# Di- and Trivalent Ytterbium Complexes Containing Linked Amino- and Amidocyclopentadienyl Ligands

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**Keywords:** Ytterbium / Chelates / Metallocenes / Cyclopentadienyl ligands

Reactions of the aminocyclopentadienes $(C_5Me_4H)SiMe_2NHR$ (R = Et, allyl, *n*Pr, *t*Bu) with $[YbI_2(THF)_2]$ in the presence of two equivalents of potassium 1,2-diphenylethenide in THF at room temperature gave the diamagnetic half-sandwich complexes $[Yb(\eta^5\text{-}C_5Me_4SiMe_2NHR)L_n(\mu\text{-}I)]_2$ (L = THF, *n* = 2, L = DME, *n* = 1). The *tert*-butylamido derivative $[Yb(\eta^5\text{-}C_5Me_4SiMe_2NHtBu)(THF)_2(\mu\text{-}I)]_2$ was characterized by X-ray structural analysis as a dinuclear complex containing a nonchelating aminocyclopentadienyl ligand. Deprotonation of the aminocyclopentadiene $(C_5H_4tBu)SiMe_2NHtBu$ with two equivalents of potassium 1,2-diphenylethenide in THF, followed by reaction with $[YbI_2(THF)_2]$ at 60 °C, gave the trivalent ytterbium ate complex $[K(DME)][Yb\{(\eta^5{:}\eta^1\text{-}C_5H_3tBu\text{-}3)SiMe_2NtBu\}_2]$. A single crystal X-ray diffraction study of this complex shows polymeric chains consisting of trivalent ytterbocene units with two chelating amidocyclopentadienyl ligands coordinated to potassium ions. Metalation of the aminoindene $(C_9H_7)SiMe_2NHtBu$ under the same conditions and treatment with $[YbI_2(THF)_2]$ in THF at ambient temperature resulted in the formation of the divalent ytterbocene complex $[Yb\{\eta^5\text{-}(1\text{-}C_9H_6)SiMe_2NHtBu\}_2(THF)_2]$. The reaction of ytterbium naphthalenide $[Yb(C_{10}H_8)(THF)_2]$ with one equivalent of $(C_9H_7)SiMe_2NHtBu$ afforded the bis(indenyl) compound which was isolated as its 2,2′-bipyridyl adduct $[Yb\{\eta^5\text{-}(1\text{-}C_9H_6)SiMe_2NHtBu\}_2(bipy)]$. It was shown by single-crystal structural analysis to exhibit a bent metallocene structure with noncoordinating amino side-chains. The reaction of $(C_5Me_4H)CH_2SiMe_2NHtBu$, which contains a longer $CH_2SiMe_2$ bridge, with $[Yb(C_{10}H_8)(THF)_2]$ gave the complex $[Li_{0.5}][Yb(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NtBu)(THF)_2(\mu\text{-}I)_{0.5}]$. Single crystal X-ray structure analysis revealed the presence of polymeric chains consisting of dinuclear iodo-bridged $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NtBu)]$ units with a chelating linked amidocyclopentadienyl ligand, intermolecularly bridged by lithium ions. The lithium ions are bonded in an $\eta^5$-manner to both units, forming a lithocene structure. When $YbCl_3$ was reacted with $Li_2[(C_5H_3tBu\text{-}3)SiMe_2NCH_2CH_2X]$ (X = $NMe_2$, OMe), heterobimetallic complexes $Li[Yb\{(\eta^5{:}\eta^1\text{-}C_5H_3tBu\text{-}3)SiMe_2NCH_2CH_2X\}_2]$ with a helical metallocene structure were isolated. The single crystal structure analysis of one of the three possible diastereomers of $Li\{Yb[(\eta^5{:}\eta^1\text{-}C_5H_3tBu\text{-}3)SiMe_2NCH_2CH_2NMe_2]_2\}$, viz. the thermodynamically stable (*R*,*R*)/(*S*,*S*) epimer was performed. When $YbCl_3$ was reacted with one equivalent of $Li_2[(C_5H_3tBu\text{-}3)SiMe_2NCH_2CH_2NMe_2]$ and reduced "in situ" with one equivalent of sodium 1,2-diphenylethenide in THF, the ytterbium(II) metallocene complex $[Li(THF)]_2[Yb\{(\eta^5\text{-}C_5H_3tBu\text{-}3)\text{-}SiMe_2NH(CH_2CH_2NMe_2)\}_2(\mu\text{-}Cl)_2]$ was isolated, which exhibits a structure with the two amino functions coordinating to the lithium ions and the chloro ligands bridging both the lithium and ytterbium centers.



## Introduction

In contrast to the organometallic chemistry of divalent samarium,[1] that of divalent ytterbium is less developed.[2] In the context of developing lanthanide complexes supported by a linked amidocyclopentadienyl ligand,[3] we have started to explore the synthetic access to complexes of divalent ytterbium. Ytterbium(II) is diamagnetic, thus amenable to NMR spectroscopy, and its large ionic radius (1.02 Å, coordination number 6[4]) should allow coordination of the $SiMe_2$-linked amidocyclopentadienyl ligand for the larger lanthanides.[5] The tendency of divalent ytterbium complexes to undergo facile ligand-exchange reactions in solution to form homoleptic derivatives[6] makes linked amidocyclopentadienyl ligands an attractive ligand system that provides access to half-sandwich-type ytterbium(II) derivatives.[2c] We describe here our attempts at coordinating a linked amidocyclopentadienyl ligand to a divalent ytterbium center. During the course of our work, Hou et al. have independently reported the synthesis of linked anilidocyclopentadienyl lanthanide(II) complexes $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NPh)(THF)_n]$ (Ln = Sm, Yb, *n* = 0−3) and $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NPh)(THF)]_2$ by the amine elimination reaction of $[Ln\{N(SiMe_3)_2\}_2(THF)_2]$ and $(C_5Me_4H)SiMe_2NHPh$.[7]

## Results and Discussion

In order to prepare complexes of divalent ytterbium containing a linked amidocyclopentadienyl ligand, the meta-

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thesis of the dilithium derivatives $Li_2(C_5Me_4SiMe_2NtBu)$ and $Li_2[(C_5H_3tBu\text{-}3)SiMe_2NCH_2CH_2NMe_2]$ with $[YbI_2(THF)_2]$ in THF or toluene was first explored, but no tractable products could be isolated. Moreover, all attempts to prepare dipotassium derivatives of the ligand system,[8] for example by exchange reaction of the dilithium derivatives with two equivalents of KO*t*Bu in hexane or toluene, were also unsuccessful. The complete double metalation of the aminocyclopentadienes $(C_5Me_4H)SiMe_2NHR$ (R = Et, allyl, *n*Pr, *t*Bu) was achieved by reaction with two equivalents of potassium 1,2-diphenylethenide in THF at room temperature, as indicated by the disappearance of the characteristic color of the radical anion $[PhCHCHPh]^{\cdot -}$ upon addition of the aminocyclopentadiene. When these "in-situ" prepared dipotassium derivatives were reacted with $[YbI_2(THF)_2]$ in THF, the half-sandwich iodide complexes $[Yb(\eta^5\text{-}C_5Me_4SiMe_2NHR)L_n(\mu\text{-}I)]_2$ (**1**, R = *t*Bu, L = THF, *n* = 2; **2**, R = *n*Pr, L = THF, *n* = 2; **3,** R = Et, L = DME, *n* = 1; **4,** R = allyl, L = DME, *n* = 1) were obtained in good yields as yellow to orange crystals, after filtration and recrystallization from THF/hexane or DME.

The diamagnetic[9] complexes **1**–**4** are soluble in THF, DME, and pyridine, but insoluble in aliphatic and aromatic hydrocarbons. Bright-yellow crystals of **1** suitable for X-ray diffraction analysis were obtained by cooling a concentrated THF/hexane solution to 0 °C. An ORTEP diagram of the structure of **1** is shown in Figure 1. The crystal and structure refinement data are compiled in Table 1. The crystal structure determination revealed **1** to be a centrosymmetric iodo-bridged dimer with *trans*-disposed aminocyclopentadienyl ligands, similar to the structure adopted by its pentamethylcyclopentadienyl analogue $[Yb(\eta^5\text{-}C_5Me_5)(THF)_2(\mu\text{-}I)]_2$.[10] Each ytterbium center is coordinated to an $\eta^5$-cyclopentadienyl ring, two bridging iodides and two THF ligands. The pendant amino groups are not coordinated. The value of the Yb-$Cp_{Cent}$ distance in **1** [2.412(6) Å]

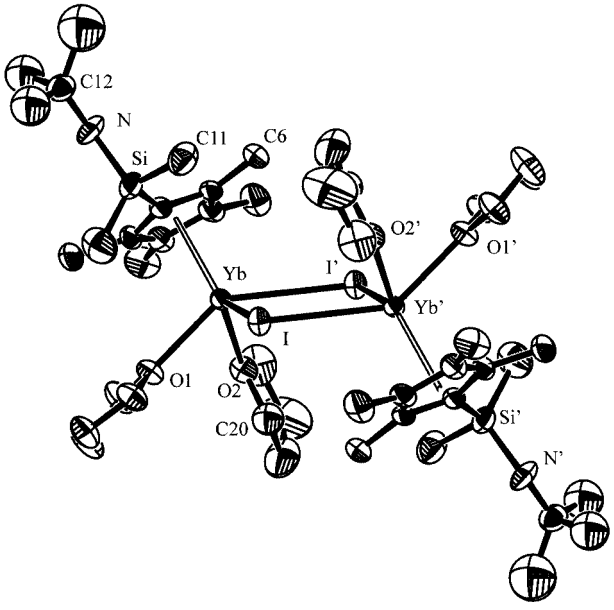


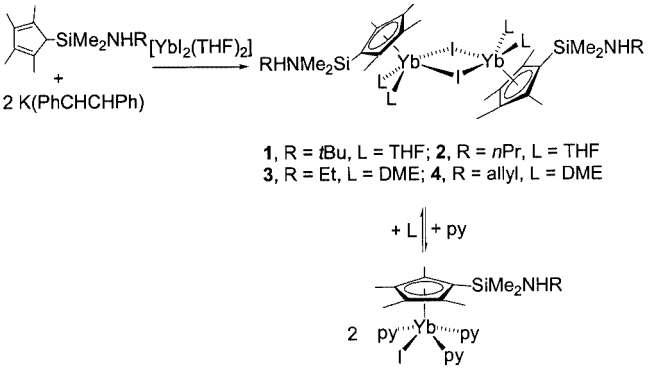

Figure 1. ORTEP drawing and numbering scheme of the molecular structure of **1** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms are omitted for the sake of clarity; selected bond lengths (Å) and bond angles (°): Yb–O2 2.434(5), Yb–O1 2.486(4), Yb-C2 2.664(6), Yb–C3 2.680(6), Yb–C1 2.681(7), Yb–C4 2.722(6), Yb–C5 2.723(7), Yb–$Cp_{cent}$ 2.412(6), Yb–I 3.0985(5), Yb–I′ 3.3008(5); O2–Yb–O1 75.3(2), O2–Yb–I 116.9(1), O1–Yb–I 88.1(1), O2–Yb–I′ 77.5(1), O1–Yb–I′ 140.8(1), I–Yb–I′ 79.69(1)

Table 1. Crystallographic and refinement parameters for complexes **1**, **5**, and **7**

| Compound | **1** | **5** | **7** |
|---|---|---|---|
| Chemical formula | $C_{23}H_{43}INO_2SiYb$ | $C_{34}H_{64}KN_2O_2Si_2Yb$ | $C_{40}H_{52}N_4Si_2Yb$ |
| $M$ [g mol$^{-1}$] | 693.61 | 801.19 | 818.08 |
| Crystal system | triclinic | orthorhombic | orthorhombic |
| Space group | $P\bar{1}$ (No. 2) | *Pccn* (No. 56) | $P2_12_12_1$ (No.19) |
| Crystal size [mm] | 0.65 × 0.55 ×0.53 | 1.10 × 0.70 × 0.29 | 0.88 × 0.62 × 0.48 |
| $a$ [Å] | 9.1196(4) | 9.5770(7) | 12.586(1) |
| $b$ [Å] | 10.6554(9) | 19.1900(10) | 17.388(1) |
| $c$ [Å] | 15.370(1) | 22.372(2) | 18.831(2) |
| α [deg] | 92.542(6) | 90 | 90 |
| β [deg] | 105.143(4) | 90 | 90 |
| γ [deg] | 99.724(5) | 90 | 90 |
| $V$ [Å$^3$] | 1414.8(2) | 4111.6(5) | 4121.1(6) |
| Z | 2 | 4 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.628 | 1.294 | 1.319 |
| $F$(000) | 682 | 1660 | 1672 |
| μ(Mo-$K_\alpha$) [mm$^{-1}$] | 4.455 | 2.462 | 2.358 |
| $T$ [K] | 296(2) | 296(2) | 293(2) |
| 2θ range [°] | 3–28 | 3–28 | 3–29.5 |
| $N$, $N_0$ | 8082, 6765 | 7922, 4935 | 39793, 10827 |
| $R_{int.}$ | 0.0319 | 0.0419 | 0.0359 |
| No. of parameters | 263 | 206 | 410 |
| GOF | 0.856 | 1.001 | 1.067 |
| $R$, $R_w$ (observed data) | 0.0393, 0.1110 | 0.0560, 0.1261 | 0.0337, 0.0827 |
| $R$,$R_w$ (all data) | 0.0581, 0.1241 | 0.1322, 0.1538 | 0.0446, 0.0885 |

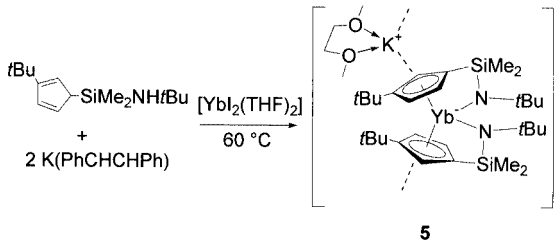
is very close to that previously observed for the related complex $[Yb(\eta^5\text{-}C_5Me_5)(THF)_2(\mu\text{-}I)]_2$,[10] but somewhat shorter than the comparable distance in the mononuclear complex $[Yb\{\eta^5{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\}I(THF)_2]$.[11] The Yb−O bond lengths fall into the range normally observed for derivatives of divalent ytterbium.[12] Significant differences in the Yb−I and Yb−I′ bond lengths have been found for **1** [3.0985(5) and 3.3008(5) Å respectively]. The shorter Yb−I distance is similar to the values previously observed for related dimeric $Yb^{II}$ complexes,[10,13] but the Yb−I′ distance appears to be very long. The I−Yb−I′ bond angle in **1** is significantly smaller than that in the $C_5Me_5$ analogue.[10] The structures of (cyclopentadienyl)-iodo complexes of divalent ytterbium are known to be influenced by the nature of both the $\eta^5$-bonded carbocyclic ligands and the Lewis base: some of them are dimeric $\{[Yb(\eta^5\text{-}C_5Me_5)L_2(\mu\text{-}I)]_2$ (L = THF, DME)[10]$\}$, while others are monomeric in the solid state ($[Yb(\eta^5\text{-}C_9H_7)I(DME)]$,[6a] $[Yb\{\eta^5{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\}I(THF)_2]$[11]).

The $^1H$ and $^{13}C$ NMR spectra of **1**−**4** in [D$_5$]pyridine at room temperature indicate complete dissociation of the THF or DME molecules, as their signals appear at the positions of the free ligands. All signals of the aminocyclopentadienyl ligands give rise to two sets of signals. The nearly constant intensity ratio for all pairs of signals of a given complex varies with the amino substituent: for **1** the signals are of approximately equal intensities, while for the complexes **2**−**4** the ratios are in the range of 1:2.0−2.6. This finding can be explained by the partial dissociation of the dimeric complex $[Yb(\eta^5\text{-}C_5Me_4SiMe_2NHR)L_2(\mu\text{-}I)]_2$ in pyridine into mononuclear species $[Yb(\eta^5\text{-}C_5Me_4SiMe_2NHR)I(py)_3]$ (Scheme 1). This behavior is in agreement with the unsymmetric structure of the $Yb_2I_2$ core in the crystal structure of **1**. Absorption bands in the region of 3370−3390 cm$^{-1}$ in the IR spectra of the complexes **1**−**4** indicate the presence of NH groups. Since *trans*-stilbene has been isolated from the reaction mixtures in almost quantitative yield, THF can regarded as the only source for the proton abstraction.




Scheme 1

Temperature was found to have an important influence on the above-mentioned complexation reaction, giving different types of products (Scheme 2). When the aminocyclopentadiene $(C_5H_4tBu)SiMe_2NHtBu$ was deprotonated with two equivalents of potassium 1,2-diphenylethenide in THF and then reacted with $[YbI_2(THF)_2]$ at 60 °C, an ate complex of trivalent ytterbium $[K(DME)][Yb\{(\eta^5{:}\eta^1\text{-}C_5H_3tBu\text{-}3)SiMe_2NtBu\}_2]$ (**5**) was obtained as orange, paramagnetic crystals after recrystallization from DME. The absence of any absorption bands for the NH group in the IR spectrum of **5** indicates coordination of the amido group to the ytterbium atom.




Scheme 2

Orange crystals of **5** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into the DME solution at room temperature. An ORTEP diagram of the structure is shown in Figure 2. The compound crystallizes in a polymeric chain structure; crystal structure and refinement data are compiled in Table 1. X-ray diffraction study of **5** shows a polymeric chain consisting of anionic ytterbium(III) metallocene units bridged by $[K(DME)]^+$ ions. The $Yb^{III}$ center is coordinated to two chelating amidocyclopentadienyl ligands to form an anionic metallocene unit with both pendant amido groups coordinated to the ytterbium. The thermodynamically favored (*R*,*R*)/(*S*,*S*) diastereomer is observed. The Yb−C bond lengths in **5** are remarkably scattered [2.571(7) for Yb−C(1) to 2.963(8) Å for Yb−C(3)]. The bond lengths Yb−C(1), Yb−C(2),

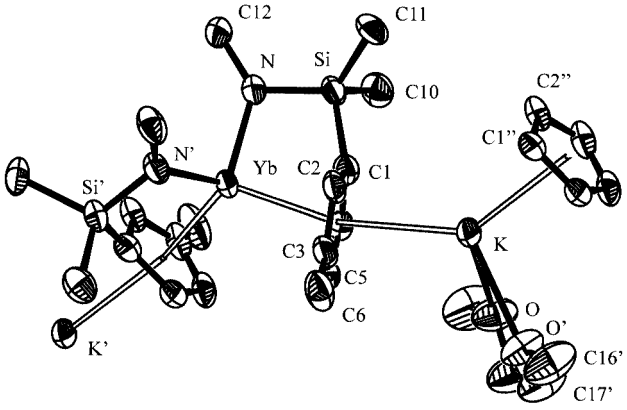
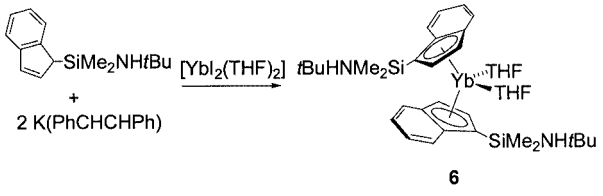



Figure 2. ORTEP drawing and numbering scheme of the molecular structure of **5** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms as well as the methyl carbon atoms of the *t*Bu groups are omitted for the sake of clarity; selected bond lengths (Å) and bond angles (°): Yb−N 2.237(6), Yb−N′ 2.237(6), Yb−C1 2.571(7), Yb−C5 2.673(7), Yb−C2 2.689(8), Yb−C4 2.908(7), Yb−C3 2.963(8), K−O 2.766(6), K−O′ 2.766(6), K−C1 3.083(7), K−C2 3.062(8), K−C3 3.148(7), K−C5 3.183(7), K−C4 3.225(8), C1−C5 1.39(1), C1−C2 1.42(1), C2−C3 1.40(1), C3−C4 1.38(1), C4−C5 1.40(1); N−Yb−N′ 106.6(3), $Cp_{cent1}$−Yb−$Cp_{cent2}$ 114.5(3)

Yb−C(5) are slightly longer than those in the $Yb^{III}$ complex $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N\textit{t}Bu)(THF)(\mu\text{-}H)]_2$ [3c] and are similar to the values of Yb−C bonds in other bis(cyclopentadienyl)ytterbium(III) complexes.[14] The Yb−C(3) and Yb−C(4) distances are extremely long indicating a significant ring slippage toward $\eta^3$-bonding. Such an approach to $\eta^3$-coordination is well documented for fluorenyl complexes of the lanthanides.[15] This bonding situation can be explained by the strain resulting from the repulsion of the bulky *t*Bu groups in the cyclopentadienyl ring and those of the amido group. The $Cp_{Cent1}-Yb-Cp_{Cent2}$ bond angle in **5** [114(1)°] is smaller than the values previously described for bis(cyclopentadienyl) complexes of trivalent ytterbium, which normally fall into the range 127−143°.[14,16] The Yb−N distance in **5** is very close to that previously reported for $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N\textit{t}Bu)(THF)(\mu\text{-}H)]_2$ [3c] and is similar to values observed for the $Yb^{II}$ complexes $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NPh)(THF)]_n$ and $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NPh)(THF)]_2$,[7a] accounting for the difference of ionic radii of $Yb^{II}$ and $Yb^{III}$.[4] The potassium ion is coordinated to one molecule of DME. The potassium-ring distances are in the range of 3.083(7)−3.225(8) Å and are slightly longer than those reported for $[K(py)_2](C_5Me_5)$[17a] and $K[C_5H_4(SiMe_3)]$.[17b] This finding may indicate a more pronounced ionic interaction of the potassium ions with the metallocene ate units. The oxidation of $Yb^{II}$ to $Yb^{III}$ at elevated temperature cannot be satisfactorily explained at this time. We believe, however, that the stability of the bis(chelate) is higher for the monoanionic $Yb^{III}$ species than for the dianionic $Yb^{II}$ complex.

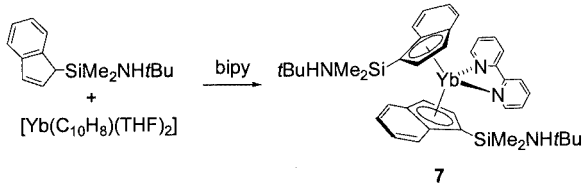
Metalation of the aminoindene $(C_9H_7)SiMe_2N\textit{H}tBu$ under the same conditions and treatment with $[YbI_2(THF)_2]$ in THF at ambient temperature resulted in the $Yb^{II}$ compound $[Yb\{\eta^5\text{-}(1\text{-}C_9H_6)SiMe_2N\textit{H}tBu\}_2(THF)_2]$ (**6**; Scheme 3). Complex **6** was isolated as highly sensitive ruby-red crystals, soluble in THF, DME and aromatic hydrocarbons but insoluble in hexane.




Scheme 3

In the $^1H$ NMR spectrum of **6** in $[D_6]$benzene the methyl protons of the $SiMe_2$ groups appear as two singlets. The signals in each pair are of equal intensities and the ratio of intensities of the couples is 3:2. The *t*Bu protons are recorded as two singlets in the same ratio as the sets of the $SiMe_2$ protons. All indenyl protons are inequivalent due to the planar chirality, giving rise to six signals. The fact that signals corresponding to the THF molecules are somewhat broadened and high-field shifted (δ = 1.25 and 3.05 ppm for β- and α-$CH_2$) confirms their coordination to the ytterbium atom in benzene solution. The $^1H$ and $^{13}C$ NMR spectra of **6** apparently reflect the presence of rotational isomers in solution, as has previously been reported for the indenyl-derived ytterbocenes $[Yb\{\eta^5\text{-}(C_9H_6\text{-}1\text{-}SiHR_2\text{-}2\text{-}R')\}_2(L)_2]$ (R = Me, Ph, R′ = donor ligand).[18]

Ytterbium naphthalenide $[Yb(C_{10}H_8)(THF)_2]$[19a] has been shown to be a convenient precursor for the synthesis of various types of both di- and trivalent organoytterbium compounds.[19] The reactions of $[Yb(C_{10}H_8)(THF)_2]$ with aminocyclopentadienes $(C_5Me_4H)SiMe_2NHR$ (R = Me, Et, allyl, *n*Pr, *i*Pr, *t*Bu) and $(C_5H_5\textit{t}Bu)SiMe_2N\textit{H}tBu$ in THF or DME at room temperature result in the isolation of yellow-orange powders (Scheme 4). These compounds are diamagnetic, corresponding to the $Yb^{II}$ oxidation state; $^1H$, $^{13}C$ NMR and IR spectra show the presence of the aminocyclopentadiene ligands in deprotonated form. However microanalysis failed to give reproducible data and all attempts to obtain samples suitable for X-ray crystal structure analysis failed. Reaction of one equivalent of $(C_9H_7)SiMe_2N\textit{H}tBu$ with $[Yb(C_{10}H_8)(THF)_2]$ resulted in the ytterbocene $[Yb\{\eta^5\text{-}(1\text{-}C_9H_6)SiMe_2N\textit{H}tBu\}_2(THF)_2]$ which was isolated in crystalline form as a complex with 2,2′-bipyridyl $[Yb\{\eta^5\text{-}(1\text{-}C_9H_6)SiMe_2N\textit{H}tBu\}_2(bipy)]$ (**7**). Complex **7** is soluble in THF, DME and pyridine, sparingly soluble in toluene and insoluble in hexane.




Scheme 4

Black crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a THF/toluene/hexane solution at room temperature. An ORTEP diagram of the structure of **7** is shown in Figure 3. The crystal and structure refinement data are compiled in Table 1. Single-crystal structural analysis shows that complex **7** adopts a bent metallocene structure with noncoordinating amino side chains and one coordinated 2,2′-bipyridyl ligand. The average value of the Yb−C bond lengths is 2.72 Å. The $Yb-Ind_{Cent}$ bond lengths are 2.440(8) and 2.449(11) Å, and are similar to values for other bis(indenyl) complexes of divalent ytterbium.[20] The bond angle $Ind_{cent}-Yb-Ind_{cent}$ in **7** is slightly larger [132(1)°] than those in complexes $[Yb(\eta^5\text{-}C_9H_7)_2(THF)_2]$ [128.6[20a] and 129.31(5)[20b]] probably due to a lower steric strain resulting from the coordination of a planar 2,2′-bipyridyl ligand instead of two THF molecules. The Yb−N distances [2.454(3) and 2.476(4) Å] are close to those reported for the complex $[YbI(bipy)_2(DME)_2]$.[21]

In the $^1H$ NMR spectra of **7** in $[D_8]$THF the protons of the $SiMe_2$ groups give rise to four singlets of equal intensity, the *t*Bu protons are recorded as two singlets (1:1 ratio) and the indenyl protons appear as a complex set of six multiplets of different intensities (12 protons together). The bipyridyl protons are observed as a set of eight significantly broadened signals of different intensities.[22] This is probably due to the exchange of bipyridyl by THF within the

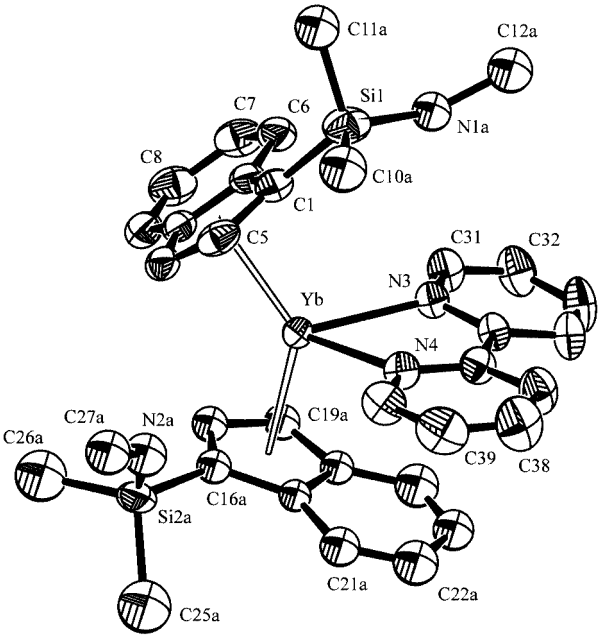
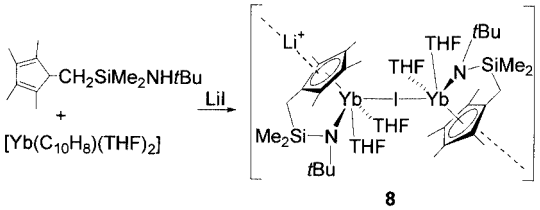



Figure 3. ORTEP drawing and numbering scheme of the molecular structure of **7** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms as well as the methyl carbon atoms of the *t*Bu groups are omitted for the sake of clarity; for the distorted groups, only one of the two split positions are shown; selected bond lengths (Å) and bond angles (°): Yb-$Ind_{cent}$ 2.440(8), 2.45(1), Yb−C1 2.760(4), Yb−C2 2.755(4), Y−C3 2.722(4), Y−C4 2.680(4), Y−C5 2.695(4), Y−C16A 2.71(1), Y−C17A 2.77(1), Y−C18A 2.79(1), Y−C19A 2.69(1), Y−C20A 2.69(1), Yb−N3 2.454(3), Yb−N4 2.476(4); $Ind_{cent}$−Yb−$Ind_{cent}$ 132.1(3), N3−Yb−N4 66.1(1)

coordination sphere of ytterbium. The $^1H$ and $^{13}C$ NMR spectra of **7** display nonequivalence of the indenyl ligands as a consequence of either chirality or the presence of two rotational isomers in the [$D_8$]THF solution.

The reaction of $(C_5Me_4H)CH_2SiMe_2NHtBu$[23] with $[Yb(C_{10}H_8)(THF)_2]$ was carried out in THF. Cooling of the THF/hexane mixture at 0 °C produced yellow crystals of the composition $[Li_{0.5}][Yb(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2N tBu)(THF)_2(\mu\text{-}I)_{0.5}]$ (**8**; Scheme 5). $[Yb(C_{10}H_8)(THF)_2]$ has been shown to contain an admixture of LiI,[19] and the reaction in the presence of LiI gave complex **8**. It is soluble in THF and DME and insoluble in aromatic and aliphatic hydrocarbons. In the $^1H$ NMR spectrum of **8** in [$D_5$]pyridine the protons of the $SiMe_2$, *t*Bu, and $CH_2$ groups appear as singlets, and the methyl groups of the $C_5Me_4$ ring give rise to two singlets. The chemical shifts of the signals of the α- and β-methylene protons of THF




Scheme 5

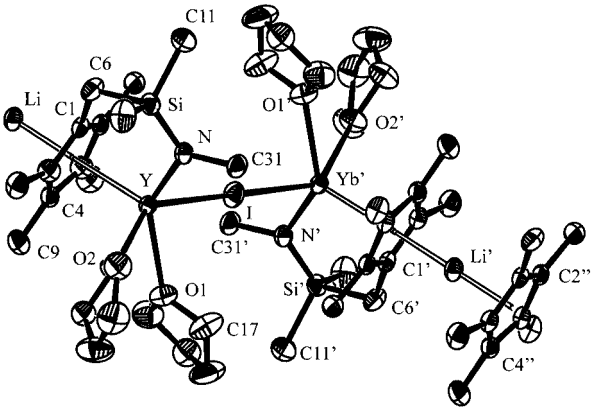



Figure 4. ORTEP drawing and numbering scheme of the molecular structure of **8** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms as well as the methyl carbon atoms of the *t*Bu groups are omitted for the sake of clarity; selected bond lengths (Å) and bond angles (°): Yb−$Cp_{cent}$ 2.45(3), Yb−C1 2.697(3), Yb−C2 2.713(3), Yb−C3 2.770(3), Yb−C4 2.775(3), Yb−C5 2.740(3), Yb−N 2.356(3), Yb−O1 2.559(3), Yb−O2 2.545(3), Yb−I 3.295(1), Li−C1 2.292(3), Li−C2 2.275(3), Li−C3 2.255(3), Li−C4 2.251(4), Li−C5 2.265(3); $Cp_{cent}$−Yb−I 106.1(1), $Cp_{cent}$−Yb−N 104.4(1), $Cp_{cent}$−Yb−O1 118.8(1), $Cp_{cent}$−Yb−O2 104.8(1)

molecules and their well-resolved structure indicate THF dissociation in pyridine solution.

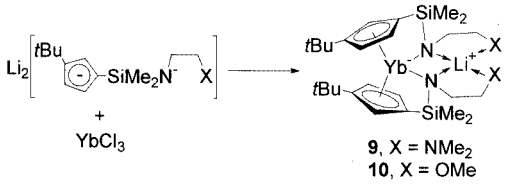
Yellow crystals suitable for X-ray diffraction analysis were obtained by recrystallization of **8** from a THF/hexane mixture at 0 °C. An ORTEP diagram of the structure of **8** is shown in Figure 4. The compound crystallizes in a polymeric chain structure; crystal and structure refinement data are compiled in Table 2. Complex **8** exhibits the unusual

Table 2. Crystallographic and refinement parameters for complexes **8** and **9**

| Compound | **8** | **9** |
|---|---|---|
| Chemical formula | $C_{24}H_{45}I_{0.5}Li_{0.5}NO_2SiYb$ | $C_{30}H_{56}LiN_4Si_2Yb$ |
| $M$ [g mol$^{-1}$] | 647.66 | 708.95 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ (No. 2) | $C2/c$ (No. 15) |
| Crystal size [mm] | 0.74 × 0.13 × 0.09 | 0.55 × 0.53 × 0.45 |
| $a$ [Å] | 10.589(4) | 11.5816(9) |
| $b$ [Å] | 11.877((5) | 16.327(1) |
| $c$ [Å] | 12.316(5) | 18.393(2) |
| α [deg] | 85.990(6) | 90 |
| β [deg] | 66.808(6) | 94.207(7) |
| γ [deg] | 87.279(6) | 90 |
| $V$ [Å$^3$] | 1420(1) | 3468.6(5) |
| Z | 2 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.515 | 1.358 |
| $F(000)$ | 648 | 1460 |
| μ(Mo-$K_\alpha$) [mm$^{-1}$] | 3.897 | 2.789 |
| $T$ [K] | 296(2) | 296(2) |
| 2θ range [°] | 3−29 | 3−29 |
| $N$, $N_0$ | 12826, 6838 | 9641, 4590 |
| $R_{int.}$ | 0.0247 | 0.0252 |
| No. of parameters | 387 | 221 |
| GOF | 0.987 | 1.055 |
| $R$, $R_w$ (observed data) | 0.0273, 0.0634 | 0.0364, 0.0852 |
| $R$,$R_w$ (all data) | 0.0344, 0.0660 | 0.0516, 0.0904 |

structure of an "inverted" sandwich complex. The $Yb^{II}$ ion is coordinated to the linked amidocyclopentadienyl group, the bridging iodo, and two THF ligands, giving a distorted square-pyramidal coordination geometry. The iodine atom bridges two ytterbium atoms of the neighboring molecules, while the lithium ions connect the cyclopentadienyl ligands, forming zigzag chains. Both the ytterbium and lithium ions are symmetrically $\eta^5$-bonded to the tetramethylcyclopentadienyl ligand. The average Yb−C bond length in **9** is slightly longer than those in complexes $[Yb(\eta^5\text{-}C_5Me_5)I(L)_n]_2$ [10] and $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NPh)(THF)]_2$.[7a] The Li−C contacts are similar to those found in lithium complexes of substituted $\eta^5$-cyclopentadienyls.[24] The Yb−N bond length in **8** [2.356(3) Å] is close to that in $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NPh)(THF)]_2$.[7a] The Yb−I bond length [3.295(1) Å] is slightly longer than the value reported for the monomeric complex $[Yb\{\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\}I(THF)_2]$[11] and significantly longer than that in the dimeric complexes $[Yb(\eta^5\text{-}C_5Me_5)I(L)_n]_2$ [10] and $[Yb\{C(SiMe_3)_3\}I(OEt_2)]_2$.[13]

Recently we have shown that reactions of yttrium and lutetium chlorides with dilithium derivatives of tridentate amidocyclopentadienyl ligands result in the formation of chiral lanthanocene complexes with a unique heterobimetallic core.[25] Ytterbium trichloride reacted with $Li_2[(C_5H_3t\text{Bu-}3)SiMe_2NCH_2CH_2X]$ (X = $NMe_2$, OMe) in THF or DME regardless of the reagent ratio, solvent, and the isolation method, to give heterobimetallic complexes $Li[Yb\{\eta^5{:}\eta^1\text{-}C_5H_3t\text{Bu-}3)SiMe_2NCH_2CH_2X\}_2]$ (X = $NMe_2$, **9**; OMe, **10**) with a helical metallocene structure (Scheme 6). Complexes **9** and **10** are soluble in THF, DME and toluene and have been characterized by IR spectroscopy as well as microanalysis.




Scheme 6

Yellow crystals of **9** suitable for X-ray diffraction analysis were obtained by recrystallization from toluene at −30 °C. An ORTEP diagram of the structure of **9** is shown in Figure 5. The crystal and structure refinement data are compiled in Table 2. The single crystal structure analysis of one of the three possible diastereomers of **9**, viz. the thermodynamically stable (*R*,*R*) or (*S*,*S*) epimer, was performed and confirmed the bent metallocene structure with $C_2$-symmetry, similar to that described for a related yttrium complex.[25a] The *t*Bu substituents on the two cyclopentadienyl ligands are oriented *trans* to each other. The ytterbium atom is coordinated by two linked amidocyclopentadienyl ligands, forming a distorted tetrahedral coordination environment. The average value of Yb−C distances is similar to those in bis(cyclopentadienyl) derivatives of trivalent ytterbium,[16] and slightly longer than that in complex

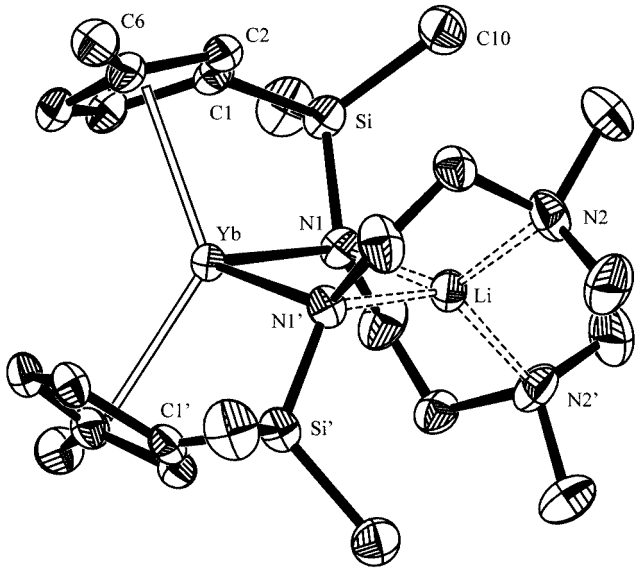
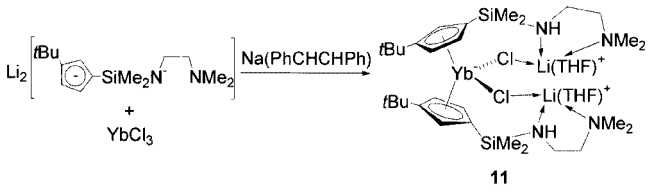



Figure 5. ORTEP drawing and numbering scheme of the molecular structure of **9** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms as well as the methyl carbon atoms of the *t*Bu groups are omitted for the sake of clarity; selected bond lengths (Å) and bond angles (°): Yb−N1 2.279(3), Yb−C1 2.535(4), Yb−C2 2.672(4), Yb−C3 2.818(4), Yb−C4 2.713(4), Yb−C5 2.548(4), Li−N1 2.193(7), Li−N2 2.124(7); $Cp_{cent}$−Yb−$Cp_{cent}$ 127.8(1), N1−Yb−N1′ 92.1(2), Li−N1−Yb 85.6(2), N2−Li−N2′ 111.6(5), N1−Li−N2 89.3(2)

$[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2Nt\text{Bu})(THF)(\mu\text{-}H)]_2$.[3c] The scattering of Yb−C bond lengths [2.534(4)−2.818(4) Å] is somewhat higher than those in complexes (*R*,*R*)-, (*R*,*S*)-$Li[Y\{(\eta^5{:}\eta^1\text{-}C_5H_3t\text{Bu-}3)SiMe_2NCH_2CH_2NMe_2\}_2]$[25a] and $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2Nt\text{Bu})(THF)(\mu\text{-}H)]_2$.[3c] The Yb−C bond lengths distal to the silicon bridge [C(3), C(4)] are longer than the distances for the proximal carbon atoms [C(1), C(2), C(5)]. The Yb−N bond length [2.279(3) Å] is substantially longer than that in $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2Nt\text{Bu})(THF)(\mu\text{-}H)]_2$,[3c] while the Li−N bond lengths are similar to the corresponding values in related yttrium complexes.[25a] The $Cp_{cent}$−Yb−$Cp_{cent}$ bond angle (127.8(1)°] in **9** is slightly less than the $Cp_{cent}$−Y−$Cp_{cent}$ bond angle in (*R*,*R*)-$Li[Y(\eta^5{:}\eta^1\text{-}C_5H_3t\text{Bu-}3)SiMe_2NCH_2CH_2NMe_2]_2$.[25]

Reduction of **9** and **10** with potassium metal or sodium 1,2-diphenylethenide gave a mixture of inseparable products, while reduction of $YbCl_3$ and $Li_2[(C_5H_3t\text{Bu-}3)SiMe_2NCH_2CH_2NMe_2]$ (1:1 molar ratio) prepared "in situ" with one equivalent of sodium 1,2-diphenylethenide in THF resulted in an ate complex of divalent ytterbium $[Li(THF)]_2[Yb\{(\eta^5\text{-}C_5H_3t\text{Bu-}3)SiMe_2N(H)CH_2CH_2NMe_2\}_2(\mu\text{-}Cl)_2]$ (**11**), isolated as bright-red crystals in 46% yield. (Scheme 7).

Complex **11** is soluble in THF and pyridine, sparingly soluble in toluene and in hexane. According to NMR spectroscopy **11** was found to be diamagnetic, indicating the divalency of the ytterbium atom. The $^1H$ NMR and IR spectroscopic data of **11** suggest the presence of protonated amino groups. This indicates that reduction of the $Yb^{III}$ species by sodium 1,2-diphenylethenide occurs together




11

Scheme 7

with protonation of the amido groups. THF molecules seem the most likely source for proton abstraction because *trans*-stilbene was isolated from the reaction mixture in nearly quantitative yield. In the $^1$H NMR spectrum of **11** in [$D_8$]toluene at 20 °C, the methyl protons on the silicon atom are observed as two singlets, while the protons of both methylene groups of the $CH_2CH_2$ bridge appear as broad signals. The protons of the *t*Bu and dimethylamino groups also give rise to two singlets. The significantly broadened signals of both α- and β-methylene protons of THF are shifted to higher field than those of free THF. At −60 °C the $^1$H NMR spectrum shows four singlets for the protons of the $SiMe_2$ groups. The signal of the methylene group $SiNC\mathit{H}_2$ splits into two singlets, and the methylene protons of the $C\mathit{H}_2NMe_2$ group appear as four broad multiplets. Despite the poor crystal quality, a preliminary X-ray crystal structure determination confirmed the connectivity in **11**.[26] Furthermore, the divalent oxidation state of the ytterbium atom could be inferred from the Yb−C distances, ranging from 2.70(2) Å to 2.87(2) Å [Yb−C(Cp)$_{av.}$= 2.78 Å]. In the trivalent ytterbium metallocene **9**, the corresponding values range from 2.535(4) Å to 2.814(4) [Yb−C(Cp)$_{av.}$= 2.657 Å]. The Yb−Cl distances in **11** were found to be 2.753(5) Å and 2.774(6) Å. The unusual bent metallocene structure includes a pseudo-tetrahedrally coordinated Yb$^{II}$ center, bonded to two η$^5$-*tert*-butylcyclopentadienyl rings and two chloro ligands. Each of the amino functions coordinates a [Li(THF)]$^+$ moiety which is linked to the ytterbium center via a bridging chloride ligand.

## Conclusion

The attempts to prepare divalent ytterbium complexes with an $SiMe_2$-linked amidocyclopentadienyl ligand by metathesis of their dipotassium salts with [$YbI_2(THF)_2$] in THF or DME resulted in the formation of dimeric iodo (**1**−**4**) or metallocene-type (**6**) complexes with noncoordinating amino groups. Forcing conditions allow coordination of the amino functions, but the resulting Yb$^{III}$ metallocene ate complexes **5** contain oxidized ytterbium centers. Treatment of the naphthalene ytterbium complex with amino-substituted indene or reduction of the Yb$^{III}$ ate complexes gave the metallocene complexes **7** and **11**. The ligand $(C_5Me_4CH_2SiMe_2N\mathit{t}Bu)^{2-}$ allowed the isolation of the Yb$^{II}$ ate complex **8** which contains a chelating linked amidocyclopentadienyl ligand. Our results are in contrast to the smooth complexation of the anilido ligand $(C_5Me_4SiMe_2NPh)^{2-}$ at divalent ytterbium centers as reported by Hou et al.[7] The coordination of the amidocyclopentadienyl ligands at the large divalent ytterbium center apparently requires electron-withdrawing amido substituents, whereas the sterically bulky *tert*-butyl group appears to severely hinder the chelation reaction.

## Experimental Section

**General:** All experiments were performed under argon using standard Schlenk or glove-box techniques. Solvents were purified, dried, and condensed in vacuo prior to use. $^1$H, $^{13}$C, and $^{29}$Si NMR: Bruker DRX 400; all spectra were obtained at 25 °C. Elemental analyses: Microanalytical laboratory of this department.

**[Yb(η$^5$-$C_5Me_4SiMe_2NH\mathit{t}Bu$)(THF)$_2$(μ-I)]$_2$ (1):** A solution of $(C_5Me_4H)SiMe_2NH\mathit{t}Bu$ (0.298 g, 1.19 mmol) in THF (5 mL) was added at room temperature to a solution of potassium 1,2-diphenylethenide, prepared in situ from *trans*-stilbene (0.430 g, 2.38 mmol) and potassium (0.093 g, 2.38 mmol) in THF (35 mL). The reaction mixture was stirred for 3 h, then slowly treated with [$YbI_2(THF)_2$] (0.679 g, 1.19 mmol) at room temperature with vigorous stirring. The reaction mixture was left stirring overnight. The brownish-yellow reaction mixture was filtered, THF was evaporated in vacuo, and the dark-yellow residue was heated at 60 °C in vacuo for 3 h to sublime off stilbene. The solid residue was recrystallized from the THF/hexane mixture at 0 °C. The mother liquor was decanted from the bright-yellow crystals which were dried in vacuo to afford 0.620 g (76%) of **1**. $^1$H NMR ([$D_5$]pyridine): δ = 0.34, 0.62 (s, 2 × 6 H, $SiCH_3$), 0.71, 1.15 (s, 2 × 1 H, NH), 1.17, 1.32 [s, 2 × 9 H, $C(CH_3)_3$], 1.61 (m, 2 × 8 H, β-$CH_2$, THF), 1.92, 2.07, 2.12, 2.21 [s, 4 × 6 H, $C_5(CH_3)_4$], 3.65 (m, 2 × 8 H, α-$CH_2$, THF) ppm. $^{13}$C{$^1$H} NMR ([$D_5$]pyridine): δ = 7.3, 7.7 (Si$\mathit{C}H_3$), 12.4, 12.8 (ring $\mathit{C}H_3$), 15.9, 16.3 (ring $\mathit{C}H_3$), 26.8 (β-$CH_2$, THF), 34.8, 35.1 [$C(\mathit{C}H_3)_3$], 51.0 [$\mathit{C}(CH_3)_3$, 68.9 (α-$CH_2$, THF), 106.2 (ring C attached to $SiMe_2$), 122.3, 126.1 (ring C) ppm. IR (KBr): $\tilde{\nu}$ = 3382 w, 2964 s, 2921 s, 2858 s, 1622 m, 1592 m, 1443 m, 1379 m, 1256 s, 1216 m, 1043 s, 984 m, 832 s, 800 s, 644 m cm$^{-1}$. $C_{46}H_{88}I_2N_2O_4Si_2Yb_2$ (1387.2): calcd. C 39.82, H 6.34, N 2.02; found C 39.39, H 6.47, N 2.30.

**[Yb(η$^5$-$C_5Me_4SiMe_2NHCH_2CH_2CH_3$)(THF)$_2$(μ-I)]$_2$ (2):** A solution of $(C_5Me_4H)SiMe_2NHCH_2CH_2CH_3$ (0.322 g, 1.36 mmol) in THF (5 mL) was added at room temperature to a solution of potassium 1,2-diphenylethenide, prepared in situ from *trans*-stilbene (0.489 g, 2.72 mmol) and potassium (0.106 g, 2.72 mmol) in THF (35 mL). The reaction mixture was stirred for 3 h, then slowly treated with [$YbI_2(THF)_2$] (0.780 g, 1.36 mmol) at room temperature with vigorous stirring. The reaction mixture was left stirring overnight. The brownish-yellow reaction mixture was filtered, THF was evaporated in vacuo, and the dark-yellow residue was heated at 60 °C in vacuo for 3 h to sublime off stilbene. The solid residue was recrystallized from DME at 0 °C. The mother liquor was decanted from the yellow crystals which were dried in vacuo to afford 0.670 g (79%) of **2**. $^1$H NMR ([$D_5$]pyridine): δ = 0.41, 0.52 (s, 2 × 6 H, $SiCH_3$), 0.78, 1.17 (m, 2 × 1 H, NH), 0.95 (m, 2 × 3 H, $NCH_2CH_2C\mathit{H}_3$), 1.50 (m, 2 × 2 H, $NCH_2C\mathit{H}_2CH_3$), 1.62 (s, 2 × 8 H, β-$CH_2$, THF), 2.03, 2.06, 2.18, 2.24 (s, 4 × 6 H, $C_5(CH_3)_4$], 2.88 (m, 2 × 2 H, $NC\mathit{H}_2$), 3.65 (s, 2 × 8 H, α-$CH_2$, THF) ppm. $^{13}$C{$^1$H} NMR ([$D_5$]pyridine): δ = 3.4, 3.9 (Si$\mathit{C}H_3$), 12.4, 12.7 (ring $\mathit{C}H_3$), 15.2, 15.6 (ring $\mathit{C}H_3$), 26.5 (β-$CH_2$, THF), 28.9 ($CH_2CH_2\mathit{C}H_3$), 45.4 ($CH_2\mathit{C}H_2CH_3$), 46.4 ($\mathit{C}H_2CH_2CH_3$), 68.5 (α-$CH_2$, THF), 106.4 (ring C attached to $SiMe_2$), 118.1, 121.0 (ring

C) ppm. IR (KBr): $\tilde{\nu}$ = 3378 w, 2969 s, 2918 s, 2860 s, 1642 m, 1582 m, 1449 m, 1379 m, 1250 s, 1116 m, 1043 s, 984 m, 832 s, 810 s, 646m $cm^{-1}$. $C_{44}H_{84}I_2N_2O_4Si_2Yb_2$ (1360.6): calcd. C 38.84, H 6.17, N 2.05; found C 38.99, H 6.11, N 2.49.

**[Yb(η$^5$-$C_5Me_4SiMe_2NHCH_2CH_3$)(DME)(μ-I)]$_2$ (3):** A solution of $(C_5Me_4H)SiMe_2NHCH_2CH_3$ (0.412 g, 1.84 mmol) in THF (5 mL) was added at room temperature to a solution of potassium 1,2-diphenylethenide, prepared in situ from *trans*-stilbene (0.665 g, 3.69 mmol) and potassium (0.144 g, 3.69 mmol) in THF (30 mL). The reaction mixture was stirred for 3 h, then slowly treated with $[YbI_2(THF)_2]$ (1.050 g, 1.83 mmol) at room temperature with vigorous stirring. The reaction mixture was left stirring overnight. The resulting dark-orange reaction mixture was filtered, THF was evaporated in vacuo, and the brown residue was heated at 60 °C in vacuo for 2 h to sublime off stilbene. The solid residue was recrystallized from DME/hexane mixture at 0 °C. The mother liquor was decanted from the orange crystals which were dried in vacuo to afford 0.640 g (59%) of **3**. $^1$H NMR ([D$_5$]pyridine): δ = 0.40, 0.52 (s, 2 × 6 H, $SiCH_3$), 0.92, 1.07 (m, 2 × 1 H, NH), 1.19 (m, 2 × 3 H, $NCH_2CH_3$), 2.01, 2.03, 2.08, 2.16 [s, 4 × 6 H, $C_5(CH_3)_4$], 2.94 (m, 2 × 2 H, $NCH_2CH_3$) 3.26 (s, 2 × 6 H, $OCH_3$, DME), 3.49 (s, 2 × 4 H, $OCH_2CH_2O$, DME) ppm. $^{13}$C{$^1$H} NMR ([D$_5$]pyridine): δ = 4.5, 4.9 ($SiCH_3$), 11.2, 11.7 (ring $CH_3$), 14.9, 15.3 (ring $CH_3$), 35.0, 35.6 ($NCH_2CH_3$), 48.1, 48.9 ($NCH_2$), 59.8 ($OCH_3$, DME), 73.3 ($OCH_2$, DME), 107.3 (ring C attached to $SiMe_2$), 124.2, 128.7 (ring C) ppm. IR (KBr): $\tilde{\nu}$ = 3383 w, 2963 s, 2916 s, 2860 s, 1449 m, 1385 m, 1319 m, 1249 s, 1104 s, 1058 s, 1020 s, 981 m, 917 m, 825 s, 789 s, 698 m, 636w $cm^{-1}$. $C_{34}H_{68}I_2N_2O_4Si_2Yb_2$ (1224.5): calcd. C 33.34, H 5.55, N 2.28; found C 33.71, H 5.21, N 2.27.

**[Yb(η$^5$-$C_5Me_4SiMe_2NHCH_2CH{=}CH_2$)(DME)(μ-I)]$_2$ (4):** A solution of $(C_5Me_4H)SiMe_2NHCH_2CH{=}CH_2$ (0.300 g, 1.27 mmol) in THF (5 mL) was added at room temperature to a solution of potassium 1,2-diphenylethenide, prepared in situ from *trans*-stilbene (0.457 g, 2.53 mmol) and potassium (0.099 g, 2.54 mmol) in THF (30 mL). The reaction mixture was stirred for 3 h, then slowly treated with $[YbI_2(THF)_2]$ (0.720 g, 1.26 mmol) at room temperature with vigorous stirring. The reaction mixture was left stirring overnight. The brownish-red reaction mixture was filtered, THF was evaporated in vacuo, and the brown residue was heated at 60 °C in vacuo for 2 h to sublime off stilbene. The solid residue was recrystallized from DME/hexane mixture at 0 °C. The mother liquor was decanted from the orange crystals which were dried in vacuo to afford 0.500 g (66%) of **4**. $^1$H NMR ([D$_5$]pyridine): δ = 0.39, 0.54 (s, 2 × 6 H, $SiCH_3$), 1.10, 1.60 (br. s, 2 × 2 H, NH), 2.01, 2.05, 2.23, 2.32 [s, 4 × 6 H, $C_5(CH_3)_4$], 3.31 (s, 2 × 6 H, $OCH_3$, DME), 3.49 (s, 2 × 4 H, $OCH_2CH_2O$, DME), 3.54, 3.56 (m, 2 × 2 H, $NCH_2CH$), 5.08, 5.29 (m, 2 × 2 H, $CH{=}CH_2$), 6.04−6.11 (m, 2 × 1 H, $CH_2CH{=}CH_2$) ppm. $^{13}$C{$^1$H} NMR ([D$_5$]pyridine): δ = 3.4, 3.9 ($SiCH_3$), 12.3, 12.6 (ring $CH_3$), 15.2, 15.4 (ring $CH_3$), 46.2, 46.9 ($NCH_2$), 59.3 ($OCH_3$, DME), 72.8 ($OCH_2$, DME), 106.4, 110.2 (ring C attached to $SiMe_2$), 113.5, 114.7 ($CH{=}CH_2$), 121.3, 123.7 (ring C), 141.8, 142.9 ($CH{=}CH_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3384 w, 2984 s, 2914 s, 2857 s, 1634 m, 1574 m, 1450 m, 1252 s, 1045 s, 986 m, 950 m, 832 s, 798 s, 695 m, 645m $cm^{-1}$. $C_{36}H_{68}I_2N_2O_2Si_2Yb_2$ (1248.5): calcd. C 34.63, H 5.48, N 2.30; found C 34.56, H 5.67, N 2.38.

**[K(DME)][Yb{(η$^5$:η$^1$-$C_5H_3$*t*Bu-3)$SiMe_2N$*t*Bu}$_2$] (5):** A solution of $(C_5H_4$*t*Bu)$SiMe_2NH$*t*Bu (0.700 g, 2.78 mmol) in THF (5 mL) was added to a solution of potassium 1,2-diphenylethenide, prepared in situ from *trans*-stilbene (1.000 g, 5.55 mmol) and potassium (0.216 g, 5.55 mmol) in THF (30 mL) at room temperature and stirred for 3 h. $[YbI_2(THF)_2]$ (1.580 g, 2.78 mmol) was slowly added at room temperature with vigorous stirring. The reaction mixture was stirred for 3 h at room temperature and at 60 °C for 6 h. The dark orange solution was filtered, THF was evaporated in vacuo, and the brown residue was heated to 60 °C in vacuo for 2 h to remove stilbene (by sublimation). The residue was redissolved in 20 mL of DME and recrystallized by slow condensation of hexane into the DME solution at room temperature. The mother liquor was decanted from the orange crystals which were washed with hexane and dried in vacuo to give 0.850 g (77%) of **5**. IR (KBr): $\tilde{\nu}$ = 2970 s, 2902 s, 2869 s, 1460 m, 1358 m, 1257 s, 1158 s, 1097 s, 1010 s, 838 s, 723 m, 525 m, 433m $cm^{-1}$. $C_{34}H_{64}KN_2O_2Si_2Yb$ (801.2): calcd. C 50.97, H 7.98, N 3.49; found C 51.24, H 8.03, N 3.68.

**[Yb{η$^5$-(1-$C_9H_6$)$SiMe_2NH$*t*Bu}$_2$(THF)$_2$] (6):** A solution of $(C_9H_7)SiMe_2NH$*t*Bu (0.500 g, 2.04 mmol) in THF (5 mL) was added at room temperature to a solution of potassium 1,2-diphenylethenide, prepared in situ from *trans*-stilbene (0.730 g, 4.05 mmol) and potassium (0.159 g, 4.06 mmol) in THF (30 mL). The reaction mixture was stirred for 3 h, then slowly treated with $[YbI_2(THF)_2]$ (1.160 g, 2.03 mmol) at room temperature with vigorous stirring. The reaction mixture was left stirring overnight. The dark red reaction mixture was filtered, THF was evaporated in vacuo, and the brown residue was heated to 60 °C in vacuo for 4 h (to sublime off stilbene). The solid residue was recrystallized from toluene at −30 °C. The mother liquor was decanted from the red crystals which were dried in vacuo to afford 0.370 g (46%) of **6**. $^1$H NMR ([D$_6$]benzene): δ = 0.28, 0.39, 0.73, 0.86 (s, 4 × 3 H, $SiCH_3$), 0.81, 1.00 (br. s, 2 × 1 H, NH), 1.12, 1.16 [s, 2 × 9 H, $C(CH_3)_3$], 1.25 (br. s, 2 × 4 H, β-$CH_2$ THF), 3.05 (br. s, 2 × 4 H, α-$CH_2$ THF), 6.37, 6.81, 7.04, 7.40, 7.70, 7.88 (m, 2 × 6 H, $C_9H_6$) ppm. $^{13}$C{$^1$H} NMR (101 MHz, [D$_8$]THF): δ = 1.2 ($SiCH_3$), 23.3 (β-$CH_2$, THF), 31.1 [$C(CH_3)_3$], 47.1 [$C(CH_3)_3$], 65.2 (α-$CH_2$, THF), 95.2 (ring C attached to $SiMe_2$), 100.2, 114.9, 115.7, 117.8, 120.6, 124.8, 129.3, 132.6 ($C_9H_6$) ppm. IR (Nujol): $\tilde{\nu}$ = 3382 w, 1322 m, 1222 s, 1154 m, 1025 s, 966 w, 839 s, 764 s, 717 s, 642 w $cm^{-1}$. $C_{38}H_{60}N_2O_2Si_2Yb$ (806.1): calcd. C 56.61, H 7.58, N 3.47; found C 55.80, H 6.97, N 3.08.

**[Yb{η$^5$-(1-$C_9H_6$)$SiMe_2NH$*t*Bu}$_2$(bipy)] (7):** A solution of $(C_9H_7)SiMe_2NH$*t*Bu (0.548 g, 2.23 mmol) in THF (5 mL) was added to a suspension of $[Yb(C_{10}H_8)(THF)_2]$ (1.000 g, 2.24 mmol) in THF (35 mL) at room temperature with vigorous stirring and the reaction mixture was left standing overnight. The solution was filtered and THF was evaporated in vacuo. The brown residue was washed with hexane to remove naphthalene and redissolved in THF (20 mL). A solution of 2,2′-bipyridyl (0.690 g, 4.48 mmol) in toluene (5 mL) and hexane (3 mL) was added. Slow evaporation of the solvents at room temperature resulted in the precipitation of black crystals. The mother liquor was decanted and the crystals were washed with cold hexane and dried in vacuo to give 0.610 g (67%) of **7**. $^1$H NMR ([D$_8$]THF): δ = 0.11, 0.21, 0.53, 0.55 (s, 4 × 3 H, $SiCH_3$), 0.62, 1.21 (br. s, 2 × 1 H, NH), 0.92, 1.09 [s, 2 × 9 H, $C(CH_3)_3$], 5.93, 6.36, 6.43, 6.61, 6.95, 7.15 (m, together 12 H, $C_9H_6$), 7.84, 7.90, 8.02, 8.19, 8.24, 8.39, 8.43, 8.59 (br. s, together 8 H, bipy) ppm. $^{13}$C{$^1$H} NMR ([D$_8$]THF): δ = 2.2, 2.6, 2.9, 3.0 ($SiCH_3$), 32.8, 33.0 [$C(CH_3)_3$], 48.6, 48.9 [$C(CH_3)_3$], 97.7, 98.3 (C-1, $C_9H_6$), 101.8, 102.3 (C-3, $C_9H_6$), 116.5, 116.7, 117.0, 117.3 (C-6, C-7, $C_9H_6$), 120, 120.3 (C-5, $C_9H_6$), 121.6, 121.9 (C-8, $C_9H_6$), 124.1, 124.6 (C-2, $C_9H_6$), 129.6, 130.2 (C-4, $C_9H_6$), 132.2, 135.5 (C-9, $C_9H_6$), 128.2 (bipy), 136.1 (bipy), 138.0 (bipy), 148.1 (bipy), 153.7 (bipy) ppm. IR (KBr): $\tilde{\nu}$ = 3384 w, 3065 m, 2962 s, 1582 m, 1455 m, 1378 m, 1226 m, 1019 s, 849 m, 759 s, 716 m, 621 w, 450 w $cm^{-1}$. $C_{40}H_{52}N_4Si_2Yb$ (818.1): calcd. C 58.72, H 6.41, N 6.84; found C 58.80, H 6.39, N 7.63.

**[$Li_{0.5}$][Yb(μ−$η^5$: $η^1$-$C_5Me_4CH_2SiMe_2NtBu$)$(THF)_2$(μ-I)$_{0.5}$] (8):** A solution of $(C_5Me_4H)CH_2SiMe_2NHtBu$ (0.667 g, 2.51 mmol) in THF (5 mL) was added to a suspension of $[Yb(C_{10}H_8)(THF)_2]$ (1.120 g, 2.51 mmol) in THF (25 mL) at room temperature and the reaction mixture was stirred for 8 h. The brown reaction mixture was filtered, THF was evaporated in vacuo, and the residue extracted with hexane (2 × 20 mL) to remove naphthalene. The resulting solid was recrystallized from a THF/hexane mixture at 0 °C. The mother liquor was decanted and the yellow crystals were dried in vacuo to yield 0.310 g (19%) of **8**. $^1$H NMR ([$D_5$]pyridine): δ = 0.73 (s, 6 H, $SiCH_3$), 1.52 [s, 9 H, $C(CH_3)_3$], 1.60 (m, 8 H, β-$CH_2$, THF), 1.73, 2.10 [s, 6 H, $C_5(CH_3)_4$], 2.37 (s, 2 H, $CH_2$), 3.64 (m, 8 H, α-$CH_2$, THF) ppm. $^{13}C\{^1H\}$ NMR ([$D_5$]pyridine): δ = 10.6 ($SiCH_3$), 12.4, 12.9 (ring $CH_3$), 20.6 ($CH_2$), 26.5 (β-$CH_2$, THF), 36.0 [$C(CH_3)_3$], 54.3 [$C(CH_3)_3$], 68.5 (α-$CH_2$, THF), 109.7, 109.9 (ring C), 137.2 (ring C attached to $CH_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2927 s, 2854 s, 1461 m, 1377 m, 1236 w, 1187 w, 1058 s, 1022 m, 987 m, 832 m, 733 w $cm^{-1}$. $C_{24}H_{45}I_{0.5}Li_{0.5}NO_2SiYb$ (647.7): calcd. C 44.51, H 7.00, N 2.16; found C 44.86, H 7.75, N 2.26.

**Li[Yb{(η$^5$:η$^1$-$C_5H_3t$Bu-3)$SiMe_2NCH_2CH_2NMe_2$}$_2$] (9):** Solid $Li_2(C_5H_3tBuSiMe_2NCH_2CH_2NMe_2)$ (0.670 g, 2.41 mmol) was slowly added at room temperature to a suspension of $YbCl_3$ (0.670 g, 2.40 mmol) in THF (50 mL) with vigorous stirring and the reaction mixture was stirred for a further 18 h. The resulting orange solution was filtered, THF was removed in vacuo, and the crude product was extracted with toluene (2 × 20 mL). LiCl was filtered off and the volume of the solution was reduced to 10 mL. After crystallization at −30 °C for 48 h, the mother liquor was decanted off from the yellow crystals which were dried in vacuo at room temperature to afford 0.530 g (62%) of **9**. IR (KBr): $\tilde{\nu}$ = 2995 s, 2826 m, 2783 m, 1458 m, 1360 m, 1244 s, 1176 m, 1094 s, 1020 s, 952 m, 800 s, 653 w $cm^{-1}$. $C_{30}H_{56}LiN_4Si_2Yb$ (708.9): calcd. C 50.85, H 7.90, N 7.90; found C 50.34, H 7.76, N 8.11.

**Li{Yb[(η$^5$:η$^1$-$C_5H_3t$Bu-3)$SiMe_2NCH_2CH_2OMe$]$_2$} (10):** Solid $Li_2(C_5H_3tBuSiMe_2NCH_2CH_2OMe)$ (1.150 g, 4.33 mmol) was slowly added at room temperature to a suspension of $YbCl_3$ (1.170 g, 4.34 mmol) in DME (40 mL) under vigorous stirring and the reaction mixture was left stirring overnight. The yellow solution was filtered and the volume of the filtrate was then reduced to 10 mL. After crystallization at 0 °C for 3 days, the mother liquor was decanted from the yellow crystals which were dried in vacuo at room temperature to afford 1.010 g (71%) of **10** as yellow crystals. IR (KBr): $\tilde{\nu}$ = 2949 s, 2898 m, 2819 m, 1459 m, 1359 m, 1239 s, 1176 m, 1075 s, 935 m, 819 s, 763 s, 719 s, 571 m, 426 w $cm^{-1}$. $C_{28}H_{50}LiN_2O_2Si_2Yb$ (682.4): calcd. C 49.28, H 7.32, N 4.10; found C 48.88, H 7.24, N 4.23.

**[Li(THF)]$_2$[Yb{(η$^5$-$C_5H_3t$Bu-3)$SiMe_2NHCH_2CH_2NMe_2$}$_2$(μ-Cl)$_2$] (11):** Solid $Li_2(C_5H_3tBuSiMe_2NCH_2CH_2NMe_2)$ (0.878 g, 3.15 mmol) was slowly added at room temperature to a suspension of $YbCl_3$ (0.882 g, 3.15 mmol) in THF (40 mL) under vigorous stirring and the reaction mixture was stirred overnight. The resulting orange solution was cooled to 0 °C and treated with a solution of sodium 1,2-diphenylethenide, prepared from *trans*-stilbene (0.567 g, 3.15 mmol) and sodium (0.072 g, 3.15 mmol) in THF (30 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. After filtration, THF was removed in vacuo and the resulting crude product was recrystallized from THF/hexane at −30 °C. The bright red crystals were dried in vacuo to give 1.350 g (46%) of **11**. $^1$H NMR ([$D_8$]toluene): δ = 0.11, 0.48 (s, 6 H, $SiCH_3$), 0.87, 1.75 (m, 1 H, NH), 1.48 (br. s, 8 H, β-$CH_2$, THF), 1.53 (br. s, 4 H, $SiNCH_2CH_2N$), 1.64 [s, 18 H, $C(CH_3)_3$], 1.97 [s, 6 H, $N(CH_3)_2$], 2.29 (br. s, 4 H, $NCH_2CH_2N$), 3.60 (br. s, 8 H, α-$CH_2$, THF), 6.06, 6.13, 6.72 (s, 2 H, ring H) ppm. $^{13}C\{^1H\}$ NMR ([$D_8$]toluene): δ = −2.1, 1.5 ($SiCH_3$), 25.3 (β-$CH_2$, THF), 31.9 [$C(CH_3)_3$],32.6 [$C(CH_3)_3$, 38.8 [$N(CH_3)_2$], 44.4 ($SiNCH_2$), 61.8 ($CH_2NMe_2$), 67.3 (α-$CH_2$, THF), 109.2 (ring C attached to $SiMe_2$), 113.8, 113.1 (ring C), 137.1 (ring C attached to *tBu*) ppm. IR (KBr): $\tilde{\nu}$ = 3380 w, 3050 w, 2960 s, 2826 m, 2783 m, 1458 m, 1360 m, 1240 s, 1176 m, 1050 s, 1090 s, 1024 s, 962 m, 800 s $cm^{-1}$. $C_{38}H_{74}Cl_2Li_2N_4O_2Si_2Yb$ (933.0): calcd. C 48.91, H 7.93, N 6.00; found C 48.39, H 8.27, Yb 6.42.

**X-ray Structure Determination of 1, 5, 7, 8, and 9:** The crystal and structure refinement data are listed in Table 1 and 2. Data for **1**, **5**, **8** and **9** were collected on an Enraf−Nonius CAD-4 diffractometer (graphite monochromator, Mo-$K_\alpha$ radiation, λ = 0.71073 Å). Data corrections were carried out using the program WINGX[27a] in the program system WinGX.[27b] Data for **7** were collected on a Bruker AXS diffractometer with area detector. Data correction was carried out using the program system SAINT.[27c] All structures were solved by direct methods using SHELXS-86[27d] and difference Fourier syntheses. All independent reflections were used in the refinement against all $F_o^2$ data using the program SHELXL-97.[27e] All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were included in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-195744 (**1**), CCDC-195745 (**5**), CCDC-195746 (**7**), CCDC-195747 (**8**), and CCDC-195748 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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