)	Y(1)−C(29)−H(29)	92.0(2)

(23) (a) Gun'ko, Y. K.; Bulychev, B. M.; Solovechick, G. L.; Belsky, V. K. *J. Organomet. Chem.* **1992**, *424*, 289. (b) Laske, D. A.; Duchateau, R.; Teuben, J. H.; Spek, A. L. *J. Organomet. Chem.* **1993**, *462*, 149. (c) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (d) Marks, T. J.; Kennely, W. J. *Inorg. Chem.* **1972**, *11*, 2540.

(24) Den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *323*, 181.

(25) (a) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531. (b) Booij, M. *Ph.D. Thesis*, University of Groningen, 1989.

(26) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Green, J. C.; Payne, M. P. *Magn. Reson. Chem.* **1987**, *25*, 544. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

(27) 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.

(28) Duchateau, R.; Teuben, J. H.; Frijns, J. H. G.; Budzelaar, P. H. M. to be published.

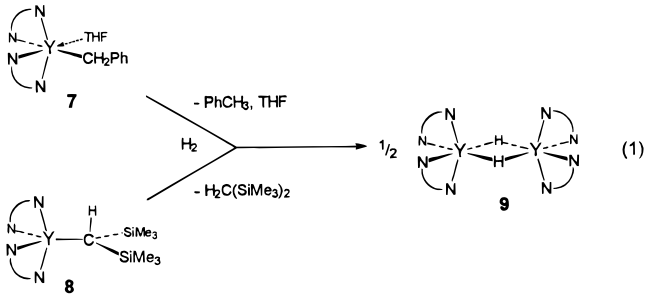
Table 2. Selected Bond Distances and Angles for {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (9)

Distances (Å)			
Y(1)−N(1)	2.389(3)	Y(2)−N(5)	2.360(3)
Y(1)−N(2)	2.343(3)	Y(2)−N(6)	2.327(3)
Y(1)−N(3)	2.327((3)	Y(2)−N(7)	2.347(3)
Y(1)−N(4)	2.365(3)	Y(2)−N(8)	2.398(3)
Y(1)−C(1)	2.752(4)	Y(2)−C(27)	2.736(4)
Y(1)−C(8)	2.738(4)	Y(2)−C(34)	2.760(4)
Y(1)−H(0)	2.11(3)	Y(2)−H(0)	2.19(3)
Y(1)−H(0′)	2.16(3)	Y(2)−H(0′)	2.17(3)
N(1)−C(1)	1.338(5)	N(5)−C(27)	1.332(5)
N(2)−C(1)	1.329(5)	N(6)−C(27)	1.336(5)
N(3)−C(8)	1.329(5)	N(7)−C(34)	1.332(5)
N(4)−C(8)	1.333(5)	N(8)−C(34)	1.340(5)
Angles (deg)			
N(1)−Y(1)−N(2)	57.92(10)	H(0)−Y(1)−H(0′)	69.0(12)
N(5)−Y(2)−N(6)	58.33(10)	H(0)−Y(2)−H(0′)	67.5(12)
N(3)−Y(2)−N(4)	58.13(10)	Y(1)−H(0)−Y(2)	111.9(15)
N(7)−Y(2)−N(8)	57.85(10)	Y(1)−H(0′)−Y(2)	111.0(15)
C(1)−Y(1)−C(8)	126.80(13)		
C(27)−Y(2)−C(34)	124.45(13)		

The monomeric complex is best described as trigonal-planar with the yttrium in the center, considering the benzamidinate ligands to occupy one coordination vertex (C(1)−Y(1)−C(15) = 122.71(13)°; C(1)−Y(1)−C(29) = 119.23(14)°, C(15−Y(1)−C(29) = 117.76(15)°; sum of the angles, 359.7(2)°). With torsion angles of −2.2(2)° (N(1)−Y(1)−N(2)−C(1)) and −1.4(2)° (N(3)−Y(1)−N(4)−C(15)), both benzamidinate ligands form planar rings with the yttrium atom.

The almost identical C−N distances in the benzamidinate ligands (C−N$_{av}$ = 1.337(6) Å, Table 2), corresponding to a bond order of 1.5,[29] indicate full electron delocalization within the NCN fragment, whereas the rather short Y−N distances (Y−N$_{av}$ = 2.338(4) Å) suggest π-interaction of the ligands with yttrium.[27] The dihedral angles N(1)−C(1)−C(2)−C(3) (69.6(6)°) and N(3)−C(15)−C(16)−C(17) (−85.3(5)°) and the C(1)−C(2) (1.492(7) Å) and C(15)−C(16) (1.499(6) Å) distances, which correspond to C(sp^2)−C(sp^2) single bonds,[29] exclude conjugation between the phenyl ring and the NCN fragment. The Y(1)−C(29) σ-bond (2.431(5) Å) is significantly shorter than in Cp*$_2$YCH(SiMe$_3$)$_2$ (2.468(7) Å)[27] and compares well with the Y−C σ-bond in Cp*$_2$YMe.THF (2.44(2) Å).[24] The trigonal-planar molecule is formed by three closely interlocking ligands around yttrium to adopt a geometry with minimal steric repulsions. The molecule appears in solution to be very flexible since, instead of many resonances due to various inequivalent SiMe$_3$ groups with inequivalent methyl substituents, the ^{1}H and ^{13}C NMR spectra of **8$_{OMe}$** only show one singlet resonance for the methyl groups of the benzamidinates and one singlet for the bis(trimethylsilyl)methyl ligand. The rapid equilibration of the various methyl substituents may result from an easy cogwheel type rotation of the ligands around the respective Y−C axes (Y(1)−C(1), Y(1)−C(15), Y(1)−C(29)). The bonding of the alkyl group (CH(SiMe$_3$)$_2$) also supports the view that the configuration around the metal is mainly determined by steric interactions among the ligands. As observed for all crystallographically characterized lanthanoid bis(trimethylsilyl)methyl compounds, C(29) has an almost planar geometry (Si(5)−C(29)−Si(6) = 121.8(3)°, Y(1)−C(29)−Si(5) = 115.6(2)°; Y(1)−C(29)−Si(6) = 116.1(2)°; sum of the angles, 353.5(2)°). The position of the α-H, H(29), could not be determined with high accuracy, but in contrast to Cp*$_2$YCH(SiMe$_3$)$_2$,[27] there is no indication that H(29) is forming a strong α-agostic interaction with the yttrium atom. In addition, the large obtuse and identical Y−C−Si angles (115−116°) in **8$_{OMe}$** also exclude other agostic (γ, δ) interactions with other parts of the bis(trimethylsilyl)methyl ligand, in contrast to what has been observed in Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = Y,[27] Ce,[2d] Nd[2c]) and [Me$_2$Si(C$_5$Me$_4$)(C$_5$R$_4$)]$_2$LnCH(SiMe$_3$)$_2$ (Ln = Nd, R = Me;[6a] Ln = Lu, R = H[6c]) systems. Assuming that benzamidinate ligands are 4 electron donors, the absence of agostic interactions in the formally 10 electron complex **8$_{OMe}$** is rather surprising. Similarly, [OEP]YCH(SiMe$_3$)$_2$ (OEP = octaethylporphyrin) did not show any agostic interactions either.[8a] One feature that **8$_{OMe}$** and [OEP]YCH(SiMe$_3$)$_2$ have in common is that both complexes are stabilized by nitrogen-based hard Lewis basic ancillary ligands. A possible explanation for the absence of agostic interactions in these complexes is that these hard basic ligands render the complexes significantly more ionic. The empty yttrium orbitals will be more contracted on the metal and therefore less available for effective overlap with C−H or C−Si electron pairs (*vide infra*).

Metal−Carbon Bond Hydrogenolysis. Synthesis and Characterization of {[*p*-X-C$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (9, X = H; 9$_{OMe}$, X = OMe). (a) Synthesis. In contrast to the facile hydrogenolysis of Cp*$_2$YCH(SiMe$_3$)$_2$,[2b] which is completed within hours at 0 °C, hydrogenolysis of **8** is slow and can be best performed in benzene under 4 bar of hydrogen at room temperature (3 days), resulting in the formation of H$_2$C(SiMe$_3$)$_2$ and {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (**9**, eq 1). This low rate may



(1)

be a consequence of a stronger Y−C σ-bond in **8**, combined with less effective charge stabilization in the heterolytic transition state as a result of the lower electron-donating capacity of the benzamidinate anion compared to Cp* and the more ionic character of the bis(benzamidinate) system.[6c,8a,30] Another possibility is that the driving force for hydrogenolysis is reduced due to the lower stability of the initially formed monomeric hydride, compared to Cp*$_2$YH. Steric crowding as reason for the low reaction rate is not realistic, since two benzamidinate ligands are not likely to occupy more space than two Cp* ligands (*vide infra*). The influence of electronic properties of the ancillary ligand system on the reactivity of a complex is clearly illustrated by the fact that even under drastic conditions no hydro-

(29) Burke-Laing, M.; Laing, M. *Acta Crystallogr.* **1976**, *32B*, 3216.

(30) Nolan, S. P.; Stern, D.; Hedden, D.; Marks, T. J. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series 248; American Chemical Society: Washington, DC, 1990.

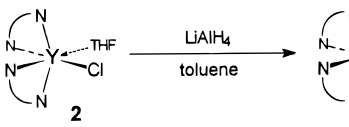
genolysis was observed for the sterically unsaturated [OEP]LnCH(SiMe$_3$)$_2$ (Ln = Y, Lu).[8a]

The hydride **9** is the first example of a fully characterized cyclopentadienyl-free yttrium hydride. In contrast with the other bis(*N,N′*-bis(trimethylsilyl)benzamidinate complexes described above, it is sparingly soluble in benzene and essentially insoluble in aliphatic hydrocarbons. It is extremely oxygen and moisture sensitive but thermally quite stable and shows no sign of decomposition after several days at 100 °C in benzene-d_6. A remarkable observation made during the thermolysis study is that H/D scrambling or metalation of benzene-d_6, which is a very easy process for {Cp*$_2$Ln(μ-H)}$_2$ (Ln = Sc, Y, lanthanides) systems,[2b,c,f,25,31] was not observed. This clearly reflects the different electronic situation in **9** when compared with {Cp*$_2$Y(μ-H)}$_2$. Probably, like the absence of agostic interactions and the slow hydrogenolysis, the lack of H/D exchange can be related as well to the increased ionic character of the bis(benzamidinato)yttrium system.

Hydrogenolysis of [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph.THF (**7**) in benzene-d_6 also gives **9**, although the coordinated THF retards the rate considerably. ^{1}H NMR spectroscopy showed that within 2 days at 50 °C, 44% of **7** had been converted into **9**. Remarkably, **9** shows no tendency to form a THF adduct, while no indication for ether splitting could be obtained either. In contrast, {[C$_5$H$_4$Me]$_2$Y(μ-H)·THF}$_2$ and {[1,3-C$_5$H$_3$Me$_2$]$_2$Y(μ-H)·THF}$_2$, reported by Evans *et al.*, were isolated as stable THF adducts,[32] whereas bis-Cp* yttrium and lanthanide hydrides, {Cp*$_2$Ln(μ-H)}$_2$ (Ln = Y, lanthanides), give very fast C−O activation with ethers, yielding the alkoxo or μ-oxo compounds.[2f,25b,31] Independent NMR tube experiments confirmed that **9** does not react with THF (1−5 equiv) in benzene-d_6. However, when dissolved in neat THF, C−O bond activation, similar as found for {Cp*$_2$Ce(μ-H)}$_2$,[31c,33] was observed. A more extensive discussion of the stability and reactivity of **9** will be given elsewhere.[34] Analogously, reaction of **8$_{OMe}$** with hydrogen resulted in the formation of H$_2$C(SiMe$_3$)$_2$ and the corresponding hydride {[*p*-MeO-C$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (**9$_{OMe}$**).[35]

Since the yield of **9** by hydrogenolysis of **8** appeared to be quite variable, other synthetic strategies for the formation of the hydride **9** were investigated. Attempts to prepare it through thermolysis of an *in situ* prepared alkyl complex, [PhC(NSiMe$_3$)$_2$]$_2$YR (R = *t*-Bu, *n*-Bu), treatment of the chloride **2** with NaH,[36] and treatment of the borohydride **3** with NR$_3$, to abstract BH$_3$·NR$_3$,[37] all failed.

A related method also remained unsuccessful but gave a very interesting view on the high lability of the benzamidinate ligands. The reaction of **2** with LiAlH$_4$ was expected to give [PhC(NSiMe$_3$)$_2$]$_2$Y(AlH$_4$) which, on treatment with an amine should afford **9** and AlH$_3$·NR$_3$.[23b] Instead, ligand exchange took place resulting in formation of the monomeric bis(*N,N′*-bis(trimethylsilyl)benzamidinato)aluminum hydride, [PhC(NSiMe$_3$)$_2$]$_2$AlH (eq 2), confirming the high affinity of the strong Lewis acid Al^{3+} for nitrogen donors.[38]



(2)

(b) Characterization. The ^{1}H NMR spectrum of **9** displays a characteristic Y−H coupling (triplet, $^1J_{Y-H}$ = 27.6 Hz), consistent with a (time-averaged) symmetric dimeric structure in solution. The Y−H resonance (δ 8.28 ppm) is at extreme lowfield compared to other yttrium hydrides (2.02−5.45 ppm), while the coupling constant (27.6 Hz) is quite similar.[6c,e,10b,25,32] As observed for all complexes described in this paper, the single resonance (^{1}H, ^{13}C NMR) for the SiMe$_3$ groups indicates fluxional benzamidinate ligands in **9** at room temperature. From the coalescence temperature and $\Delta\nu_c$, the Gibbs energy for rotation of the benzamidinate ligands around the yttrium center was calculated ($\Delta G^{\ddagger}_{Tc}$ = 48 ± 1 kJ·mol^{-1}) and found to be intermediate to those for **4** and **6**. Assuming that the bonding mode of the ancillary ligands is comparable in the complexes examined, the differences in fluxionality (and $\Delta G^{\ddagger}_{Tc}$ values) can be explained by the different steric crowding in the complexes (*vide supra*) and suggests that the steric bulk increases from **6** → **9** → **4**.

The chemical shift and coupling constant for the α-carbon resonance in **8$_{OMe}$** (dd, δ 42.9 ppm, $^1J_{C-H}$ = 88 Hz, $^1J_{Y-C}$ = 31 Hz) and the hydride resonance in **9$_{OMe}$** (t, δ 8.31 ppm, $^1J_{Y-H}$ = 27.8 Hz) are almost identical to those found for **8** (dd, δ 43.5 ppm, $^1J_{C-H}$ = 88 Hz, $^1J_{Y-C}$ = 30 Hz) and **9** (t, δ 8.28 ppm, $^1J_{Y-H}$ = 27.6 Hz). It is clear that the electronic influence of the *para*-methoxy substituent of the benzamidinate ligands in **8$_{OMe}$** and **9$_{OMe}$** is negligible like earlier assumed on the fact that the aryl group is almost perpendicular to the NCN plane.

The molecular structure of **9** was determined by a low-temperature X-ray diffraction analysis. An ORTEP drawing of **9** is shown in Figure 3, and selected bond

(31) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134. (b) Deelman, B.-J. Ph.D. Thesis, University of Groningen, 1994. (c) Deelman, B.-J.; Booij, M.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1995**, *14*, 2306.

(32) (a) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008. (b) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (c) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279. (d) Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439.

(33) The quantitative formation of ethane (Töpler pomp determination), together with olefinic resonances in the ^{1}H NMR of the product mixture, suggests the formation of an enolate [Y]−OCH=CH$_2$ species. Minor amounts of ethylene formed suggest a second C−O activation reaction of the enolate species, probably forming a μ-oxo species: ref 31b,c.

(34) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291.

(35) An important observation is the lack of reactivity of the hydride toward the *p*-anisyl functionality within **9$_{OMe}$**. Like alkyllithium reagents, {Cp*$_2$Y(μ-H)}$_2$ is well-known for its facile *ortho*-metalation reactions with heteroatom-containing arenes, PhX (X = OMe, SMe, NMe$_2$, CH$_2$NMe$_2$, PMe$_2$). For instance, the reaction of {Cp*$_2$Y(μ-H)}$_2$ with anisole is instantaneous at room temperature, yielding Cp*$_2$Y(η^2-(*C,O*)-C$_6$H$_4$-2-OMe): (a) Reference 25. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306 and references cited therein. (c) Brandsma, L.; Verkruysse, H. *Preparative Polar Organometallic Chemistry;* Springer-Verlag: Berlin, 1987; Vol. 1.

(36) (a) Schumann, H.; Genthe, W. *J. Organomet. Chem.* **1981**, *213*, C7. (b) Schumann, H.; Genthe, W.; Hahn, E.; Hossain, M. B.; van der Helm, D. *J. Organomet. Chem.* **1986**, *299*, 67. (c) Qian, C.; Deng, D.; Ni, C.; Zhang, Z. *Inorg. Chim. Acta* **1988**, *146*, 129.

(37) James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1967**, *6*, 1979.

(38) The characterization, determination of the X-ray crystal structure, and reactivity of the aluminum hydride [PhC(NSiMe$_3$)$_2$]$_2$AlH is beyond the scope of this paper and will be reported elsewhere. Duchateau, R.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.*, submitted for publication.

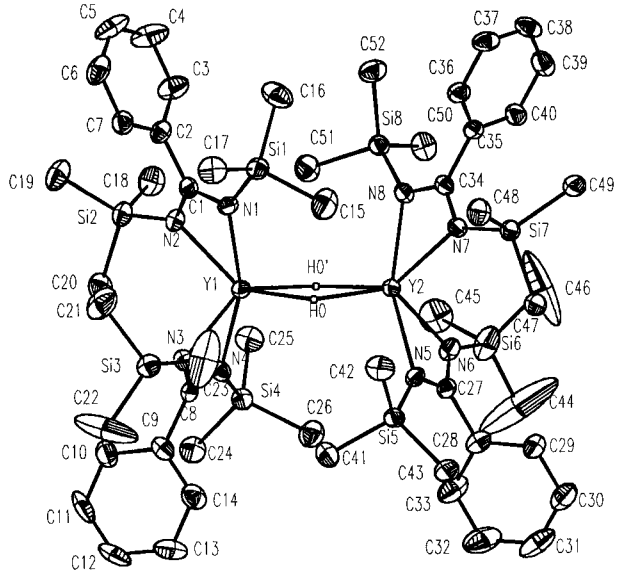


Figure 3. ORTEP drawing of the molecular structure of $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ (**9**). Hydrogen atoms on the benzamidinate ligands are omitted for clarity.

distances and angles are listed in Table 2. Details concerning the data collection are listed in Table 5.

The molecule is a dimer formed by two edge-sharing severely distorted octahedral yttrium fragments, each coordinated by two chelating benzamidinate ligands. Two bridging hydrogen atoms form the shared edge. The structure is very similar to the closely related $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH)\}_2$, reported earlier,[39] and like there, the axial bonds Y(1)−N(1) (2.389(3) Å) and Y(1)−N(4) (2.365(3) Å) are longer than the equatorial Y(1)−N(2) (2.343(3) Å) and Y(1)−N(3) (2.327(3) Å) bonds. With N(1)−Y(1)−N(2) and N(3)−Y(1)−N(4) bond angles of 57.92(10) and 58.13(10)°, the bite angles of the benzamidinate ligands are very similar to those in $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH)\}_2$ (57.92(13) and 58.12(13)°)[39] and in $\mathbf{8_{OMe}}$ (58.85(12), 58.50(12)°). The larger N(1)−Y(1)−N(4) (160.94(10)°) and N(2)−Y(1)−N(3) (102.51(10)°) angles and smaller H(0)−Y(1)−H(0′) angle (69.0(12)°) compared with the corresponding angles in $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH)\}_2$ (N(5)−Y(3)−N(8) = 149.33(15)°; N(6)−Y(3)−N(7) = 98.70(14)°; C(29)−Y(3)−C(29a) = 78.83(15)°)[39] show that the yttrium centers in **9** tend to adopt prism geometry. With equal N−C distances within the benzamidinate ligands (see Table 2), it is clear that the π-electrons within the NCN fragments are delocalized, just like in $\mathbf{8_{OMe}}$ and $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH)\}_2$. The hydride bridges are symmetrical in the crystal structure (with identical Y(1)−H(0) (2.11(3) Å) and Y(1)−H(0′) (2.16(3) Å), and they appear to remain so in solution, judging from the triplet signal for the hydrido resonances in the ^{1}H NMR spectrum of **9** (*vide supra*). The Y−H distances and Y−H−Y angles are very similar compared to values found for $\{[C_5H_4Me]_2Y(\mu\text{-}H)\cdot THF\}_2$[32a] and $\{[1,3\text{-}Me_2C_5H_3]Y(\mu\text{-}H)\cdot THF\}_2$.[32c]

Assessing the Steric and Electronic Factors that Determine the Difference between the Bis(*N*,*N*′-bis(trimethylsilyl)benzamidinate) and Bis(pentamethylcyclopentadienyl) Ligand Systems. Differences in both steric bulk and electron-donating capacity

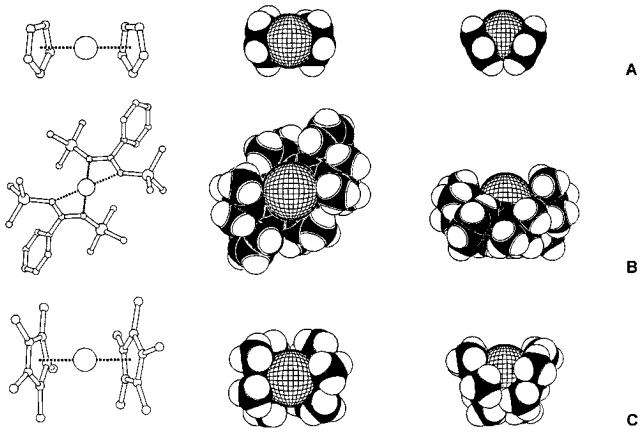


Figure 4. CPK models of Cp_2Y (A), $[PhC(NSiMe_3)_2]_2Y$ (B), and Cp^*_2Y (C) in two different orientations.

of the ancillary ligands as well as the charge distribution within the Y−R bond will influence the stability and reactivity of the compounds. Therefore, an attempt to compare the effects of the steric bulk and electronic structure of systems containing benzamidinate and (pentamethyl)cyclopentadienyl ligands was made using simple and commercially available computing facilities.

(a) Steric Properties. In 1970, Tolman quantified the steric effects observed in organometallic systems in terms of cone angles.[40] Due to its simplicity and usefulness, this method has become widely used for quantifying ligand sizes. While mostly applied to determine the steric bulk of phosphine and phosphido ligands, the cone angle concept has also been used for other ligands including cyclopentadienyls.[41] Two important limitations of Tolman's approach that have to be considered are that (i) conical geometry of the metal−ligand fragment is assumed and (ii) other ligands around the metal are ignored. This makes the method rather inaccurate when comparing the steric bulk of geometrically different ligands, such as dish-shaped cyclopentadienyl and rectangular benzamidinate ligands. Furthermore, when one is dealing with systems containing more than one of these ligands, the "effective steric bulk" of the ligand system is dramatically influenced by the way the ligands are oriented around the metal. Therefore, differences in steric bulk of ancillary ligand systems are described more accurately in terms of openness of the metal coordination gap, rather than comparing the difference in cone angle of the individual ligands. Brintzinger *et al.*[42] used this method to determine the differences in steric bulk of various metallocene systems (*vide infra*). As a measure for the openness of metallocenes, they introduced the term coordination aperture, defined by the angle between the two planes through the metal center that touch the inner van der Waals surface of the ligand system.

On the basis of the cone angle of Cp (136°) and PhC(NSiMe$_3$)$_2$ (137°), Edelmann *et al.* estimated that the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinate) system is sterically equivalent to the bis(cyclopentadienyl) ligand environment.[17b] It is not clear whether the limitations of the cone angle approach were taken into consideration. Since steric effects have normally a large influ-

(39) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931.

(40) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(41) White, D.; Civille, N. J. *Adv. Organomet. Chem.* **1994**, *36*, 95.

(42) Hortmann, K.; Brintzinger, H. H. *New J. Chem.* **1992**, *16*, 51.

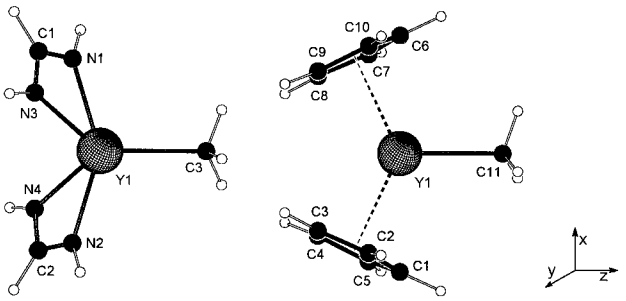


Figure 5. Perspective view of the $[HC(NH)_2]_2YCH_3$ and $[C_5H_5]_2YCH_3$ models used in INDO/1 calculations.

ence on the reactivity, the steric bulk of the various ligand systems were compared using space-filling models and Brintzinger's approach.

Figure 4 shows CPK models of the Cp_2Y (A), $[PhC(NSiMe_3)_2]_2Y$ (B), and Cp^*_2Y (C) fragments, respectively.[43] Although not leading to quantitative results, the space-filling models give an interesting picture of the relative geometric differences of the ligand systems. The bis(cyclopentadienyl) system is definitely the smallest, whereas the bis(pentamethylcyclopentadienyl) ligand environment is sterically the most demanding. On the basis of the CPK models (Figure 4), it is clear that the size of the free coordination space left by the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinate) ligand environment is considerably smaller than that of the bis(cyclopentadienyl) ligand set and resembles more that of the bis(pentamethylcyclopentadienyl) system. For the ligand systems depicted in Figure 4, the coordination apertures were determined as well. With an angle of 103°, for Cp_2Y the coordination gap is by far the largest. The assumption made above, that the steric bulk of $[PhC(NSiMe_3)_2]_2Y$ (84°) resembles more that of Cp^*_2Y (72°) than that of Cp_2Y, is supported by their coordination apertures. Clearly, this outcome differs considerably from the conclusions reached by Edelmann *et al.* who postulated that benzamidinate ligands are sterically equivalent with Cp.[17b]

(b) Electronic Properties. To compare the electronic structure of bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)- and bis(pentamethylcyclopentadienyl)yttrium systems, simple qualitative INDO/1 semi-empirical MO calculations, as implemented in the program ZINDO,[44] have been performed. To simplify the calculations, stripped and symmetrized model molecules were used: $[HC(NH)_2]_2YCH_3$ with local C_2 symmetry and $[C_5H_5]_2YCH_3$ with local C_{2v} symmetry.[45] For the fragments, $CH_3^\bullet$, $[C_5H_5]_2Y^\bullet$, and $[HC(NH)_2]_2Y^\bullet$, ROHF calculations were carried out, whereas for the complete systems, $[C_5H_5]_2YCH_3$ and $[HC(NH)_2]_2YCH_3$, RHF calculations were performed in order to get an estimate of the $Y-C_\sigma$ bond strength. No geometry optimalizations were performed. The bonding of cyclopentadienyl ligands to metal centers has extensively been studied by others and will not be further discussed.[46] To simplify the interpretation of the results, the orbitals were localized.

Table 3. AO Contributions (Squares) in Localized Ligand−Metal Bonding MO's of $[HC(NH)_2]_2YCH_3$

(contr)^2 of Y		(contr)^2 of ligand	
d_{yz}	0.06	N3, N4	
		p_x	0.28
		s	0.27
		p_z	0.16
		p_y	0.08
p_x	0.07	N1, N2	
		p_x	0.32
		s	0.27
		p_z	0.13
		p_y	0.08

The models $[HC(NH)_2]_2YCH_3$ and $[C_5H_5]_2YCH_3$ used for the INDO/1 calculations are presented in Figure 5.[45] The significant ligand to metal bonding interactions in $[HC(NH)_2]_2YCH_3$ are listed in Table 3.

For $[HC(NH)_2]_2YCH_3$ each nitrogen is bonded to the metal by one σ-orbital. The orbitals (mainly $p_x + s + p_z$) of the two equatorial nitrogens overlap with yttrium-d_{yz}, whereas the orbitals (mainly $p_x + s$) of the axial nitrogens overlap with yttrium-p_x. With bond orders of 0.74 (Y1−N1, Y1−N2) and 0.78 (Y1−N3, Y1−N4) the Y−N bonds are almost identical. Additional π-interaction of the $HC(NH)_2$ ligands with yttrium could not be observed and can therefore be assumed to be negligible.[47] Hence, benzamidinate ligands can formally be regarded as four electron donors.

The Y−C σ-bond is very similar in both systems (Table 4). The carbon contribution is mainly p_z, whereas the yttrium contribution consists of $d_{z^2} + p_z + s$. The bond orders and calculated bond dissociation enthalpies are identical. Only the Mulliken charge distributions are significantly different. Although using a Mulliken population analysis to determine the polarity of the Y−C bond should be met with reservation, it will be assumed that, because of the fact that the differences are quite large, the results obtained for the two ligand systems under consideration reflect real bonding situation. Whereas the charge at the CH_3 group remains more or less the same in both complexes, the formal yttrium charge in these systems differs significantly. Clearly, the yttrium centers in $[HC(NH)_2]_2YCH_3$ (q(Y) = +0.80 e) is considerably more positive than in $[C_5H_5]_2YCH_3$ (q(Y) = +0.48 e). Consequently, the charge separation within the Y−C bond in $[HC(NH)_2]_2YCH_3$ ($\Delta q_{(Y-C)}$ = 1.06 e) is larger than in $[C_5H_5]_2YCH_3$ ($\Delta q_{(Y-C)}$ = 0.73 e). Hence, Y−C in $[C_5H_5]_2YCH_3$ can be considered to be less polar than in the former system. It is not only the Y−C bonds in $[HC(NH)_2]_2YCH_3$ which seem to be more polar; the electron density at the $HC(NH)_2$ (q(L) = −0.27 e) is also higher than that at C_5H_5 (q(L) = −0.12 e), making $[HC(NH)_2]_2YCH_3$ more ionic than $[C_5H_5]_2YCH_3$. The larger negative charge at the benzamidinate ligands probably originates from the high electronegativity of nitrogen. As a consequence of the high positive charge of the metal in bis(benzamidinato)-yttrium complexes, the yttrium orbitals are strongly contracted on the metal, thus hampering initial interactions with substrates or C−H/C−Si bond electron pairs

(43) X-ray crystal data were used from the following. $\{Cp_2Y(\mu\text{-Me})\}_2$: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54; $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-H})\}_2$ (**9**), $Cp^*_2YCH(SiMe_3)_2$: Reference 27. CPK models were prepared using PLUTON-92: Spek, A. L. PLUTON-92; University of Utrecht: Utrecht, The Netherlands, 1992.

(44) Zerner, M. C. *ZINDO, a comprehensive semi-empirical quantum chemistry package;* University of Florida: Gainesville, FL.

(45) For details, see the Experimental Section.

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

(47) INDO/1 ROHF calculations on $[HC(NH)_2]^\bullet$ showed that the N and C π-orbitals are involved in π-bonding within the ligand, resulting in complete charge delocalization within the NCN fragment of the benzamidinate ligand.

Table 4. Y−C σ-Bond: AO Contributions (Squares), Bond Orders (b.o.), Mulliken Formal Charges (q), and Calculated Bond Dissociation Enthalpies

complex	(contr)^2 of C		(contr)^2 of Y		b.o.	q(CH$_3$)	q(Y)	$\Delta q_{(Y-C)}$	q(L)	E_{calcd}
$[C_5H_5]_2YCH_3$	p_z	0.459	d_{z^2}	0.142	1.03	-0.25	+0.48	0.73	-0.12	120
	s	0.149	p_z	0.138						
			s	0.108						
$[HC(NH)_2]_2YCH_3$	p_z	0.471	d_{z^2}	0.144	1.03	−0.26	+0.80	1.06	−0.27	120
	s	0.148	p_z	0.118						
			s	0.116						

and causing low hydrogenolysis rates and lack of H/D exchange and agostic interactions.

Conclusions

It is clear that benzamidinate ligands can effectively stabilize Y−X (X = heteroatom, C, H) bonds, and in this respect they form robust alternatives for (pentamethyl)-cyclopentadienyl ligands. The bis(benzamidinate) ligand system has a very pronounced shape, quite different from the bis(pentamethylcyclopentadienyl) ligand set as follows from X-ray structure determinations. It appears that in solution the bis(benzamidinate) system is very flexible ($\Delta G^{\ddagger}_{Tc}$(rotation) = 39−57 kJ·mol^{-1}) giving freely rotating nonrigid structures at room temperature. The complexes described show a strong similarity with their bis(pentamethylcyclopentadienyl)yttrium analogs: [PhC-(NSiMe$_3$)$_2$]$_2$YCl·THF (**2**) readily undergoes salt metathesis reactions to form new Y−X and Y−C bonds. Hydrogenolysis of the alkyl complexes [PhC(NSiMe$_3$)$_2$]$_2$-YR (R = CH$_2$Ph.THF (**7**), CH(SiMe$_3$)$_2$ (**8**)) leads to the hydride {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (**9**). The thermal stability of all complexes is high, showing no disproportionation or ligand transfer at elevated temperatures, and even the steric bulk of the bis(benzamidinate) coordination is comparable with that of the bis(pentamethylcyclopentadienyl) ligand set. However, several important differences were observed as well. One outstanding aspect of the new ancillary ligand system is that the benzamidinates are transferred more easily than Cp or Cp* ligands. This is demonstrated in the reaction of **2** with LiAlH$_4$, where both benzamidinate ligands are transferred from yttrium to aluminum. The main difference between both groups of compounds arises from the higher ionicity of the bis(benzamidinate) system. The larger negative charge on the ancillary ligand system leads to a more positively charged yttrium atom. As a result, the yttrium orbitals are more contracted on the metal, which possibly causes the lower tendency of the yttrium atom to engage in agostic interactions and activation or precomplexation of substrates (e.g. H$_2$) leading to the low hydrogenolysis rate and lack of H/D exchange.

Experimental Section

General Comments. All compounds are extremely oxygen and moisture sensitive. Manipulations were carried out under nitrogen using glovebox (Braun MB-200) and Schlenk techniques. Hydrogen (Hoek-Loos 99.9995%) was used as purchased. Solvents were distilled from Na (toluene), K (THF), or Na/K alloy (ether, pentane, hexane, benzene) and stored under nitrogen. Benzene-d_6 was dried over Na/K alloy and distilled prior to use. LiAlH$_4$ (Aldrich) was suspended in THF, yielding a 1.75 M solution after filtration. YCl$_3$·3.5THF was prepared by continuous extraction of anhydrous YCl$_3$[48] with THF. [PhC(NSiMe$_3$)$_2$]Li[49] and [*p*-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]Li[49b,50] were prepared according to literature procedures. NMR spectra were recorded on a Varian VXR 300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75.4 MHz, ^{89}Y NMR at 14.697 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 30 °C, were referenced internally using the residual solvent resonances. ^{89}Y NMR spectra were measured at 25 °C using 10 mm sample tubes containing 2.5 mL of 4.5−5.5 M solutions in benzene-d_6. Because of the negative nuclear Overhauser effect of ^{89}Y, the decoupler was not used. The very long relaxation times commonly observed for ^{89}Y made it necessary to use delays between π/2 pulses of 300 s. Obtaining data was further hindered by acoustic ringing (seen as a rolling baseline). Chemical shifts are reported with respect to a 2.0 M sample of YCl$_3$ in D$_2$O (δ = 0 ppm). To achieve a signal-to-noise ratio of at least 30, 100−300 transients were accumulated. 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.

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$Y(μ-Cl)$_2$Li·2THF (1). [PhC(NSiMe$_3$)$_2$]Li (95.6 mL, 1.0 M solution in pentane, 95.6 mmol) was added to a suspension of YCl$_3$·3.5THF (21.4 g , 47.8 mmol) in THF (300 mL) at −30 °C. The mixture was warmed to room temperature and stirred for 24 h after which time the solvent was evaporated and the compound dried thoroughly. Extraction with ether (200 mL) and subsequent concentration and cooling to −30 °C yielded **1** (27.7 g, 33.0 mmol, 69%) as a colorless microcrystalline material. ^{1}H NMR (benzene-d_6, δ): 7.22 (m, 4H, Ar), 7.05 (m, 6H, Ar), 3.90 (s, 4H, THF-α-CH_2), 1.43 (s, 4H, THF-β-CH_2), 0.14 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 183.9 (s, Ph*C*[NSiMe$_3$]$_2$), 143.8 (s, Ar), 128.1 (s, Ar), 126.3 (s, Ar), 70.2 (s, THF-α-*C*H$_2$), 25.5 (s, THF-β-*C*H$_2$), 2.5 (s, PhC[NSi(*C*H$_3$)$_3$]$_2$). The crystalline product appeared to gradually loose THF. Therefore no satisfactory elemental analysis could be obtained.

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YCl·THF·0.25(pentane) (2). Method a. [PhC(NSiMe$_3$)$_2$]Li (190 mL, 1.0 M solution in pentane, 0.19 mol) was added to a suspension of YCl$_3$·3.5THF (43 g, 96 mmol) in THF (200 mL) at −30 °C. The mixture was warmed to room temperature and stirred for 24 h after which time the solvent was evaporated and the compound dried thoroughly. The residue was subsequently refluxed with pentane (400 mL) to cause the LiCl to separate out. The solvent was evaporated again under vacuum, and the residue was transferred to a Schlenk tube equipped with a frit and continuously extracted with pentane. The pentane solution then was concentrated until crystallization started. Cooling to −30 °C yielded **2** (52.0 g, 70.1 mmol, 73%) as colorless crystals. **Method b.** A suspension of **1** (5.3 g, 6.3 mmol) in pentane (80 mL) was refluxed for 2 h. Then the volatiles were pumped off *in vacuo*, and the product was extracted with pentane (100 mL). Concentration and cooling to −30 °C

(48) Freeman, J. H.; Smith, M. L. *J. Inorg. Nucl. Chem.* **1958**, *7*, 224.

(49) (a) Sanger, A. R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 351. (b) Boeré, R. T.; Oakley, R. T.; Reed, R. W. *J. Organomet. Chem.* **1987**, *331*, 161.

(50) Wedler, M.; Knösel, F.; Noltemeyer, M.; Edelmann, F. T.; Behrens, U. *J. Organomet. Chem.* **1990**, *388*, 21.

yielded **2** (4.1 g, 5.5 mmol, 87%) as colorless needles. IR (KBr/Nujol, cm^{-1}): 2951 (vs), 2857 (s), 1601 (w), 1578 (w), 1447 (s), 1412 (vs), 1343 (sh), 1316 (m), 1294 (m), 1248 (s), 1169 (m), 1074 (m), 1030 (m), 1009 (s), 986 (vs), 922 (m), 839 (vs), 791 (s), 758 (vs), 725 (s), 704 (s), 685 (s), 604 (m), 482 (s), 440 (m). ^{1}H NMR (benzene-d_6, δ): 7.12 (m, 10H, Ar), 4.20 (s, 4H, THF-α-CH_2), 1.55 (s, 4H, THF-β-CH_2), 1.23 (m, 1.5H, pentane), 0.88 (m, 1.5H, pentane), 0.13 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 183.9 (s, Ph*C*[NSiMe$_3$]$_2$), 143.5 (s, Ar), 128.1 (s, Ar), 126.2 (s, Ar), 71.8 (s, THF-α-*C*H$_2$), 25.3 (s, THF-β-*C*H$_2$), 22.7 (s, pentane), 14.2 (s, pentane), 2.5 (s, PhC[NSi-(*C*H$_3$)$_3$]$_2$). ^{89}Y NMR (benzene-d_6, δ): 426. Anal. Calcd (found) for $C_{30}H_{54}ClN_4OSi_4Y\cdot0.25C_5H_{12}$): C, 50.62 (50.49); H, 7.75 (7.75); Cl, 4.90 (4.80); Y, 11.99 (12.11).

Preparation of [p-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$YCl·THF (2_{OMe}). Analogous to the preparation of **2**, this compound was obtained from YCl$_3$·3.5THF (8.3 g, 18.5 mmol) and 2 equiv (10.9 g, 37.9 mmol) of [*p*-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]Li·OEt$_2$ in THF (110 mL). After crystallization from pentane (50 mL) [*p*-MeOC$_6$H$_4$C-(NSiMe$_3$)$_2$]$_2$YCl·THF (**2$_{OMe}$**) was isolated as a colorless microcrystalline material (10.1 g, 13.0 mmol, 70%). IR (KBr/Nujol, cm^{-1}): 2936 (vs), 2837 (s), 1609 (s), 1576 (w), 1512 (s), 1452 (vs), 1416 (vs), 1379 (vs), 1292 (s), 1246 (s), 1171 (s), 1121 (w), 1197 (m), 1067 (w), 1038 (m), 1015 (m), 1001 (m), 986 (s), 939 (w), 843 (vs), 837 (vs), 758 (s), 745 (s), 727 (s), 683 (w), 644 (m), 629 (m), 604 (w), 529 (w), 500 (m), 426 (m). ^{1}H NMR (benzene-d_6, δ): 7.15 (d, 4H, Ar, $^3J_{H-H}$ = 6.0 Hz), 6.67 (d, 4H, Ar, $^3J_{H-H}$ = 6.8 Hz), 3.87 (s, 4H, THF-α-CH_2), 3.22 (s, 6H, OCH_3), 1.40 (s, 4H, THF-β-CH_2), 0.17 (s, 36H, PhC[NSi-(CH_3)$_3$]$_2$). ^{13}C NMR (benzene-d_6, δ): 183.7 (s, Ph*C*[NSiMe$_3$]$_2$), 159.8 (s, Ar), 136.0 (s, Ar), 127.6 (dd, Ar, $^1J_{C-H}$ = 159 Hz, $^2J_{C-H}$ = 7 Hz), 113.4 (dd, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 3 Hz), 69.8 (t, THF-α-*C*H$_2$, $^1J_{C-H}$ = 148 Hz), 54.6 (q, O*C*H$_3$, $^1J_{C-H}$ = 144 Hz), 25.4 (t, THF-β-*C*H$_2$, $^1J_{C-H}$ = 133 Hz), 2.50 (q, PhC[NSi(*C*H$_3$)$_3$]$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{32}H_{58}ClN_4O_3Si_4Y$: C, 49.05 (48.67); H, 7.40 (7.46).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YBH$_4$·THF (3). LiBH$_4$ (0.8 g, 36.7 mmol) was added to a solution of **2** (2.5 g, 3.4 mmol) in toluene (100 mL) at room temperature. After the mixture was stirred for 14 h, the toluene was removed *in vacuo* and the white residue was extracted with pentane (100 mL). Repeated recrystallization from pentane (50 mL), concentration, and cooling to −30 °C yielded colorless crystals of **3** (1.9 g, 2.7 mmol, 79%). IR (KBr/Nujol, cm^{-1}): 2955 (vs), 2926 (vs), 2872 (s), 2855 (s), 2448 (m), 2220 (w), 2170 (w), 1445 (s), 1439 (s), 1433 (vs), 1427 (vs), 1408 (s), 1246 (s), 1182 (w), 1009 (m), 986 (s), 918 (w), 839 (vs), 787 (m), 760 (s), 731 (m), 702 (m), 683 (m). ^{1}H NMR (benzene-d_6, δ): 7.18 (m, 4H, Ar), 7.04 (m, 6H, Ar), 4.06 (m, 4H, THF-α-CH_2), 1.40 (m, 4H, THF-β-CH_2), 1.32 (q, 4H, BH_4, $^1J_{B-H}$ = 80 Hz), 0.10 (s, 36H, PhC[NSi-(CH_3)$_3$]$_2$). ^{13}C NMR (benzene-d_6, δ): 182.9 (s, Ph*C*[NSiMe$_3$]$_2$), 143.0 (s, Ar), 128.4 (d, Ar, $^1J_{C-H}$ = 164 Hz), 128.0 (d, Ar, $^1J_{C-H}$ = 163 Hz), 126.1 (d, Ar, $^1J_{C-H}$ = 133 Hz), 72.3 (t, THF-α-*C*H$_2$, $^1J_{C-H}$ = 129 Hz), 25.2 (t, THF-β-*C*H$_2$, $^1J_{C-H}$ = 129 Hz), 2.5 (q, PhC[NSi(*C*H$_3$)$_3$]$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{30}H_{58}BN_4OSi_4Y$: C, 51.26 (50.98); H, 8.32 (8.40); Y, 12.65 (12.93).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YN(SiMe$_3$)$_2$ (4). A solution of **2** (2.6 g, 3.5 mmol) in toluene (75 mL) was treated with NaN(SiMe$_3$)$_2$ (0.64 g, 3.5 mmol) at room temperature and stirred overnight. Then the volatiles were removed *in vacuo* and the residue extracted with pentane (75 mL). Concentration and cooling to −30 °C yielded **4** (2.1 g, 2.7 mmol, 77%) as a colorless microcrystalline solid. IR (KBr/Nujol, cm^{-1}): 2932 (vs), 2905 (vs), 1433 (vs), 1381 (s), 1248 (s), 1167 (w), 1134 (w), 1101 (w), 1074 (w), 988 (s), 943 (w), 916 (w), 872 (s), 845 (vs), 781 (m), 760 (m), 727 (m), 700 (m), 685 (m), 627 (m), 610 (m), 517 (w), 482 (s), 438 (m). ^{1}H NMR (benzene-d_6, δ): 7.18 (m, 4H, Ar), 7.01 (m, 6H, Ar), 0.49 (s, 18H, N(Si(CH_3)$_3$)$_2$), 0.11 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$). ^{13}C NMR (benzene-d_6, δ): 183.8 (s, Ph*C*[NSiMe$_3$]$_2$), 142.2 (s, Ar), 128.4 (dt, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz), 128.0 (d, Ar, $^1J_{C-H}$ = 163.5 Hz), 126.5 (d, Ar, $^1J_{C-H}$ = 152 Hz), 4.6 (q, N(Si(*C*H$_3$)$_3$)$_2$, $^1J_{C-H}$ = 116 Hz), 2.8 (q, PhC[NSi(*C*H$_3$)$_3$]$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{32}H_{64}N_5Si_6Y$: C, 49.51 (48.99); H, 8.31 (8.32); Y, 11.45 (11.06).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YOAr (OAr = 2,6-(CMe$_3$)$_2$-4-MeC$_6$H$_2$) (5). ArOLi·OEt$_2$ (1.25 g, 4.2 mmol) was added to a solution of **2** (3.1 g, 4.2 mmol) in toluene (40 mL) at room temperature. After the solution was stirred for 14 h, the solvent was pumped off and the residue was extracted with pentane (50 mL). Concentration and slow cooling to −30 °C yielded **5** (3.4 g, 4.1 mmol, 97%) as large colorless crystals. IR (KBr/Nujol, cm^{-1}): 2940 (vs), 2851 (vs), 2726 (m), 2672 (m), 1464 (vs), 1439 (s), 1377 (vs), 1262 (s), 1248 (s), 1155 (m), 1121 (w), 986 (w), 934 (w), 916 (m), 845 (s), 760 (m), 721 (m), 700 (w), 660 (w). ^{1}H NMR (benzene-d_6, δ): 7.21 (m, 6H, Ar), 7.02 (m, 6H, Ar), 2.35 (s, 3H, CH_3), 1.75 (s, 18H, C(CH_3)$_3$), 0.03 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$). ^{13}C NMR (benzene-d_6, δ): 184.2 (s, PhC[NSi(*C*H$_3$)$_3$]$_2$), 159.9 (s, Ar), 142.5 (s, Ar), 137.0 (s, Ar), 128.8 (dt, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz), 128.1 (d, Ar, $^1J_{C-H}$ = 160 Hz), 126.6 (d, Ar, $^1J_{C-H}$ = 154 Hz), 126.1 (d, Ar, $^1J_{C-H}$ = 143 Hz), 124.7 (q, Ar, $^2J_{C-H}$ = 6 Hz), 34.8 (s, *C*(CH$_3$)$_3$), 32.6 (q, C(*C*H$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 21.6 (q, *C*H$_3$, $^1J_{C-H}$ = 124 Hz), 2.7 (q, PhC[NSi(*C*H$_3$)$_3$]$_2$, $^1J_{C-H}$ = 119 Hz). ^{89}Y NMR (benzene-d_6, δ): 412. Anal. Calcd (found) for $C_{41}H_{69}N_4OSi_4Y$: C, 58.89 (58.84); H, 8.44 (8.55); Y, 10.63 (10.67).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$Y(μ-Me)$_2$Li·TMEDA (6). An ethereal (50 mL) solution of **2** (3.0 g, 4.0 mmol) was cooled to −80 °C and treated with MeLi (6.7 mL, 8.0 mmol). Upon warming of the solution to room temperature, salt precipitated. After addition of TMEDA (1.2 mL, 8.0 mmol), the volatiles were removed *in vacuo* and the residue was extracted with pentane (50 mL). Cooling to −30 °C yielded **6** (2.5 g, 3.3 mmol, 82%) as large colorless crystals. IR (KBr/Nujol, cm^{-1}): 3100 (m), 3246 (w), 3079 (s), 2930 (vs), 2857 (vs), 2795 (s), 1508 (m), 1495 (s), 1458 (vs), 1377 (vs), 1358 (s), 1292 (s), 1240 (vs), 1181 (w), 1159 (w), 1130 (w), 1098 (w), 1071 (m), 1003 (s), 993 (s), 951 (m), 934 (w), 918 (m), 845 (vs), 833 (vs), 785 (s), 758 (s), 700 (s), 689 (m), 677 (s), 604 (m), 475 (s), 440 (m), 403 (m). ^{1}H NMR (benzene-d_6, δ): 7.32 (m, 4H, Ar), 7.05 (m, 6H, Ar), 2.04 (s, 12H, TMEDA-CH_3), 1.67 (s, 4H, TMEDA-CH_2), 0.21 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$), −0.48 (s, 6H, CH_3). ^{13}C NMR (benzene-d_6, δ): 182.7 (s, Ph*C*[NSi(CH$_3$)$_3$]$_2$), 144.2 (s, Ar), 127.8 (dd, Ar, $^1J_{C-H}$ = 159 Hz, $^2J_{C-H}$ = 7 Hz), 127.4 (dt, Ar, $^1J_{C-H}$ = 155 Hz, $^2J_{C-H}$ = 7 Hz), 126.7 (dt, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz), 56.9 (q, TMEDA-*C*H$_3$, $^1J_{C-H}$ = 134 Hz), 46.3 (t, TMEDA-*C*H$_2$, $^1J_{C-H}$ = 134 Hz), 10.1 (q, *C*H$_3$, $^1J_{C-H}$ = 116 Hz), 3.1 (q, PhC-[NSi(*C*H$_3$)$_3$]$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd (found) for $C_{34}H_{68}LiN_6Si_4Y$: C, 53.09 (53.19); H, 8.91 (8.89); N, 10.93 (10.94); Y, 11.56 (11.74).

Preparation of [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph.THF (7). At −80 °C, a solution of **2** (3.6 g, 4.9 mmol) in toluene (45 mL) was treated with KCH$_2$Ph (0.65 g, 5.0 mmol). The suspension was allowed to warm to room temperature and then stirred until all the KCH$_2$Ph had reacted. The volatiles were pumped off, and after being dried thoroughly, the residue was extracted with pentane (50 mL). Concentration and cooling gave **7** as an oily product. Repeated recrystallization from pentane (30 mL) and slow cooling to −30 °C yielded **7** (2.2 g, 2.8 mmol, 58%) as block-shaped pale yellow crystals. IR (KBr/Nujol, cm^{-1}): 3061 (w), 2926 (vs), 2857 (vs), 1589 (m), 1483 (m), 1447 (vs), 1429 (vs), 1398 (s), 1316 (w), 1296 (w), 1244 (s), 1215 (m), 1007 (m), 984 (s), 914 (m), 899 (m), 845 (s), 797 (m), 785 (m), 758 (s), 735 (m), 698 (m), 683 (m), 482 (m). ^{1}H NMR (benzene-d_6, δ): 7.15 (m, 15H, Ar), 3.91 (s, 4H, THF-α-CH_2), 2.25 (d, 2H, CH_2Ph, $^2J_{Y-H}$ = 3 Hz), 1.39 (s, 4H, THF-β-CH_2), 0.18 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$). ^{13}C NMR (benzene-d_6, δ): 183.6 (s, Ph*C*[NSi(CH$_3$)$_3$]$_2$), 155.1 (s, Ar), 143.3 (s, Ar), 128.7 (d, Ar, $^1J_{C-H}$ = 158 Hz), 128.1 (d, Ar, $^1J_{C-H}$ = 160 Hz), 126.3 (d, Ar, $^1J_{C-H}$ = 159 Hz), 124.0 (d, Ar, $^1J_{C-H}$ = 153 Hz), 116.7 (d, Ar, $^1J_{C-H}$ = 157 Hz), 70.9 (t, THF-α-*C*H$_2$, $^1J_{C-H}$ = 149 Hz), 53.4 (dt, *C*H$_2$Ph, $^1J_{C-H}$ = 118 Hz; $^1J_{Y-C}$ = 31 Hz), 25.3 (t, THF-β-*C*H$_2$, $^1J_{C-H}$ = 135 Hz), 2.7 (q, PhC[NSi(*C*H$_3$)$_3$]$_2$), $^1J_{C-H}$ = 118 Hz).

^{89}Y NMR (benzene-d_6, δ): 549. Anal. Calcd (found) for $C_{37}H_{61}N_4OSi_4Y$: C, 57.04 (57.05); H, 7.89 (7.97); Y, 11.41 (11.55).

Preparation of [PhC(NSiMe$_3$)$_3$]$_2$YCH(SiMe$_3$)$_2$ (8). Li-CH(SiMe$_3$)$_2$ (3.3 g, 19.8 mmol) was added to a solution of **2** (15.2 g, 20.5 mmol) in toluene (200 mL) at −80 °C. The suspension was slowly warmed to room temperature and stirred overnight. The reaction mixture was evaporated *in vacuo*, and the residual sticky solid was dissolved in 150 mL of pentane. After filtration, the pentane was removed, leaving a viscous oil which slowly solidified yielding **8** (12.8 g, 16.5 mmol, 83%) as a colorless crystalline material. IR (KBr/Nujol, cm^{-1}): 2936 (vs), 2481 (w), 2363 (w), 2338 (w), 2101 (w), 2010 (w), 1887 (w), 1773 (w), 1601 (w), 1578 (w), 1435 (vs), 1378 (s), 1292 (w), 1248 (s), 1165 (m), 1074 (m), 1009 (s), 986 (s), 920 (m), 845 (vs), 785 (s), 760 (s), 723 (s), 702 (s), 683 (s), 664 (m), 594 (m), 486 (m), 440 (m). ^{1}H NMR (benzene-d_6, δ): 7.15 (m, 4H, Ar), 6.97 (m, 6H, Ar), 0.47 (s, 18H, CH(Si(CH_3)$_3$)$_2$), 0.07 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$), −0.94 (d, 1H, CH(SiMe$_3$)$_2$, $^2J_{Y-H}$ = 1.8 Hz). ^{13}C NMR (benzene-d_6, δ): 184.6 (s, PhC[NSiMe$_3$]$_2$), 141.9 (s, Ar), 128.6 (dt, Ar, $^1J_{C-H}$ = 164 Hz, $^2J_{C-H}$ = 7 Hz), 128.2 (d, Ar, $^1J_{C-H}$ = 163 Hz), 126.5 (d, Ar, $^1J_{C-H}$ = 155 Hz), 43.5 (dd, CH(SiMe$_3$)$_2$, $^1J_{C-H}$ = 88 Hz, $^1J_{Y-C}$ = 30 Hz), 5.2 (q, CH(Si(CH$_3$)$_3$)$_2$, $^1J_{C-H}$ = 116 Hz), 2.9 (q, PhC[NSi(CH$_3$)$_3$]$_2$, $^1J_{C-H}$ = 119 Hz). ^{89}Y NMR (benzene-d_6, δ): 721. Anal. Calcd (found) for $C_{33}H_{65}N_4Si_6Y$: C, 51.12 (51.07); H, 8.45 (8.48); Y, 11.47 (11.59).

Preparation of [p-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (8$_{OMe}$). Compound **8$_{OMe}$** was prepared by a similar procedure as **8** starting from **2$_{OMe}$** (3.2 g, 4.1 mmol) and LiCH(SiMe$_3$)$_2$ (0.7 g, 4.2 mmol). Repeated recrystallization from pentane yielded **8$_{OMe}$** (2.2 g, 2.6 mmol, 63%) as colorless crystals. IR (KBr/Nujol, cm^{-1}): 2940 (vs), 2874 (s), 2749 (w), 1609 (s), 1576 (w), 1512 (s), 1408 (vs, br), 1292 (s), 1248 (vs), 1171 (s), 1107 (w), 1034 (s), 988 (s), 843 (vs), 758 (vs), 741 (vs), 723 (s), 685 (m), 669 (m), 644 (s), 633 (m), 604 (w), 596 (w), 534 (w), 503 (s), 426 (m), 407 (w). ^{1}H NMR (benzene-d_6, δ): 7.11 (d, 4H, Ar, $^3J_{H-H}$ = 8.8 Hz), 6.62 (d, 4H, Ar, $^3J_{H-H}$ = 8.8 Hz), 3.20 (s, 6H, OCH_3), 0.50 (s, 18H, CH(Si(CH_3)$_3$)$_2$), 0.13 (s, 36H, PhC-[NSi(CH_3)$_3$]$_2$), −0.91 (d, 1H, CH(SiMe$_3$)$_2$, $^2J_{Y-H}$ = 1.3 Hz). ^{13}C NMR (benzene-d_6, δ): 184.8 (s, p-MeO-C$_6$H$_4$$C$[NSiMe$_3$]$_2$), 160.0 (s, Ar), 134.6 (s, Ar), 127.9 (dd, Ar, $^1J_{C-H}$ = 159 Hz, $^2J_{C-H}$ = 7 Hz), 113.4 (dd, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz), 54.6 (q, OCH$_3$, $^1J_{C-H}$ = 144 Hz), 42.9 (dd, CH(SiMe$_3$)$_2$, $^1J_{C-H}$ = 88 Hz, $^1J_{Y-C}$ = 31 Hz), 5.2 (q, CH(Si(CH$_3$)$_3$)$_2$, $^1J_{C-H}$ = 118 Hz), 2.9 (q, PhC[NSi(CH$_3$)$_3$]$_2$, $^1J_{C-H}$ = 119 Hz). Anal. Calcd (found) for $C_{35}H_{69}N_4O_2Si_6Y$: C, 50.32 (50.38); H, 8.33 (8.39).

Preparation of {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (9). A solution of **8** (2.5 g, 3.2 mmol) in benzene (50 mL) was cooled to −196 °C and brought under 1 atm of dihydrogen. The flask with the frozen solution was warmed to room temperature and stirred under H_2 for 3 days. Then the solvent was evaporated until crystallization started. Cooling to 6 °C afforded **9** (1.4 g, 1.1 mmol, 71%) as colorless crystals. IR (KBr/Nujol, cm^{-1}): 3023 (sh), 2925 (vs), 2870 (vs), 1946 (w), 1927 (w), 1896 (w), 1879 (w), 1773 (w), 1447 (vs), 1400 (vs), 1300 (s), 1257 (s), 1246 (vs), 1170 (m), 995 (s), 918 (m), 841 (vs), 785 (s), 758 (vs), 723 (s), 700 (s), 685 (m), 660 (m), 482 (m). ^{1}H NMR (benzene-d_6, δ): 8.28 (t, 1H, Y−H−Y, $^1J_{Y-H}$ = 27.6 Hz), 7.39 (m, 4H, Ar), 7.09 (m, 6H, Ar), 0.21 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$). ^{13}C NMR (benzene-d_6, δ): 184.9 (s, PhC[NSiMe$_3$]$_2$), 143.1 (s, Ar), 128.3 (dt, Ar, $^1J_{C-H}$ = 164 Hz, $^2J_{C-H}$ = 6 Hz), 126.3 (d, Ar, $^1J_{C-H}$ = 162 Hz), 3.2 (q, PhC[NSi(CH$_3$)$_3$]$_2$, $^1J_{C-H}$ = 119 Hz). Anal. Calcd (found) for $C_{52}H_{94}N_8Si_8Y_2$: C, 50.62 (50.59); H, 7.68 (7.65); Y, 14.41 (14.46).

NMR-Scale Preparation of {[p-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$Y-(μ-H)}$_2$ (9$_{OMe}$). An NMR tube equiped with a Teflon needle valve was charged with **8$_{OMe}$** (34 mg, 0.04 mmol) in benzene-d_6 (0.7 mL). After the solution had been cooled to −196 °C and evacuated, dihydrogen was added (1 atm) and subsequently the solution warmed at 50 °C for 12 h. ^{1}H NMR spectroscopy showed that all **8$_{OMe}$** had been converted into **9$_{OMe}$**. ^{1}H NMR (benzene-d_6, δ): 8.31 (t, 1H, Y−H−Y, $^1J_{Y-H}$ = 27.8 Hz), 7.35 (d, 4H, Ar, $^3J_{H-H}$ = 8.6 Hz), 6.76 (d, 6H, Ar, $^3J_{H-H}$ = 9.0 Hz), 3.23 (s, OCH_3), 0.29 (s, 36H, PhC[NSi(CH_3)$_3$]$_2$). ^{13}C NMR (benzene-d_6,δ): 185.1 (s, PhC[NSiMe$_3$]$_2$), 159.8 (s, Ar), 136.1 (s, Ar), 127.5 (dt, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz), 113.5 (dd, Ar, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 10 Hz), 54.6 (q, OCH$_3$, $^1J_{C-H}$ = 144 Hz), 3.2 (q, PhC[NSi(CH$_3$)$_3$]$_2$, $^1J_{C-H}$ = 118 Hz).

Molecular Orbital Calculations. All molecular orbital calculations were performed with ZINDO94, installed on a HP-750 workstation. The theoretical Γ's, provided by the program, were used.[44] The bond lengths and angles of the models [HC(NH)$_2$]$_2$YCH$_3$ and [C$_5$H$_5$]$_2$YCH$_3$ were taken from X-ray crystal data, and the models were restricted to C_2 and C_{2v} symmetry, respectively. The Y−C$_\sigma$ bond distance was set at 2.48 Å. A full list of the Cartesian coordinates and Mulliken analyses of [HC(NH)$_2$]$_2$YCH$_3$ and [C$_5$H$_5$]$_2$YCH$_3$ can be found in the Supporting Information.

X-ray Crystallographic Analysis of [p-MeOC$_6$H$_4$C-(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (8$_{OMe}$). A suitable colorless polyfacial crystal was glued on top of a glass fiber in a drybox and transferred into the cold nitrogen stream of the low-temperature unit[51] mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a MicroVAX-2000 computer. The crystals reflected well but showed a relatively very high background scattering, probably caused by fluorescence of the Y atoms. Unit cell parameters and orientation matrix were determined from a least-squares treatment of the SET4 setting angles[52] of 22 reflections in the range 14.76° < θ < 21.61°. The unit cell was identified as monoclinic, space group $P2_1/a$. Reduced cell calculations did not indicate any higher metric lattice symmetry,[53] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[54] The intensity of three standard reference reflections, monitored every 2 h of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics, indicating crystal and electronic stability. A 360° Ψ-scan for a reflection close to axial (42$\bar{2}$) showed a variation in intensity of less than 8% about the mean value. Intensity data were corrected for Lorentz and polarization effects and scale variation but not for absorption. Standard deviation $\sigma(I)$ in the intensities was increased according to an analysis of the excess variance of the reference reflection: Variance was calculated on the basis of counting statistics and the term (P^2I^2), where P (=0.0078) is the instability constant[55] as derived from the excess variance in the reference reflections. Equivalent reflections were averaged and stated observed if satisfying the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[56] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms refined with block-diagonal least-squares procedures (CRYLSQ)[57] minimizing the function $Q = \Sigma_{\mathbf{h}}[w(|F_o| - k|F_c|)^2]$. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms which coordinates were included in the refinement. Final refinement on F_o 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 converged at R_F = 0.051 (wR = 0.029). Weights were introduced in the final refinement cycles. A final difference Fourier map did not show any significant residual

(51) Van Bolhuis, F. *J. Appl. Crystallogr.* **1971**, *4*, 263.
(52) De Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.
(53) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.
(54) (a) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264. (b) Le Page, Y. *J. Appl. Crystallogr.* **1988**, *21*, 983.
(55) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245.
(56) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory;* University of Nijmegen: Nijmegen, The Netherlands, 1992.
(57) Olthof-Hazekamp, R. *QRYLSQ, Xtal3.0 Reference Manual;* Hall, S. R., Stewart, J. M., Eds.; University of Western Australia and Maryland; Lamb: Perth, Australia, 1992.

Table 5. Details of the X-ray Structure Determination of [*p*-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (8_{OMe}) and {PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (9)

	8_{OMe}	9
formula	$C_{35}H_{69}N_4O_2Si_6Y$	$(C_{26}H_{47}N_4Si_4Y)_2$
M_n	835.38	1233.86
cryst system	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$
a, Å	22.637(2)	13.526(1)
b, Å	18.032(1)	14.052(1)
c, Å	12.020(1)	20.027(2)
α, deg		104.385(8)
β, deg	101.833(8)	108.934(7)
γ, deg		93.455(8)
V, Å^3	4802.2(7)	3446.2(5)
D_{calc}, g·mol^{-3}	1.155	1.189
Z	4	2
F(000)	1784	1304
μ(Mo $K\alpha$), cm^{-1}	13.98	18.6
cryst size, mm	0.20 × 0.25 × 0.33	0.37 × 0.45 × 0.50
T, K	130	130
θ range, deg: min, max	1.13, 27.0	1.12, 25.6
λ (Mo $K\alpha$), Å	0.71073	0.71073
monochromator	graphite	graphite
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.85 + 0.34 \tan\theta$	$\Delta\omega = 0.75 + 0.34 \tan\theta$
data set	h, −28→28; k, 0→23; l, 0→15	h, 0→16; k, −17→17; l, −24→22
tot. data	11 326	13 522
unique data	10 461	12 931
obsd data ($I \geq 2.5\sigma(I)$)	5673	8746
$R1$ (=$\Sigma(I - \bar{I})/\Sigma I$)	0.049	0.031
$R2$ (=$\Sigma\sigma/\Sigma I$)	0.070	0.049
no. of equiv reflcns	1028	1182
no. of refined params	709	990
final agreement factors		
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.051	0.043
$wR = [\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma w\|F_o\|^2]^{1/2}$	0.029	0.037
weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$ [a]	1.841	1.761
resid electron density in final diff Fourier map, e/Å^3	−0.79, 0.65	−0.60, 0.70
max shift/σ in final cycle	0.3988	0.2504
av shift/σ in final cycle	0.021 10	0.0122

[a] m = no. of observations and n = no. of variables.

features. Crystal data and experimental details of the structure determination are compiled in Table 5. Scattering factors were taken from Cromer and Mann.[58] Anomalous dispersion factors taken from Cromer and Liberman.[59] All calculations were carried out on the HP9000/735 computer at the University of Groningen with the program packages Xtal,[60] PLATON[61] (calculation of geometric data), and ORTEP[62] (preparation of illustrations).

X-ray Crystallographic Analysis of {[PhC(NSiMe$_3$)$_2$]$_2$Y(μ-H)}$_2$ (9). The general procedure for solving the structure was as outlined above. Precise lattice parameters and their standard deviation were derived from the angular settings of 22 reflections in the range 11.81° < σ < 16.88°. The triclinic unit cell (space group $P\bar{1}$) was checked for higher symmetry.[53,54] A correction for absorption was judged not to be necessary in view of the observed small intensity variation (9%) for a 360° Ψ-scan of the close to axial reflection (20$\bar{4}$). The structure was solved by Patterson methods and extension of the model was accomplished by direct methods, applied to difference structure factors using the program DIRDIF.[56] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms refined with block-diagonal least-squares procedures (CRYLSQ)[57] minimizing the function $Q = \Sigma_{\mathbf{h}}[w(|F_o| - k|F_c|)^2]$. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms. Following the inclusion of the positional parameters of hydrogen atoms, the remainder of the structure refined smoothly. High thermal displacement motion was sited for the C(44) and C(46) atoms, suggesting some degree of disorder, but no resolvable disorder could be stated. The methyl hydrogen atoms bonded to the C(44) and C(45) atoms did not refine well and were ultimately included in the final refinement riding on their carrier atoms with their positions calculated by using sp^3 hybridization at the C atom as appropriate with a fixed C−H distance of 0.96 Å. Final refinement on F_o 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 converged at $R_F = 0.043$ ($wR = 0.037$). Weights were introduced in the final refinement cycles. A final difference Fourier map did not show unusual residual peaks. The crystal exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter.[63] Crystal data and experimental details of the structure determination are compiled in Table 5.

Acknowledgment. This work was financially supported by Shell Research B.V. Amsterdam, which is gratefully acknowledged. The ^{89}Y NMR spectra were recorded by J. H. G. Frijns (Shell Research B.V. Amsterdam), who is gratefully acknowledged.

Supporting Information Available: Listing of the Cartesian coordinates and Mulliken population analyses of [C$_5$H$_5$]$_2$YCH$_3$ and [HC(NH)$_2$]$_2$YCH$_3$ and all atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles for **8_{OMe}** and **9** (35 pages). Ordering information is given on any current masthead page.

OM950813+

(58) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(59) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(60) Hall, S. R.; Flack, H. D.; Stewart, J. M. *Xtal3.2 Reference Manual*; Universities of Western Australia and Maryland; Lamb: Perth, Australia, 1992.
(61) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(62) Johnson, C. K. *ORTEP*; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.
(63) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.