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Rare-Earth Metal Alkyl and Hydride Complexes Supported by a Linked Anilido–cyclopentadienyl Ligand: Synthesis, Structure, and Reactivity

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Trimethylsilylmethyl complexes of the type [Ln(η^5-$C_5Me_4CH_2SiMe_2NC_6H_4R$-4-κN)($CH_2SiMe_3$)(thf)$_n$] containing a dianionic ligand [$C_5Me_4CH_2SiMe_2NC_6H_4R$-4]$^{2-}$ with a *para*-substituted anilido group and a CH_2SiMe_2 link were prepared. The yttrium complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(CH_2SiMe_3)(thf)$_2$] (**2a**) reacts with H_2 to generate the corresponding dimeric hydride [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)-(μ-H)(thf)]$_2$ (**5a**). Pyridine inserts into the Y–H bond in a 1,2-fashion to afford the stable 2-hydropyridyl complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(η^1-NC_5H_6)(py)$_2$] (**6a**). Upon reaction with *t*BuC≡CH, protonolysis takes place to give the dimeric alkynyl complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(μ-C≡C*t*Bu)(thf)]$_2$ (**7a**).

Introduction

Linked amido–cyclopentadienyl ligands $(C_5R_4ZNR')^{2-}$, commonly known as "constrained geometry ligands", have gained considerable importance as ancillary ligands for group 4 metal polymerization catalyst precursors.[1] Since the first report on scandium alkyl and hydride complexes containing a linked *tert*-butylamido tetramethylcyclopentadienyl ligand by Bercaw et al.,[2] this type of chelate ligands have also been utilized widely in group 3 metal chemistry.[3,4d–4h,11] Work by Hou et al. suggests that the anilido group rather than the ubiquitous *tert*-butylamido group for the amido donor R′ imparts a higher activity to the metal center in alkyne dimerization catalysis and related reactions,[5b,10] probably because of the electron-withdrawing property of the phenyl group in conjunction with a different steric profile. We have recently reported that yttrium hydride complexes supported by a linked amido–cyclopentadienyl ligand [Ln(η^5-C_5Me_4ZNR'-κN)(μ-H)(thf)$_n$]$_2$ (Ln = Y, Lu) are active hydrosilylation catalysts for 1-alkene and styrene and that the amido substituent R′ as well as the link Z exert considerable influence on both activity and regioselectivity; the longer CH_2SiMe_2 link delivers the most-active catalyst.[5] We report here on the synthesis, structure, and reactivity of yttrium hydride complexes that contain a CH_2SiMe_2-linked anilido–cyclopentadienyl ligand.

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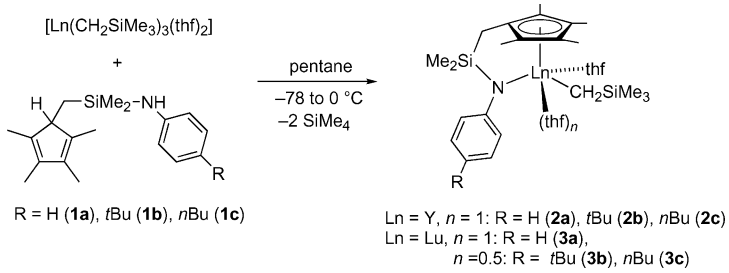
Results and Discussion

Alkyl Complexes

The trimethylsilylmethyl complexes [Ln(η^5-$C_5Me_4CH_2$-$SiMe_2NC_6H_4R$-4-κN)(CH_2SiMe_3)(thf)$_n$] [Ln = Y, n = 2: R = H (**2a**), *t*Bu (**2b**), *n*Bu (**2c**); Ln = Lu, n = 2: R = H (**3a**); n = 1.5: R = *t*Bu (**3b**), *n*Bu (**3c**)] were synthesized by adding the diprotonated ligand [$(C_5Me_4H)CH_2SiMe_2NHC_6H_4R$-4] to a suspension of [Ln(CH_2SiMe_3)$_3$(thf)$_2$] in pentane cooled to –78 °C and isolated as colorless powders (Scheme 1).

Complexes **2a** and **3a** containing an anilido group are sparingly soluble in aliphatic hydrocarbon solvents, but soluble in aromatic solvents. The ^{1}H NMR spectra at room temperature show five singlets for the methyl groups attached to the silicon atoms ($SiMe_3$, $SiMe_2$), for those on the cyclopentadienyl ring, and for the methylene group of the linker. The methylene group attached to the yttrium center in **2a** gives rise to a doublet at δ = –0.91 ppm ($^2J_{YH}$ = 2.7 Hz), whilst a sharp singlet is observed at δ = –0.84 ppm for the corresponding signal in the lutetium complex **3a**. Three signals are detected for the protons at the phenyl ring with an integral ratio of 1:2:2, which indicates free rotation of the ring about the C–N single bond. This rotation is slowed down by cooling, as five distinct signals are observed at –70 °C. Two separate signals for the α- and the β protons of thf are found at this temperature, whereas the signals arising from the diastereotopic groups of the anilido–cyclopentadienyl ligand do not split. The C_s symmetry is due to the *trans* coordination of two thf molecules.

Crystals of **2a** suitable for diffraction were obtained from a saturated toluene solution at –30 °C, and Figure 1 shows two views of the molecule. The compound was found to



Scheme 1.

adopt a distorted square-pyramidal coordination geometry in the solid state; two molecules of thf, the alkyl group, and the nitrogen atom form the base of the structure.

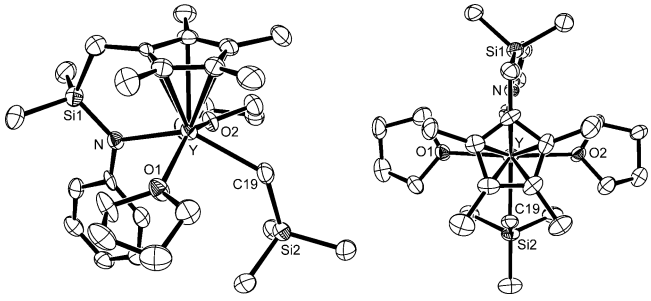


Figure 1. ORTEP view of the alkyl complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(CH_2SiMe_3)(thf)$_2$] (**2a**) (left: standard view; right: top view). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y–N 2.312(5), Y–C19 2.451(6), Y–O1 2.428(4), Y–O2 2.419(4), Y–Cp_{cent} 2.342(6), N–C13 1.382(8); N–Y–O1 83.77(16), N–Y–O2 83.02(16), O1–Y–O2 145.05(15), N–Y–C19 140.8(2).

The phenyl ring is arranged parallel to the plane defined by the Si, N, and Y atoms. The bulky $SiMe_3$ group is bent away from the cyclopentadienyl ring (Cp_{cent}–Y–C19–Si2 179°). In other four-coordinate linked amido–cyclopentadienyl complexes such as [Y(η^5-$C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2$-κN,N′)($CH_2SiMe_3$)(thf)] ($Cp_{cent}$–Y–C–Si 89°),[6] [Y(η^5-$C_5Me_4SiMe_2N$*t*Bu-κN)($CH_2SiMe_3$)(thf)] ($Cp_{cent}$–Y–C–Si 90.1°),[7] or [Y(η^5-$C_5Me_4CH_2SiMe_2N$*t*Bu-κN)(CH_2SiMe_3)(thf)] (Cp_{cent}–Y–C–Si 94.1°), this group is found to be turned to the side.[5a] The Y–C_{ring} and Y–O bonding distances are in the usual range for yttrium amido–cyclopentadienyl complexes. The Y–N bond length of 2.312(5) Å is long and comparable to bimetallic rare-earth metal complexes of the type [LiY(η^5-$C_5R_4SiMe_2NCH_2CH_2X$-κN)$_2$] (C_5R_4 = C_5Me_4, C_5H_3*t*Bu; X = NMe_2, OMe),[4d] [LiY(η^5-$C_5Me_4SiMe_2NC_5H_4$N-2-κN)$_2$], and [CuY(η^5-$C_5Me_4SiMe_2NC_5H_4$N-2-κN)$_2$] [2.319(4)–2.333(3) Å].[8] Another example of a "constrained geometry" complex bearing two molecules of thf is the linked amido–fluorenyl complex [Y{(η^3-3,6-tBu$_2$Flu)$SiMe_2N$*t*Bu-κN}(CH_2SiMe_3)(thf)$_2$], in which an η^3-coordination of the fluorenyl fragment allows the coordination of a second molecule of thf.[9]

Comparison with an analogous complex featuring a shorter $SiMe_2$ link, [Y(η^5-$C_5Me_4SiMe_2NPh$-κN)(CH_2SiMe_3)(thf)$_2$] (**A**),[10] illustrates the influence of the ligand on the molecular geometry around the metal center (Figure 2). The additional carbon atom in the backbone of **2a** induces a much smaller N–Y–C(alkyl) angle [140.8(2)° in **2a** vs. 150.89(19)° in **A**], together with a smaller Y–N–C_{ipso} angle [115.5(4)° in **2a** vs. 131.0(4)° in **A**]. Consequently, the plane

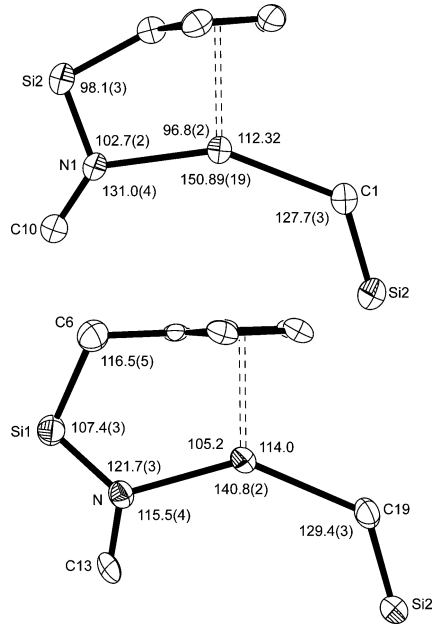
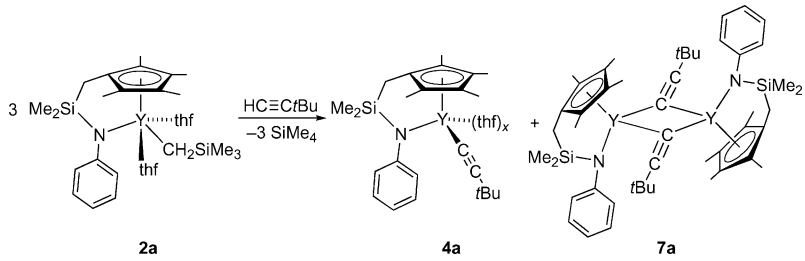


Figure 2. Comparison of structural parameters in [Y(η^5-$C_5Me_4SiMe_2NPh$-κN)(CH_2SiMe_3)(thf)$_2$][10] (**A**, top) and in [Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(CH_2SiMe_3)(thf)$_2$] (**2a**, bottom).

Table 1. Selected bond lengths [Å] in [Y(η^5-$C_5Me_4SiMe_2NPh$-κN)(CH_2SiMe_3)(thf)$_2$][10] (**A**) and in [Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(CH_2SiMe_3)(thf)$_2$] (**2a**).

	A	**2a**
Y–C(alkyl)	2.481(6)	2.451(6)
C–Si(alkyl)	1.842(6)	1.857(7)
Y–Cp_{cent}	2.336(6)	2.342(6)
Y–N	2.327(5)	2.312(5)
N–C_{ipso}	1.382(7)	1.382(8)
N–Si	1.731(5)	1.732(5)
Y–O1	2.382(3)	2.428(4)
Y–O2	2.382(3)	2.419(4)

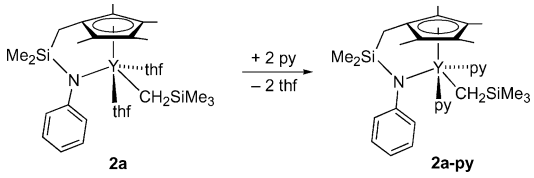


Scheme 2.

of the cyclopentadienyl ligand is perfectly perpendicular to the Y–Cp_{cent} bond in **2a** (Y–Cp_{cent}–C_{Cp} ranging from 89.22° to 90.51°), whilst Y–Cp_{cent}–C_{Cp} angles varying from 85° to 93.16° are measured in **A**. The geometry of the alkyl group and the Cp_{cent}–Y–C(alkyl) angle are, however, almost independent of the length of the backbone (Table 1).

Reaction of **2a** with HC≡C*t*Bu (Scheme 2) afforded a 1:1 mixture of the monomeric thf adduct [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(C≡C*t*Bu)(thf)$_x$] (**4a**) and the dimeric thf-free complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(C≡C*t*Bu)]$_2$ (**7a**). The similar solubility of **4a** and **7a** in several solvents prevented their separation. This behavior is different to that of [Y(η^5-$C_5Me_4CH_2SiMe_2NCH_2CH_2NMe_2$-κN,N′)(C≡C*t*Bu)(thf)], which exclusively generates the dimeric base-free complex upon recrystallization from toluene.[11]

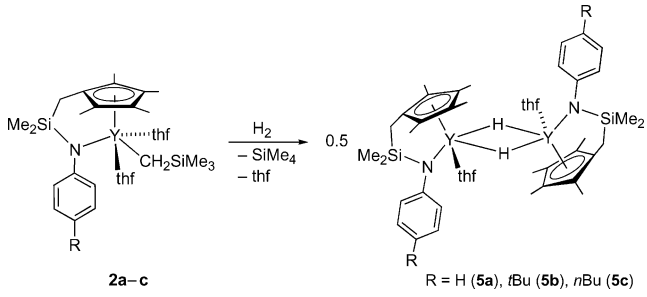
The thf ligands in **2a** are labile and can be substituted for pyridine to produce the pyridine complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(CH_2SiMe_3)(py)$_2$] (**2a-py**) (Scheme 3). The substitution is evidenced by a shift of one signal for the C_5Me_4 groups to higher field (δ = 1.38 ppm in **2a-py** relative to 1.99 ppm in **2a**). The pyridine complex decomposes overnight at room temperature by C–H activation of the coordinated pyridine with concomitant formation of tetramethylsilane. A red solution is obtained for which no alkyl signals can be detected in the ^{1}H NMR spectrum.



Scheme 3.

Hydrogenolysis of the Alkyl Complex

Hydrogenolysis of the alkyl complexes **2a**–**2c** with dihydrogen (4 bar) was carried out in toluene (for **2a**) or pentane (for **2b** and **2c**), depending on the respective solubility of the alkyl precursors. Stirring overnight afforded the hydride complexes [Y(η^5-$C_5Me_4CH_2SiMe_2NC_6H_4$R-4-κN)(μ-H)(thf)]$_2$ [(R = H (**5a**), *t*Bu (**5b**), *n*Bu (**5c**)] in good yields as sparingly soluble products (Scheme 4). Whilst complexes **5a** and **5b** are insoluble in aliphatic and aromatic hydrocarbons and poorly soluble in thf, the *n*Bu chain in the *para* position of the phenyl ring in **5c** increases its solubility in aromatic solvents. NMR spectroscopic data could nonetheless be obtained for complexes **5a** and **5b** in [D_8]thf at 50 °C. The NMR investigations show that the lutetium analogues **3a**–**3c** react in a similar manner with $PhSiH_3$ to produce the corresponding hydride species.



Scheme 4.

The dimeric structure is conserved in solution [triplets at δ = 5.10 ppm for all three complexes **5a**–**5c** in [D_8]thf with $^1J_{YH}$ = 28.4 Hz (**5a**) and 29.9 Hz (**5b** and **5c**)]. Crystals of complexes **5a**–**5c** suitable for diffraction can be grown by layering a toluene solution of the alkyl precursors **2a**–**2c** with a toluene solution of $PhSiH_3$ (5 equiv.). Structural in-

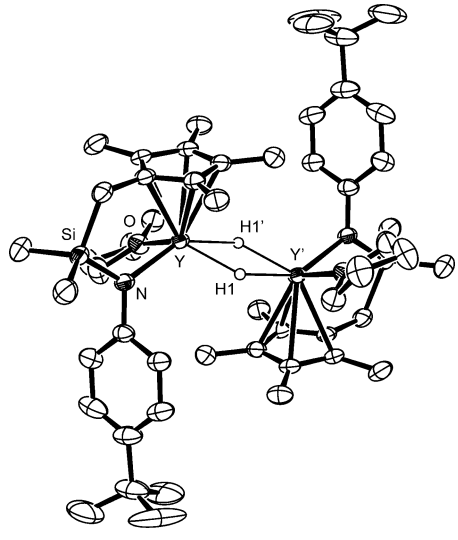
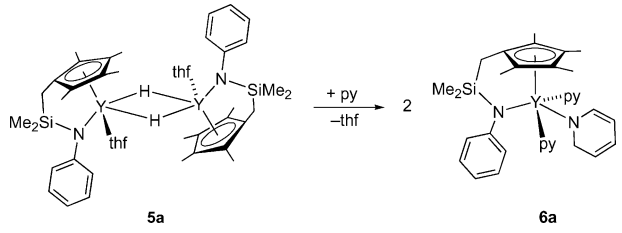


Figure 3. ORTEP view of the dimeric hydride complex [Y(η^5-$C_5Me_4CH_2SiMe_2NC_6H_4$*t*Bu-4-κN)(μ-H)(thf)]$_2$ (**5b**). Thermal ellipsoids are drawn at the 50% probability level. Only bridging hydrogen atoms are shown. Selected bond angles [Å] and angles [°]: Y–O 2.367(3), Y–N 2.262(3), Y–Cp_{cent} 2.328(3), Y···Y′ 3.6644(8); Cp_{cent}–Y–N 103.17(11).

vestigations on **5b** reveal a heterochiral molecule of C_i symmetry with cyclopentadienyl rings in a *trans* arrangement (Figure 3).

Reaction of the Hydride Complex with Pyridine

When the hydride **5a** is dissolved in pyridine, a clear yellow solution is obtained. Partial removal of pyridine under vacuum and cooling to –30 °C overnight afforded yellow single crystals suitable for X-ray diffraction. The crystal-structure analysis shows a 2-hydropyridyl complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(η^1-NC_5H_6)(py)$_2$] (**6a**) formed by 1,2-insertion of pyridine into the Y–H bond of **5a** (Scheme 5).



Scheme 5.

The kinetically controlled 1,2-insertion product was formed at room temperature. Isomerization to the thermodynamically more stable 1,4-insertion product at higher temperatures (up to 80 °C) was not observed by ^{1}H NMR spectroscopy. In a similar manner, the reaction of [Y{PhC(NSiMe$_3$)$_2$}$_2$(μ-H)]$_2$ with pyridine was reported to give the 1,2-addition product [Y{PhC(NSiMe$_3$)$_2$}$_2$(η^1-NC_5H_6)], which also did not isomerize at higher temperature (over a day at 100 °C).[12] Isomerization to the 1,4-insertion product upon heating was reported to proceed within 2 h for the 2-hydropyridyl complex [Y(DADMB)(η^1-NC_5H_6)(py)$_2$] (DADMB = 2,2-bis{(*tert*-butyldimethylsilyl)-amido}-6,6-dimethylbiphenyl [{6,6′-Me$_2$-(C$_6$H$_3$)$_2$}(2,2′-NSiMe$_2$*t*Bu)$_2$]$^{2-}$) obtained by 1,2-insertion of pyridine into the Y–H bond of the hydride precursor [Y(DADMB)(μ-H)(thf)]$_2$.[13] Similarly, Evans et al. found that the hydride complex [Y(η^5-C_5H_4R)$_2$(μ-H)(thf)]$_2$ (R = H, Me) readily reacted with pyridine in polar solvents to give the 1,2-insertion product, which rearranged to the 1,4-isomer.[14] Reaction of the hydride complex [Y{(η^3-3,6-*t*Bu$_2$Flu)SiMe$_2$N*t*Bu-κN}(μ-H)(thf)]$_2$ with excess pyridine was reported to directly afford the 1,4-addition product [Y{(η^3-3,6-*t*Bu$_2$Flu)SiMe$_2$N*t*Bu-κN}(η^1-NC_5H_6)(py)$_2$]. No evidence for the existence of the 1,2-isomer was found from the NMR spectroscopic data, possibly because of simultaneous attack at the 2- and 4-positions of the pyridine ring, and/or fast isomerization of the 1,2-product to the 1,4-isomer that occurs under the experimental conditions (70 °C).[15] In the Ziegler alkylation of pyridine with alkyllithium compounds, the 1,2-addition product was assumed as the intermediate.[16] Examination of the 1,2- or 1,4-insertion of pyridine was carried out with metal hydrides such as $LiAlH_4$,[17] MgH_2,[18] or ZnH_2.[19]

In **6a**, the linked anilido–cyclopentadienyl ligand, the two coordinated pyridine molecules, and the 2-hydropyridyl ligand form a square-based pyramidal geometry around the metal, and the structure resembles that observed in the amido–fluorenyl complex [Y{(η^3-3,6-*t*Bu$_2$Flu)SiMe$_2$N*t*Bu-κN}(η^1-NC_5H_6)(py)$_2$] (Figure 4). The Y–N bond length for the pyridine donors and the 2-hydropyridyl ligand are also comparable. The Y–N bond length for the anilido group and that of the amido group are of comparable length. As in **2a**, the phenyl ring is arranged parallel to the Si–N–Y plane. The bond lengths of the anilido–cyclopentadienyl ligand (Y–C_{Cp}, Y–N1, N1–C_{ipso}) are comparable with those in **2a**.

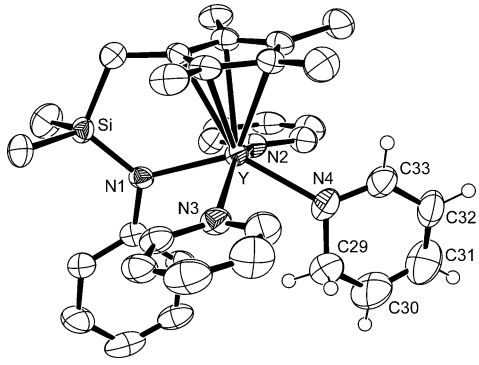


Figure 4. ORTEP view of the 2-hydropyridyl complex [Y(η^5-$C_5Me_4CH_2SiMe_2$NPh-κN)(η^1-NC_5H_6)(py)$_2$] (**6a**). Thermal ellipsoids are drawn at the 50% probability level. Only hydrogen atoms at the 2-hydropyridyl ligand are shown. Selected bond lengths [Å] and angles [°]: Y–N1 2.300(5), Y–N2 2.531(5), Y–N3 2.542(5), Y–N4 2.294(5), Y–C_{ring} 2.604(6)–2.668(5), N1–C13 1.399(7); N1–Y–N2 86.65(17), N1–Y–N3 84.09(17), N1–Y–N4 135.86(18), N2–Y–N3 150.88(15), N2–Y–N4 86.03(17), N3–Y–N4 81.64(18).

The 1,2-insertion becomes apparent in the different carbon–carbon bond lengths of the 2-hydropyridyl ligand. The bonds C29–C30 and C31–C32 are longer than the other bonds in this fragment, whilst C30–C31 and C32–C33 are found to be much shorter (Figure 5).

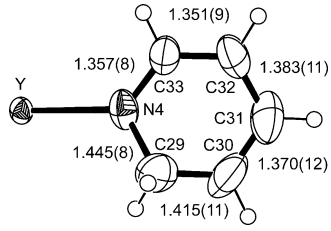
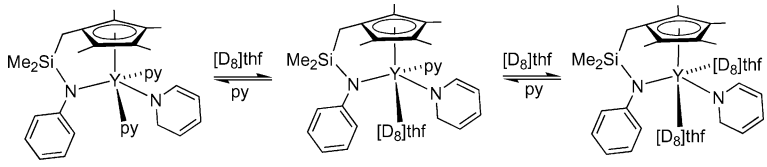


Figure 5. ORTEP view of the [Y(η^1-NC_5H_6)] fragment in **6a** showing the discrete double bonds C30=C31 and C32=C33. Thermal ellipsoids are drawn at the 50% probability level; bond lengths in Å.

The results of the structure analysis were confirmed by NMR spectroscopy. Five separate signals assigned to the 2-hydropyridyl ligand are observed in the ^{1}H NMR spectrum at room temperature. The two methylene protons as well as the methine proton in the *ortho* position give rise to a doublet each. A multiplet and a triplet are found for the protons in the *meta* position. A doublet of doublets is assigned to



Scheme 6.

the proton in the *para* position because of the different coupling to the *meta* protons ($^3J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 6.0 Hz). The signals for the methyl groups at the cyclopentadienyl ring and the methylene group of the 2-hydropyridyl ligand undergo coalescence at 0 °C. The pyridine signals are broad at room temperature, which suggests an exchange reaction according to Scheme 6.

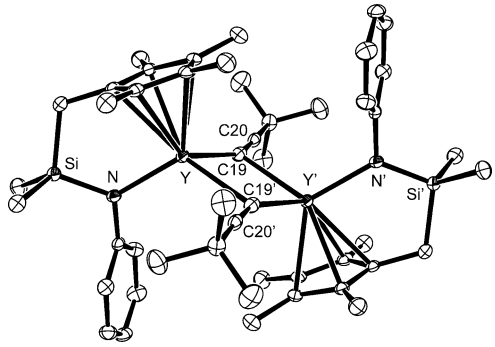
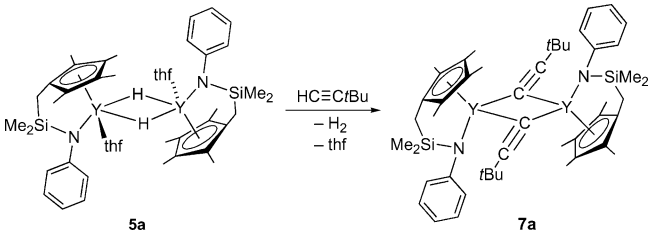


Figure 6. ORTEP view of the dimeric alkynyl complex [Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(μ-C≡C*t*Bu)]$_2$ (**7a**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Y–N 2.1924(16), Y–C19 2.477(2), Y–C19′ 2.483(2), Y···C20 3.061(2), C19–C20 1.214(3), Y–C_{ring} 2.5804(19)–2.6184(19), N–C13 1.419(2); Y–C19–Y′ 95.80(7), C19–Y–C19 84.20(7), Y–C19–C20 156.16(17), Y′–C19–C20 106.65(15), C19–C20–C21 177.1(2).

Reaction of the Hydride Complex with *tert*-Butylacetylene

At room temperature or above, the hydride complex **5a** does not undergo any reaction with 1-alkenes; e.g. styrene does not insert into the metal–hydride bond (5-fold excess). This low reactivity may partly be due to the low solubility, but we believe that the polarization of the metal–hydride bond may be reduced and the monomer–dimer equilibrium unfavorably affected.[20] On the other hand, protonolysis of **5a** with the weak Brønsted acid HC≡C*t*Bu forms the dimeric alkynyl complex [Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(μ-C≡C*t*Bu)]$_2$ (**7a**) (Scheme 7). The colorless compound is soluble in aromatic solvents. The ^{1}H NMR spectrum at room temperature consists of a set of signals for a molecule with C_i symmetry with four singlets for the cyclopentadienyl methyl groups, the $SiMe_2$ bridge, and the *tert*-butyl group. The coordination of thf was not observed. Three separate signals (two triplets and one doublet) in a 1:2:2 ratio are detected for the protons of the phenyl ring.



Scheme 7.

Single crystals of the alkynyl complex **7a** were obtained from a saturated benzene solution at room temperature. Structural investigations show that the two moieties of the structure are bridged by the alkynyl ligands, in a fashion similar to that observed in [Lu(η^5-$C_5Me_4SiMe_2NC_6H_2Me_3$–2,4,6-κN)(μ-C≡CPh)]$_2$ (Figure 6).[5b]

The phenyl ring is orientated perpendicularly to the plane defined by the Si, N, and Y atoms, which is in contrast to **2a** and **6a**. The N–C bond length in the anilido fragment [1.419(2) Å] is longer than in the complexes **2a** and **6a** [1.382(8) Å and 1.399(7) Å, respectively]. The Y–N bond length [2.1924(16) Å] is much shorter than in **2a** and **6a** [2.312(5) Å and 2.300(5) Å, respectively] and is also short relative to other amido cyclopentadienyl yttrium complexes.[5a,5c,6,7,20]

The short yttrium–carbon distance and the asymmetric coordination of the alkynyl ligand [Y–C19–C20 156.1(2)° and Y′–C19–C20 106.7(2)°, Δ = 49.4°] indicate a weak π bonding of the triple bond to the metal center (Figure 7, **I**). This would also explain the fact that in the ^{13}C{^{1}H} NMR spectrum, two doublets for the carbon atoms of the C≡C bond are detected. A coupling of the bridging carbon atom to both metal centers, as depicted in structure **II**, would give rise to only one triplet.

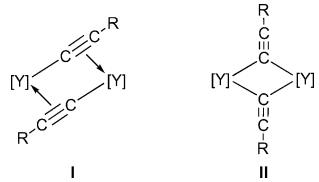


Figure 7. Bridging alkynyl bonding mode in **7a**.

The triple bond length is in the usual range for lanthanide, actinide, and transition-metal alkynyl complexes and is comparable with that of free alkynes HC≡CR (1.20 Å).[21] The asymmetric coordination of the alkynyl ligands in dimeric complexes is well known for rare-earth metal complexes,[22] but a π interaction of the triple bond with the metal center has so far been rarely detected.[22c,22d,23] In all other examples, the metal–β-carbon distance (>3.15 Å) is too long for such a secondary interaction.

Conclusions

A series of yttrium and lutetium trimethylsilylmethyl complexes bearing a CH_2SiMe_2-linked anilido–cyclopentadienyl ligand was synthesized. The sterically small anilido function was found to increase the Lewis acidity of the metal center within the "constrained geometry" ligand sphere, which generally resulted in the coordination of a second molecule of thf in solution as well as in the solid state. Conversion of the trimethylsilylmethyl complexes into the hydride species resulted in the formation of dimeric complexes of the type well studied for the *tert*-butylamido congeners.[2,3,4d–4h,7,20] Reaction of pyridine with the hydride complex gave the 1,2-insertion product, which did not rearrange to the 1,4-isomer. This 1,3-H shift seems to occur more easily when harder ancillary ligands are coordinated to the rare-earth metal.[12] Although the reason for the selective formation of the 1,2- or the 1,4-product remains obscure, a more covalent $Y–N_{amido}$ bond may impede this rearrangement. Protonolysis of the hydride with *t*BuC≡CH gave a donor-free dimer with alkynyl bridges in which the metal centers are held together by weak π donation of the carbon–carbon triple bond to the metal center.

Experimental Section

General Considerations: All operations were performed under an inert atmosphere of argon by using standard Schlenk-line or glovebox techniques. The solvents were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous rare-earth trichlorides (STREM) were used as received. $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Lu)[7,24] and $(C_5Me_4H)CH_2SiMe_2Cl$[5a] were prepared according to published procedures. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded with a Bruker DRX 400 spectrometer (^1H, 400 MHz; ^{13}C, 101 MHz) at 25 °C, unless otherwise stated. Chemical shifts for ^1H and ^{13}C spectra were referenced internally by using the residual solvent resonances and reported relative to tetramethylsilane. Elemental analyses were performed by the Microanalytical Laboratory of this department. Metal titrations were carried out in a 1 M ammonium acetate buffer with edta (5×10^{-3} M) as titrating agent and xylenol orange as indicator.

$(C_5Me_4H)CH_2SiMe_2NHPh$ (1a): A suspension of lithium anilide (5.130 g, 51.8 mmol) in thf (100 mL) was treated at –78 °C with a thf solution (70 mL) of $(C_5Me_4H)CH_2SiMe_2Cl$ (1.1870 g, 51.8 mmol). After addition, the cold bath was removed, and the solution was warmed up to room temperature and stirred overnight. After removal of the solvent under vacuum, the residue was extracted with pentane (3×15 mL). The solvent was removed under vacuum, and the remaining oil distilled under reduced pressure (148 °C, 2×10^{-1} mbar) to afford **1a** (1.0790 g, 73%) as a yellow oil. ^1H NMR ([D$_6$]benzene): δ = 0.16 (s, 6 H, $SiMe_2$), 0.96, 0.99 (d, $^2J_{HH}$ = 7.6 Hz, 2 H, CH_2Si), 1.73, 1.75, 1.76, 1.77, 1.78, 1.87 (s, 12 H, C_5Me_4), 2.45, 2.55 (m, 1 H, C_5Me_4H), 3.11, 3.20 (br. s, 1 H, NH), 6.60 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, 2-, 6-C_6H_5), 6.75 (t, $^3J_{HH}$ = 5.5 Hz, 1 H, 4-C_6H_5), 7.12 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, 3-, 5-C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): δ = –1.1, –0.9, –0.7 ($SiMe_2$), 11.3, 11.7, 11.8, 11.9, 12.6, 14.7 (C_5Me_4), 16.2, 16.8 (CH_2Si), 51.3, 51.8 ($C_5Me_4CH_2$, C attached to CH_2), 116.6, 116.7, 116.8, 118.1, 118.2 (C_6H_5), 129.5, 129.6, 134.1, 134.5, 134.6, 138.5, 138.8 ($C_5Me_4CH_2$, C attached to Me), 147.5 (1-C_6H_5) ppm. EI-MS: *m*/*z* (%) = 285 (19) [M^+], 192 (28) [$C_5Me_4CH_2SiMe_2^+$], 150 (100) [$Me_2SiNHC_6H_5^+$], 134 (14) [$C_5Me_4CH_2^+$], 120 (7) [$C_5Me_4^+$], 91 (6) [$NC_6H_5^+$], 77 (2) [$C_6H_5^+$], 58 (3) [$SiMe_2^+$]. $C_{18}H_{27}NSi$ (285.50): calcd. C 75.72, H 9.53, N 4.91; found C 75.76, H 9.29, N 4.85.

$(C_5Me_4H)CH_2SiMe_2NHC_6H_4tBu$-4 (1b): A solution of [Li(NHC_6H_4tBu)] (3.967 g, 25.6 mmol) in thf (60 mL) was treated at –78 °C with a thf solution (40 mL) of $(C_5Me_4H)CH_2SiMe_2Cl$ (5.850 g, 25.6 mmol). After addition, the cold bath was removed, and the solution was warmed up to room temperature and stirred overnight. After removal of the solvent under vacuum, the residue was extracted with pentane (3×20 mL). The solvent was removed under vacuum, and the remaining oil distilled under reduced pressure (154 °C, 2×10^{-1} mbar) to afford **1b** (7.150 g, 82%) as a yellow oil. ^1H NMR ([D$_6$]benzene): δ = 0.14 (s, 6 H, $SiMe_2$), 0.92, 0.94 (d, $^2J_{HH}$ = 7.7 Hz, 2 H, CH_2Si), 1.22 (s, 9 H, CMe_3), 1.69, 1.73 (s, 12 H, C_5Me_4), 2.45, 2.60 (m, 1 H, C_5Me_4H), 3.06, 3.15 (br. s, 1 H, NH), 6.55 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, 2-, 6-C_6H_5), 7.12 (d, $^3J_{HH}$ = 11.6 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C NMR ([D$_6$]benzene): δ = –1, –0.8, –0.6 ($SiMe_2$), 11.3, 11.7, 11.8, 11.9, 12.6 (C_5Me_4), 14.7 (CH_2Si), 31.8 (CMe_3), 33.9 (CMe_3), 51.3, 51.8 ($C_5Me_4CH_2$, C attached to CH_2), 116.4 (2-,6-C_6H_5), 126.3 (3-, 5-C_6H_5), 132.8, 134.1, 134.5, 135.5, 137.1, 138.4, 138.9, 140.4, 140.5 ($C_5Me_4CH_2$, C attached to Me), 144.9 (1-C_6H_5) ppm. EI MS: *m*/*z* (%) = 341 (14) [M^+], 206 (49) [$SiMe_2NHC_6H_4CMe_3^+$], 192 (32) [$C_5Me_4CH_2SiMe_2^+$], 148 (11) [$NHC_6H_4CMe_3^+$], 134 (100) [$C_5Me_4CH_2^+$], 133 (71) [$C_6H_4CMe_3^+$], 120 (7) [$C_5Me_4^+$], 91 (65) [$NC_6H_5^+$], 77 (66) [$C_6H_5^+$]. $C_{22}H_{35}NSi$ (341.61): calcd. C 77.35, H 10.33, N 4.10; found C 78.56, H 10.48, N, 4.12.

$(C_5Me_4H)CH_2SiMe_2NHC_6H_4nBu$-4 (1c): A solution of [Li(NHC_6H_4nBu)] (2.328 g, 15 mmol) in thf (30 mL) was treated at –78 °C with a thf solution (30 mL) of $(C_5Me_4H)CH_2SiMe_2Cl$ (3.433 g, 15 mmol). After addition, the cold bath was removed, and the solution was warmed up to room temperature and stirred overnight. After removal of the solvent under vacuum, the residue was extracted with pentane (3×20 mL). The solvent was removed under vacuum, and the remaining oil distilled under reduced pressure (240 °C, 2×10^{-1} mbar) to afford **1c** (3.380 g, 66%) as a yellow oil. ^1H NMR ([D$_6$]benzene): δ = 0.19 (s, 6 H, $SiMe_2$), 0.87 (t, $^3J_{HH}$ = 7 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 0.97, 1.00 (d, $^2J_{HH}$ = 7.6 Hz, 2 H, CH_2Si), 1.29 (sextet, $^3J_{HH}$ = 7 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.61 (quintet, $^3J_{HH}$ = 7 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.74, 1.78 (s, 12 H, C_5Me_4), 2.50, 2.59 (m, 1 H, C_5Me_4H), 2.54 (t, $^3J_{HH}$ = 7 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 3.05, 3.14 (br. s, 1 H, NH), 6.58 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2-, 6-C_6H_5), 6.98 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, 3-, 5-C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): δ = –1.0, –0.8, –0.6 ($SiMe_2$), 11.3, 11.7, 11.8, 11.9, 12.6 (C_5Me_4), 14.2 ($CH_2CH_2CH_2CH_3$), 14.7 (CH_2Si), 22.6 ($CH_2CH_2CH_2CH_3$), 34.4 ($CH_2CH_2CH_2CH_3$), 35.2 ($CH_2CH_2CH_2CH_3$), 51.3, 51.8 ($C_5Me_4CH_2$, C attached to CH_2), 116.8 (2-, 6-C_6H_5), 129.4 (3-, 5-C_6H_5), 132.1, 132.8, 134.1, 134.5,

135.5, 137.1, 138.4, 138.9 ($C_5Me_4CH_2$, C attached to Me), 145.2 (1-C_6H_5) ppm. EI MS: *m*/*z* (%) = 341 (4) [M^+], 206 (27) [$SiMe_2NHC_6H_4(CH_2)_3CH_3^+$], 192 (6) [$C_5Me_4CH_2SiMe_2^+$], 148 (11) [$NHC_6H_4(CH_2)_3CH_3^+$), 134 (17) [$C_5Me_4CH_2^+$], 133 (71) [$C_6H_4(CH_2)_3CH_3^+$), 120 (54) [$C_5Me_4^+$], 91 (10) [$NC_6H_5^+$], 77 (23) [$C_6H_5^+$]. $C_{22}H_{35}NSi$ (341.61): calcd. C 77.35, H 10.33, N 4.10; found C 76.77, H 10.40, N 4.38.

[Y(η⁵-$C_5Me_4CH_2SiMe_2NPh$-κN)(CH_2SiMe_3)(thf)₂] (2a): A pentane suspension (40 mL) of [$Y(CH_2SiMe_3)_3(thf)_2$] (1210 mg, 2.4 mmol) was treated at –78 °C with a pentane solution (20 mL) of **1a** (686 mg, 2.4 mmol). After stirring for 2 h at this temperature, the solution was warmed up to 0 °C, whereupon a white precipitate appeared. The solvent was filtered off, and the solid dried under vacuum to afford **2a** (1040 mg, 72%) as a white solid. Crystals suitable for X-ray diffraction were obtained from a saturated toluene solution at –40 °C. ^{1}H NMR ([D$_6$]benzene): δ = –0.91 (d, $^2J_{YH}$ = 2.7 Hz, 2 H, YCH_2), 0.29 (s, 9 H, $SiMe_3$), 0.51 (s, 6 H, $SiMe_2$), 1.17 (br. s, 8 H, β-thf), 1.99 (s, 6 H, C_5Me_4), 2.12 (s, 6 H, C_5Me_4), 2.23 (s, 2 H, CH_2Si), 3.57 (br. s, 8 H, α-thf), 6.68 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, 4-C_6H_5), 6.78 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, 2-,6-C_6H_5), 7.20 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, 3-,5-C_6H_5) ppm. ^{1}H NMR ([D$_8$]toluene): δ = –0.97 (d, $^1J_{YH}$ = 2.76 Hz, 2 H, YCH_2), 0.23 (s, 9 H, $SiMe_3$), 0.47 (s, 6 H, $SiMe_2$), 1.25 (br. s, 8 H, β-thf), 1.98 (s, 6 H, C_5Me_4), 2.09 (s, 6 H, C_5Me_4), 2.18 (s, 2 H, CH_2Si), 3.56 (br. s, 8 H, α-thf), 6.65 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, 4-C_6H_5), 6.73 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 2-, 6-C_6H_5), 7.15 (t, $^3J_{HH}$ = 7.9 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{1}H NMR ([D$_8$]toluene, –70 °C): δ = –0.97 (br. s, 2 H, YCH_2), 0.43 (s, 9 H, $SiMe_3$), 0.65 (s, 6 H, $SiMe_2$), 0.96 (m, 2 H, β-thf), 1.05 (m, 2 H, β-thf), 1.89 (s, 6 H, C_5Me_4), 2.25 (s, 6 H, C_5Me_4), 2.31 (s, 2 H, CH_2Si), 3.53 (m, 2 H, α-thf), 3.81 (m, 4 H, α-thf), 6.53 (d, $^3J_{HH}$ = 6.7 Hz, 1 H, 2-C_6H_5), 6.70 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, 4-C_6H_5), 6.84 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, 6-C_6H_5), 7.22 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, 3-, 5-C_6H_5), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]-benzene): δ = 3.9 ($SiMe_2$), 4.8 ($SiMe_3$), 11.5 (C_5Me_4), 11.7 (C_5Me_4), 17.0 (CH_2Si), 24.4 (d, $^1J_{YC}$ = 40.3 Hz, YCH_2), 25.3 (β-thf), 70.3 (α-thf), 115.9 ($C_5Me_4CH_2$, C attached to Me), 116.1 ($C_5Me_4CH_2$, C attached to Me), 116.7 (4-C_6H_5), 119.6 (2-,6-C_6H_5), 123.6 ($C_5Me_4CH_2$, C attached to CH_2), 130.7 (3-,5-C_6H_5), 156.2 (1-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_8$]toluene): δ = 4.4 ($SiMe_2$), 5.2 ($SiMe_3$), 12.0 (C_5Me_4), 12.2 (C_5Me_4), 17.5 (CH_2Si), 24.9 (d, $^1J_{YC}$ = 43.6 Hz, YCH_2), 25.8 (β-thf), 70.7 (α-thf), 116.4 ($C_5Me_4CH_2$, C attached to Me), 116.6 ($C_5Me_4CH_2$, C attached to Me), 117.2 (4-C_6H_5), 120.1 (2-,6-C_6H_5), 124.1 ($C_5Me_4CH_2$, C attached to CH_2), 130.7 (3-, 5-C_6H_5), 156.6 (1-C_6H_5) ppm. $C_{30}H_{52}NO_2Si_2Y$ (603.82): calcd. C 59.67, H 8.68, N 2.32, Y 14.71; found C 58.78, H 8.65, N 2.87, Y 14.68.

[Y(η⁵-$C_5Me_4CH_2SiMe_2NC_6H_4t$Bu-4-κN)($CH_2SiMe_3$)(thf)₂] (2b): A pentane suspension (10 mL) of [$Y(CH_2SiMe_3)_3(thf)_2$] (527 mg, 1 mmol) was treated at –78 °C with a pentane solution (5 mL) of **1b** (342 mg, 1 mmol). After stirring for 2 h at this temperature, the solution was warmed up to 0 °C and stirred for a further 1 h. The volatiles were removed under vacuum to yield **2b** (393 mg, 61%) as a white powder. ^{1}H NMR ([D$_6$]benzene): δ = –0.86 (d, $^2J_{YH}$ = 2.89 Hz, 2 H, YCH_2), 0.30 (s, 9 H, $SiMe_3$), 0.53 (s, 6 H, $SiMe_2$), 1.17 (br. s, 8 H, β-thf), 1.27 (s, 9 H, CMe_3), 2.03 (s, 6 H, C_5Me_4), 2.12 (s, 6 H, C_5Me_4), 2.24 (s, 2 H, CH_2Si), 3.54 (br. s, 8 H, α-thf), 6.79 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2-, 6-C_6H_5), 7.25 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 4.1 ($SiMe_2$), 4.5 ($SiMe_3$), 11.5 (C_5Me_4), 11.6 (C_5Me_4), 16.9 (CH_2Si), 24.7 (d, $^1J_{YC}$ = 42.2 Hz, YCH_2), 25.2 (β-thf), 31.8 (CMe_3), 33.9 (CMe_3), 70.1 (α-thf), 115.9 ($C_5Me_4CH_2$, C attached to Me), 116.1 ($C_5Me_4CH_2$, C attached to Me), 120.0 (4-C_6H_4), 123.9 ($C_5Me_4CH_2$, C attached to CH_2), 126.9 (2-, 6-C_6H_4), 128.3 (3-, 5-C_6H_4), 152.2 (1-C_6H_4) ppm. $C_{34}H_{60}NO_2Si_2Y$ (659.93): calcd. C 61.88, H 9.16, N 2.12, Y 13.47; found C 61.13, H 10.36, N 2.19, Y 13.44.

[Y(η⁵-$C_5Me_4CH_2SiMe_2NC_6H_4n$Bu-4-κN)($CH_2SiMe_3$)(thf)₂] (2c): A –78 °C cold pentane suspension (10 mL) of [$Y(CH_2SiMe_3)_3(thf)_2$] (319 mg, 0.6 mmol) was treated with a pentane solution (8 mL) of **1c** (205 mg, 0.6 mmol). After stirring for 2 h at this temperature, the solution was warmed up to 0 °C and stirred for a further 1 h. The volatiles were removed under vacuum to yield **2c** (279 mg, 71%) as a pale yellow powder. ^{1}H NMR ([D$_6$]benzene): δ = –0.81 (d, $^2J_{YH}$ = 3.0 Hz, 2 H, YCH_2), 0.31 (s, 9 H, $SiMe_3$), 0.53 (s, 6 H, $SiMe_2$), 0.85 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.18 (br. s, 8 H, β-thf), 1.26 (sextet, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.52 (quintet, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 2.06 (s, 6 H, C_5Me_4), 2.11 (s, 6 H, C_5Me_4), 2.25 (s, 2 H, CH_2Si), 2.48 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 3.49 (br. s, 8 H, α-thf), 6.83 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2-, 6-C_6H_5), 7.06 (d, $^3J_{HH}$ = 8.3 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 4.1 ($SiMe_2$), 4.8 ($SiMe_3$), 11.5 (C_5Me_4), 11.6 (C_5Me_4), 14.1 ($CH_2CH_2CH_2CH_3$), 16.8 (CH_2Si), 22.6 ($CH_2CH_2CH_2CH_3$), 25.3 (d, $^1J_{YC}$ = 43.2 Hz, YCH_2), 25.2 (β-thf), 34.5 ($CH_2CH_2CH_2CH_3$), 35.2 ($CH_2CH_2CH_2CH_3$), 69.8 (α-thf), 115.8 ($C_5Me_4CH_2$, C attached to Me), 116.3 ($C_5Me_4CH_2$, C attached to Me), 121.3 (4-C_6H_4), 124.1 ($C_5Me_4CH_2$, C attached to CH_2), 128.6 (2-, 6-C_6H_4), 130.2 (3-, 5-C_6H_4), 151.8 (1-C_6H_4) ppm. $C_{34}H_{60}NO_2Si_2Y$ (659.93): calcd. C 61.88, H 9.16, N 2.12, Y 13.47; found C 61.62, H 9.44, N 2.42, Y 13.52.

[Lu(η⁵-$C_5Me_4CH_2SiMe_2NPh$-κN)(CH_2SiMe_3)(thf)₂] (3a): A pentane suspension (15 mL) of [$Lu(CH_2SiMe_3)_3(thf)_2$] (356 mg, 0.6 mmol) was treated at –78 °C with a pentane solution (5 mL) of **1a** (171 mg, 0.6 mmol). After stirring for 30 min at this temperature, the solution was warmed up to 0 °C, upon which a white precipitate appeared. The solvent was filtered off, and the solid dried under vacuum to afford **3a** (230 mg, 56%) as a white powder. ^{1}H NMR ([D$_6$]benzene): δ = –0.84 (s, 2 H, $LuCH_2$), 0.26 (s, 9 H, $SiMe_3$), 0.42 (s, 6 H, $SiMe_2$), 1.17 (br. s, 8 H, β-thf), 2.06 (s, 6 H, C_5Me_4), 2.12 (s, 6 H, C_5Me_4), 2.22 (s, 2 H, CH_2Si), 3.43 (br. s, 8 H, α-thf), 6.76 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, 4-C_6H_5), 6.93 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, 2-, 6-C_6H_5), 7.15 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 4.2 ($SiMe_2$), 4.8 ($SiMe_3$), 11.4 (C_5Me_4), 11.5 (C_5Me_4), 16.3 (CH_2Si), 31.3 (s, $LuCH_2$), 25.5 (β-thf), 69.0 (α-thf), 115.3 ($C_5Me_4CH_2$, C attached to Me), 115.7 ($C_5Me_4CH_2$, C attached to Me), 119.0 (4-C_6H_5), 122.9 ($C_5Me_4CH_2$, C attached to CH_2), 123.9 (2-, 6-C_6H_5), 129.5 (3-,5-C_6H_5), 153.6 (1-C_6H_5) ppm. $C_{30}H_{52}LuNO_2Si_2$ (689.89): calcd. C 52.23, H 7.60, N 2.03, Lu 25.36; found C 49.28, H 7.60, N 3.10, Lu 24.94.

[Lu(η⁵-$C_5Me_4CH_2SiMe_2NC_6H_4t$Bu-4-κN)($CH_2SiMe_3$)(thf)$_{1.5}$] (3b): A pentane suspension (10 mL) of [$Lu(CH_2SiMe_3)_3(thf)_2$] (349 mg, 0.6 mmol) was treated at –78 °C with a pentane solution (5 mL) of **1b** (205 mg, 1 mmol). After stirring for 2 h at this temperature, the solution was warmed to 0 °C and stirred for a further 1 h. Reducing the volume of the solvent under vacuum resulted in the formation of a white solid that was filtered to afford, after drying, **3b** (338 mg, 63%). ^{1}H NMR ([D$_6$]benzene): δ = –0.82 (s, 2 H, $LuCH_2$), 0.25 (s, 9 H, $SiMe_3$), 0.43 (s, 6 H, $SiMe_2$), 1.07 (br. s, 6 H, β-thf), 1.25 (s, 9 H, CMe_3), 2.07 (s, 6 H, C_5Me_4), 2.15 (s, 6 H, C_5Me_4), 2.23 (s, 2 H, CH_2Si), 3.39 (br. s, 6 H, α-thf), 6.91 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, 2-, 6-C_6H_5), 7.21 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 4.3 ($SiMe_2$), 4.8 ($SiMe_3$), 11.4 (C_5Me_4), 11.6 (C_5Me_4), 16.3 (CH_2Si), 25.0 (β-thf), 31.4 ($LuCH_2$), 31.8 (CMe_3), 34.0 (CMe_3), 70.5 (α-thf), 115.2 ($C_5Me_4CH_2$, C attached

to Me), 115.7 ($C_5Me_4CH_2$, C attached to Me), 123.1 ($C_5Me_4CH_2$, C attached to CH_2), 124.0 (2-, 6-C_6H_4), 126.3 (3-, 5-C_6H_4), 141.7 (4-C_6H_4), 150.0 (1-C_6H_4) ppm. $C_{32}H_{56}LuNO_{1.5}Si_2$ (709.94): calcd. C 54.14, H 7.95, N 1.97, Lu 24.64; found C 52.18, H 7.72, N 2.37, Lu 24.88.

[Lu(η^5-$C_5Me_4CH_2SiMe_2NC_6H_4$*n*Bu-4κN)(CH_2SiMe_3)(thf)$_{1.5}$] (3c): A pentane suspension (10 mL) of [Lu(CH_2SiMe_3)$_3$(thf)$_2$] (349 mg, 0.6 mmol) was treated at –78 °C with a pentane solution (8 mL) of **1c** (205 mg, 0.6 mmol). After stirring for 2 h at this temperature, the solution was warmed to 0 °C and stirred for a further 1 h. The solvent was removed under vacuum to afford **3c** as a colorless oil (290 mg, 65%). ^{1}H NMR ([D$_6$]benzene): δ = –0.88 (s, 2 H, $LuCH_2$), 0.23 (s, 9 H, $SiMe_3$), 0.40 (s, 6 H, $SiMe_2$), 0.86 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.09 (br. s, 6 H, β-thf), 1.25 (sextet, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.49 (quintet, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 2.06 (s, 6 H, C_5Me_4), 2.13 (s, 6 H, C_5Me_4), 2.20 (s, 2 H, CH_2Si), 2.47 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 3.38 (br. s, 6 H, α-thf), 6.86 (d, $^3J_{HH}$ = 8.50 Hz, 2 H, 2-, 6-C_6H_5), 6.99 (d, $^3J_{HH}$ = 8.30 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 4.2 ($SiMe_2$), 4.8 ($SiMe_3$), 11.4 (C_5Me_4), 11.6 (C_5Me_4), 14.2 ($CH_2CH_2CH_2CH_3$), 16.3 (CH_2Si), 22.6 ($CH_2CH_2CH_2CH_3$), 25.0 (β-thf), 31.2 ($LuCH_2$), 34.5 ($CH_2CH_2CH_2CH_3$), 35.3 ($CH_2CH_2CH_2CH_3$), 70.9 (α-thf), 115.2 ($C_5Me_4CH_2$, C attached to Me), 115.7 ($C_5Me_4CH_2$, C attached to Me), 123.0 ($C_5Me_4CH_2$, C attached to CH_2), 124.4 (2-, 6-C_6H_4), 129.4 (3-, 5-C_6H_4), 133.5 (4-C_6H_4), 150.3 (1C_6H_4) ppm. $C_{32}H_{56}LuNO_{1.5}Si_2$ (709.94): calcd. C 54.14, H 7.95, N 1.97, Lu 24.64; found C 51.45, H 7.72, N 2.56, Lu 24.14.

[Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(C≡C*t*Bu)(thf)$_x$] (4a): A toluene solution (6 mL) of **2a** (95 mg, 0.157 mmol) was treated at room temperature with *tert*-butylacetylene (0.1 mL, 1.2 mmol) and stirred for 2 h at room temperature. Reducing the volume of solvent under vacuum and cooling to –30 °C afforded a colorless crystalline material. In addition to the signals arising from **4a**, a second set of signals was observed, which was attributed to the donor-free dimeric species [Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(C≡C*t*Bu)]$_2$ (**7a**). Signals assigned to **4a**: ^{1}H NMR ([D$_6$]benzene): δ = 0.42 (s, 6 H, $SiMe_2$), 1.12 (s, 9 H, CMe_3), 1.29 (br. s, β-thf), 1.90 (br. s, 6 H, C_5Me_4), 2.18 (br. s, 6 H, C_5Me_4), 2.26 (s, 2 H, CH_2Si), 3.83 (br. s, α-thf), 6.96 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, 4-C_6H_5), 7.05 (br.d, $^3J_{HH}$ = 8.4 Hz, 2 H, 2-, 6-C_6H_5), 7.25 (br. t, $^3J_{HH}$ = 8.0 Hz, 2 H, 3-, 5-C_6H_5) ppm.

[Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(CH_2SiMe_3)(py)$_2$] (2a-py): An NMR tube was charged with **2a** (20 mg, 0.033 mmol). [D$_6$]benzene (0.5 mL) and pyridine (0.03 mL, 0.374 mmol) were subsequently added at room temperature, and the spectrum recorded immediately. ^{1}H NMR ([D$_6$]benzene): δ = –0.59 (d, $^1J_{YH}$ = 2.2 Hz, 2 H, YCH_2), 0.00 (s, 9 H, $SiMe_3$), 0.70 (s, 6 H, $SiMe_2$), 1.38 (s, 6 H, C_5Me_4), 2.19 (s, 2 H, CH_2Si), 2.24 (s, 6 H, C_5Me_4), 6.52 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, 4-C_6H_5), 6.87 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 2-, 6-C_6H_5), 7.15 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]-benzene): δ = 3.7 ($SiMe_2$), 4.2 ($SiMe_3$), 11.3 (C_5Me_4), 12.0 (C_5Me_4), 17.2 (CH_2Si), 26.4 (d, $^1J_{YC}$ = 35.3 Hz, YCH_2), 115.3 ($C_5Me_4CH_2$, C attached to Me), 115.4 ($C_5Me_4CH_2$, C attached to Me), 116.3 (4-C_6H_5), 118.9 (2-, 6-C_6H_5), 123.9 ($C_5Me_4CH_2$, C attached to CH_2), 130.3 (3-, 5-C_6H_5), 158.1 (1-C_6H_5) ppm.

[Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(μ-H)(thf)]$_2$ (5a): Complex **2a** (815 mg, 1.3 mmol) was dissolved in toluene (30 mL) in a thick-walled glass reactor and exposed to 4 bar of H_2. After stirring the mixture for 16 h, a white solid formed. Decanting off the supernatant, washing the remaining solid with pentane (2 × 5 mL), and drying under vacuum yielded **5a** (425 mg, 71%) as a white powder. ^{1}H NMR ([D$_8$]thf): δ = –0.04 (br. s, 6 H, $SiMe_2$), 1.64 (br. s, 4 H, β-thf), 1.78 (s, 6 H, C_5Me_4), 1.87 (s, 2 H, CH_2Si), 2.02 (s, 6 H, C_5Me_4), 3.50 (br. s, 4 H, α-thf), 5.10 (t, $^1J_{YH}$ = 28.4 Hz, 1 H, YH), 6.56 (m, 3 H, 2-, 4-, 6-C_6H_5), 6.86 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, 3-, 5-C_6H_5) ppm. $C_{44}H_{68}N_2O_2Si_2Y_2$ (891.02): calcd. C 59.31, H 7.69, N 3.14, Y 19.96; found C 58.93, H 8.06, N 2.93, Y 19.22.

[Y(η^5-$C_5Me_4CH_2SiMe_2NC_6H_4$*t*Bu-4-κN)(μ-H)(thf)]$_2$ (5b): Complex **2b** (486 mg, 0.75 mmol) was dissolved in pentane (8 mL) in a thick-walled glass reactor and exposed to 4 bar of H_2. After stirring for the mixture 16 h, a white solid formed. Decanting off the supernatant, washing the remaining solid with pentane (2 × 5 mL), and drying under vacuum yielded **5b** (158 mg, 42%) as a white solid. Crystals suitable for X-ray diffraction were obtained as follows: complex **2b** was dissolved in a pentane/thf mixture in a Schlenk tube; the solution was layered with pure pentane, and a pentane solution of phenylsilane (5 equivalents) was slowly added. Crystals appeared after 3 d at 6 °C. ^{1}H NMR ([D$_8$]thf, 60 °C): δ = 0.00 (br. s, 6 H, $SiMe_2$), 1.26 (br. s, 9 H, CMe_3), 1.73 (br. s, 4 H, β-thf), 1.77 (s, 6 H, C_5Me_4), 1.94 (s, 2 H, CH_2Si), 2.02 (s, 6 H, C_5Me_4), 3.58 (br. s, 4 H, α-thf), 5.10 (t, $^1J_{YH}$ = 29.9 Hz, 1 H, YH), 6.58 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, 2-, 6-C_6H_4), 7.08 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, 3-, 5-C_6H_5) ppm. $C_{52}H_{84}N_2O_2Si_2Y_2$ (1003.23): calcd. C 62.26, H 8.44, N 2.79, Y 17.72; found C 59.96, H 8.38, N 2.80, Y 17.12.

[Y(η^5-$C_5Me_4CH_2SiMe_2NC_5H_4$*n*Bu-4-κN)(μ-H)(thf)]$_2$ (5c): Complex **2c** (396 mg, 0.6 mmol) was dissolved in pentane (10 mL) in a thick-walled glass reactor and exposed to 4 bar of H_2. After stirring the mixture for 16 h, a white solid formed. Decanting off the supernatant, washing the remaining solid with pentane (2 × 5 mL), and drying under vacuum yielded **5c** (110 mg, 36%) as a white solid. ^{1}H NMR ([D$_8$]thf): δ = 0.02 (s, 6 H, $SiMe_2$), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.32 (sextet, $^3J_{HH}$ = 7.1 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.53 (quintet, $^3J_{HH}$ = 7.1 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.77 (br. s, 4 H, thf), 1.77 (s, 6 H, C_5Me_4), 1.93 (s, 2 H, CH_2Si), 2.02 (s, 6 H, C_5Me_4), 2.46 (t, $^3J_{HH}$ = 7.1 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 3.59 (br. s, 4 H, thf), 5.11 (t, $^1J_{YH}$ = 29.9 Hz, 1 H, YH), 6.59 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 2-, 6-C_6H_4), 6.83 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = 4.1 ($SiMe_2$), 4.8 ($SiMe_3$), 11.5 (C_5Me_4), 11.6 (C_5Me_4), 14.2 ($CH_2CH_2CH_2CH_3$), 16.2 (CH_2Si), 22.8 ($CH_2CH_2CH_2CH_3$), 25.2 (β-thf), 34.6 ($CH_2CH_2CH_2CH_3$), 35.5 ($CH_2CH_2CH_2CH_3$), 72.4 (α-thf), 115.8 ($C_5Me_4CH_2$, C attached to Me), 116.3 ($C_5Me_4CH_2$, C attached to Me), 121.3 (4-C_6H_4), 124.1 ($C_5Me_4CH_2$, C attached to CH_2), 128.6 (2-, 6-C_6H_4), 130.2 (3-, 5-C_6H_4) ppm. $C_{52}H_{84}N_2O_2Si_2Y_2$ (1003.23): calcd. C 62.26, H 8.44, N 2.79, Y 17.72; found C 59.92, H 8.04, N 2.81, Y 18.07.

[Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(η^1-NC_5H_6)(py)$_2$] (6a): Complex **5a** (116 mg, 0.130 mmol) was dissolved in pyridine (5 mL), and the clear orange-red solution was stirred for 2 h at room temperature. After partial removal of the solvent and cooling the solution to –30 °C overnight, **6a** (131 mg, 83%) could be obtained as yellow crystals suitable for X-ray diffraction analysis. ^{1}H NMR ([D$_8$]thf): δ = 0.41 (s, 6 H, $SiMe_2$), 1.75 (br. s, 6 H, C_5Me_4), 1.97 (s, 2 H, CH_2Si), 2.05 (s, 6 H, C_5Me_4), 3.63 (d, $^3J_{HH}$ = 4.0 Hz, 2 H, 2-NC_5H_6), 4.40 (m, 1 H, 5-NC_5H_6), 4.75 (m, 1 H, 3-NC_5H_6), 5.74 (dd, $^3J_{HH}$ = 4.0, $^3J_{HH}$ = 6.0 Hz, 1 H, 4-NC_5H_6), 6.39 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, 4-C_6H_5), 6.52 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2-, 6-C_6H_5), 6.81 (d, $^3J_{HH}$ = 6.0 Hz, 1 H, 6-NC_5H_6), 6.93 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, 3-, 5-C_6H_5), 7.28 (m, 4 H, 3-, 5-NC_5H_5), 7.70 (m, 2 H, 4-NC_5H_5), 8.56 (m, 4 H, 2-, 6-NC_5H_5) ppm. ^{13}C{^{1}H} NMR ([D$_8$]-thf): δ = 4.2 ($SiMe_2$), 11.4 (C_5Me_4), 11.6 (C_5Me_4), 17.6 (CH_2Si), 48.4 (6-NC_5H_6), 96.1 (3-NC_5H_6), 99.3 (5-NC_5H_6), 115.9 ($C_5Me_4CH_2$, C attached to Me), 116.4 ($C_5Me_4CH_2$, C attached to

Table 2. Crystallographic and data collection parameters for compounds **2a**, **5b**, **6a**, and **7a**.

Compound	**2a**	**5b**	**6a**	**7a**
Empirical formula	$C_{30}H_{52}NO_2Si_2Y{\cdot}0.5(C_7H_8)$	$C_{57}H_{96}N_2O_2Si_2Y_2{\cdot}C_5H_{12}$	$C_{33}H_{41}N_4SiY$	$C_{48}H_{68}N_2Si_2Y_2$
M_r [g mol^{-1}]	649.90	1147.54	610.71	907.04
Crystal size	0.30 × 0.20 × 0.20	0.50 × 0.23 × 0.20	0.50 × 0.50 × 0.20	0.50 × 0.40 × 0.30
Crystal color and habit	Colorless block	Colorless rod	Yellow fragment	Colorless fragment
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	P*bca*	$P2_1/n$
a [Å]	11.018(5)	13.226(2)	16.74(2)	13.7548(19)
b [Å]	20.847(10)	16.402(3)	19.045(6)	12.4306(17)
c [Å]	15.424(7)	15.960(2)	19.741(15)	14.693(2)
α [°]	90	90	90	90
β [°]	95.77(2)	114.184(4)	90	111.536(3)
γ [°]	90	90	90	90
V [Å^3]	3525(3)	3158.4(8)	6294(9)	2336.8(6)
Z	4	4/2	8	4/2
$D_{calcd.}$ [g cm^{-3}]	1.225	1.207	1.289	1.289
T (K)	110(2)	120(2)	243(2)	273(2)
μ(Mo-K_α) [mm^{-1}]	1.750	1.906	1.919	2.555
F(000)	1388	1232	2559	952
θ Range [°]	2.36–25.12	1.69–26.07	3.19–26.01	1.74–27.14
Number of reflections collected	46746	20835	17565	29041
Number of reflections observed [$I > 2\sigma(I)$]	3177	4314	3355	4192
Number of independent reflections (R_{int})	6235 (0.3167)	6246 (0.0531)	6180 (0.1292)	5142 (0.0732)
Data/restraints/parameters	6235/0/363	6246/21/332	6180/0/358	5142/0/253
Goodness-of-fit on F^2	1.000	1.024	0.993	0.959
R_1, wR_2 [$I > 2\sigma(I)$]	0.0724, 0.1366	0.0463, 0.1127	0.0670, 0.1377	0.0286, 0.0722
R_1, wR_2 (all data)	0.1725, 0.1726	0.0809, 0.1274	0.1457, 0.1705	0.0368, 0.0737
Largest difference in peak and hole [e Å^{-3}]	0.650 and –0.474	1.131 and –0.320	1.326 and –0.865	0.902 and –0.449

Me), 116.8 (4-C_6H_5), 118.9 (2-, 6-C_6H_5), 124.7 (3-, 5-NC_5H_5), 125.1 ($C_5Me_4CH_2$, C attached to CH_2), 127.7 (4-NC_5H_6), 130.3 (3-, 5-C_6H_5), 137.1 (4-NC_5H_5), 147.4 (2-NC_5H_6), 151.3 (2-, 6-NC_5H_5), 157.3 (1-C_6H_5) ppm. $C_{33}H_{39}N_4SiY$ (608.70): calcd. C 65.12, H 6.46, N 9.20, Y 14.61; found C 64.80, H 6.29, N 9.12, Y 14.27.

[Y(η^5-$C_5Me_4CH_2SiMe_2NPh$-κN)(C≡C*t*Bu)]$_2$ (7a): A toluene suspension (15 mL) of complex **5a** (150 mg, 0.168 mmol) was treated with *tert*-butylacetylene (0.205 mL, 1.7 mmol) at 0 °C. After stirring the mixture for 2 h, the solvent was partly removed under vacuum. Cooling the mixture overnight to –30 °C afforded **7a** (135 mg, 89%) as colorless crystals suitable for X-ray diffraction. ^{1}H NMR ([D$_6$]benzene): δ = 0.57 (s, 6 H, $SiMe_2$), 1.33 (s, 9 H, CMe_3), 2.01 (s, 6 H, C_5Me_4), 2.29 (s, 2 H, CH_2Si), 2.36 (s, 6 H, C_5Me_4), 6.54 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, 4-C_6H_5), 6.60 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, 2-, 6-C_6H_5), 7.05 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, 3-, 5-C_6H_5) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 3.7 ($SiMe_2$), 11.5 (C_5Me_4), 11.9 (C_5Me_4), 17.4 (CH_2Si), 28.3 (CMe_3), 32.8 (CMe_3), 115.0 (4-C_6H_5), 115.9 ($C_5Me_4CH_2$, C attached to Me), 116.3 (d, $^2J_{YC}$ = 10.7 Hz, YC≡*C*), 117.0 ($C_5Me_4CH_2$, C attached to Me), 117.1 (2-, 6-C_6H_5), 123.0 ($C_5Me_4CH_2$, C attached to CH_2), 129.5 (d, $^1J_{YC}$ = 53.5 Hz, Y*C*≡C), 129.9 (3-, 5-C_6H_5), 157.7 (1-C_6H_5) ppm. $C_{48}H_{64}N_2Si_2Y_2$ (903.03): calcd. C 63.84, H 7.14, N 3.10, Y 19.69; found C 64.01, H 7.30, N 2.96, Y 19.43.

X-ray Crystal Structure Determination of 2a, 5b, 6a, and 7a: Relevant crystallographic data for **2a**, **5b**, **6a**, and **7a** are summarized in Table 2. The data collections were carried out on a Bruker AXS diffractometer (for **2a**, **5b**, and **7a**), and the program system SMART[25] was used for the data corrections as well as for the absorption correction. The data collection for **6a** was carried out using an Enraf NONIUS CAD4 diffractometer, and the absorption correction was carried out using ψ-scans.[26] The structures were solved by direct methods (SHELXS-86).[27] All non-hydrogen-atoms were refined with anisotropic displacement parameters. From the measured reflections, all independent reflections were used in the refinement by full-matrix least-squares against all F_o^2 data (SHELXL-97).[28] Compounds **2a** and **5b** contain cocrystallized disordered solvent molecules in the lattice. The hydrogen atoms are included in calculated positions. The position of the hydrogen atom of the Y_2H_2 core unit of **5b** was localized in a Fourier difference map and was not refined in its position. For the graphical representation, the program ORTEP-III was used as implemented in the program system WINGX.[29] CCDC-679422 (**2a**), -679423 (**5b**), -679424 (**6a**), and -679425 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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