# Synthesis and Characterisation of Ytterbium(II) Alkyls*

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The following complexes were obtained and characterised: $[Yb(CHR_2)_2(OEt_2)_2]$ **1** from $YbI_2$ and 2 $NaCHR_2$; $[Yb(CHR_2)_3Na]$ from $YbI_2$ and 3 $Na(CHR_2)$; **1** and $[Yb(CHR_2)(OR')(OEt_2)_2]$ from $[Yb(OR')_2(OEt_2)_2]$ and 2 $K(CHR_2)$; $[Yb(CHR_2)(OR')(thf)_3]$ from $[Yb(OR')_2(thf)_3]$ and 1 $K(CHR_2)$; $[Yb(CHR_2)_2(tmen)]$ from $[Yb(\eta\text{-}C_5Me_5)_2(OEt_2)]$, 2 $Li(CHR_2)$ and tmen; $[Yb(CHR_2)_2(dmpe)]$ from **1** and dmpe; $[\{Yb(CHR_2)(OEt_2)\}_2C_6H_4(NR)_2\text{-}1,4]$ from 2 **1** and $C_6H_4(NHR)_2\text{-}1,4$; $[\{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)\}_2]$ from $YbI_2$ and 1 or 2 $K(CR_3)$; $[Yb(NR_2)_2\{NC_5H_4(CH_2R)\text{-}2\}_2]$ from $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I** and 4 $NC_5H_4(CH_2R)\text{-}2$; $[Yb(NR_2)_2\{NC_5H_4(CHR_2)\text{-}2\}]$ from **I** and 4 $NC_5H_4(CHR_2)\text{-}2$; $[Yb\{NC_5H_4(CHR)\text{-}2\}_2(dme)]$ from $YbI_2$ and 2 $[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]$ and $[K\{Yb[NC_5H_4(CHR)\text{-}2]_3\}(dme)_2]$ from $YbI_2$ and 3 $[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]$ ($R = SiMe_3$, $R' = C_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4$, thf = tetrahydrofuran, tmen = $Me_2NCH_2CH_2NMe_2$, dmpe = $Me_2PCH_2CH_2PMe_2$ and dme = 1,2-dimethoxyethane). A single-crystal X-ray diffraction study established $[\{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)\}_2]$ to be a centrosymmetric dimer with each Yb atom in a distorted-tetrahedral environment and a central planar $Yb_2O_2$ ring. Variable-temperature $^1H$ NMR spectral data for $[K\{Yb[NC_5H_4(CHR)\text{-}2]_3\}(dme)_2]$ showed that the $Me_3Si$ protons become inequivalent at low temperature, $T_c = 238$ K, due to a terminal–bridging $NC_5H_4(CHR)\text{-}2$ site-exchange process.

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The stability of organolanthanide complexes has often relied on the incorporation of cyclopentadienyl ligands. Lanthanide(III) complexes containing only alkyl ligands are well established.[2] Several types of such complexes have been synthesised and structurally characterised, including (*i*) the homoleptic neutral complexes $[Ln(CHR_2)_3]$ (Ln = La or Sm, $R = SiMe_3$);[3] (*ii*) anionic complexes, *e.g.* $[Li(thf)_4][LnBu^t{}_4]$ (Ln = Sm, Eu or Lu; thf = tetrahydrofuran)[4] and $[Li(thf)_4][Ln(CHR_2)_3Cl]$ (Ln = Er or Yb);[5] (*iii*) bimetallic complexes, *e.g.* $[(R_2HC)_3La(\mu\text{-}Cl)Li(pmdien)]$[6] and $[(R_2HC)_3Ln(\mu\text{-}Me)Li(pmdien)]$ (Ln = La or Sm; pmdien = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine)[7] and (*iv*) chelate complexes, *e.g.* $[La\{CH(PPh_2)_2\}_3]$[8] and $[Sc\{CH_2(SiMe_2C_6H_4OMe\text{-}2)\}_3]$.[9] By contrast, much less work has been reported on the lanthanide(II) alkyls. Reactions of an alkyl or aryl iodide with Sm, Eu or Yb metal have yielded lanthanide(II) complexes related to Grignard reagents.[10] The obtained products were not pure but contained various lanthanide-(II) and -(III) species. More recently, several well characterised ytterbium(II) alkyls have been reported in preliminary publications using the bulky $^-CH_2R$, $^-CHR_2$ and $^-CR_3$ ligands,[11] including the first structurally authenticated lanthanide(II) alkyl $[Yb(CHR_2)\{HB(bmpz)_3\}]$ ($R = SiMe_3$, bmpz = 3-*tert*-butyl-5-methylpyrazolyl).[11b]

The work described in this paper is concerned with the use in ytterbium(II) chemistry of the bulky alkyl ligands $^-CHR_2$ and $^-CR_3$ and the potentially bidentate alkyl ligands $C_5H_4N(CHR)\text{-}2$ and $C_5H_4N(CR_2)\text{-}2$ ($R = SiMe_3$). The latter have been widely employed in transition-metal and main-group chemistry,[12] but no lanthanide metal complexes had previously been reported.

We have previously briefly communicated the preparation and NMR spectra of the ytterbium(II) alkyls $[Yb(CHR_2)_2(OEt_2)_2]$ **1** ($R = SiMe_3$), $[Yb(CHR_2)_3Na]$ **2**, $[Yb(CHR_2)(OR')(thf)_3]$ **3** ($R' = C_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4$), $[Yb(CHR_2)_2(dmpe)]$ **4** (dmpe = $Me_2PCH_2CH_2PMe_2$) and $[\{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)\}_2]$ **5**, including the crystal structure of complex **5**.[11a] We report here details including new data on complexes **1**–**5** and the synthesis and characterisation of $[Yb(CHR_2)(OR')(OEt_2)_2]$ **6**, $[Yb(CHR_2)_2(tmen)]$ **7** (tmen = $Me_2NCH_2CH_2NMe_2$), $[\{Yb(CHR_2)(OEt_2)\}_2C_6H_4(NR)_2\text{-}1,4]$ **8**, $[Yb(NR_2)_2\{NC_5H_4(CH_2R)\text{-}2\}_2]$ **9**, $[Yb(NR_2)_2\{NC_5H_4(CHR_2)\text{-}2\}_2]$ **10**, $[Yb\{NC_5H_4(CHR)\text{-}2\}_2(dme)]$ **11** (dme = 1,2-dimethoxyethane) and $[K\{Yb[NC_5H_4(CHR)\text{-}2]_3\}(dme)_2]$ **12**. Part 3 of this Series described the reactions of $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I**[13] or $[Yb(NR_2)_2(OEt_2)_2]$[14] with various Brønsted acids, carbon disulfide, or $LiNR_2$ with tmen.[1]

## Results and Discussion

*Synthesis and Characterisation of Ytterbium*(II) *Alkyls*.—The reaction of $YbI_2$ with 2 equivalents of $Na(CHR_2)$ in diethyl ether yielded orange crystals of $[Yb(CHR_2)_2(OEt_2)_2]$ **1**, equation (1). Compound **1** was fully characterised by NMR

$$YbI_2 + 2Na(CHR_2) \xrightarrow{OEt_2} \underset{\mathbf{1}}{[Yb(CHR_2)_2(OEt_2)_2]} + 2NaI \quad (1)$$

[$^1H$, $^{13}C$, $^{29}Si\text{-}\{^1H\}$, $^{171}Yb\text{-}\{^1H\}$[15] (Table 1)] spectroscopy. Owing to the lability of the diethyl ether ligands in **1**, satisfactory elemental analytical data were not obtained. Attempts to determine the molecular structure were hampered by disorder in the crystal.

The reaction of $YbI_2$ with either 2 or 3 equivalents of $Na(CHR_2)$ in hexane yielded the solvent-free, red-brown crystalline $[Yb(CHR_2)_3Na]$ **2**, equation (2). In the former case

$$YbI_2 + 3Na(CHR_2) \xrightarrow{hexane} \underset{\mathbf{2}}{[Yb(CHR_2)_3Na]} + 2NaI \quad (2)$$

the reacting $YbI_2$ was not completely consumed; the formation of **2**, rather than $Yb(CHR_2)_2$, was confirmed by elemental

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* Lanthanide(II) Alkyls, Amides, Alkoxides and Aryloxides. Part 4.[1]
No reprints available.
*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

**Table 1** The $^{171}$Yb-{$^1$H} NMR spectral chemical shift (δ) data[a] for compounds **1**, **3**–**12**, **I** and **VIII** (R = SiMe$_3$, R′ = C$_6$H$_2$Bu$^t_2$-2,6-Me-4)

| Compound | Solvent[b] | $T$/K | δ($^{171}$Yb) | $w_{\frac{1}{2}}$/Hz | $^2J$($^{171}$Yb–$^1$H)/Hz | Ref. |
|---|---|---|---|---|---|---|
| **1** [Yb(CHR$_2$)$_2$(OEt$_2$)$_2$] | C$_6$H$_5$Me | 295 | 1035 | Triplet | 30 | 11(*a*) |
| **3** [Yb(CHR$_2$)(OR′)(thf)$_3$] | C$_6$H$_5$Me | 293 | 725 | — | — | 11(*a*) |
| **4** [Yb(CHR$_2$)$_2$(dmpe)] | C$_6$H$_5$Me | 293 | 1231 | 260 | — | 11(*a*) |
| **5** [{Yb(CR$_3$)(μ-OEt)(OEt$_2$)}$_2$] | OEt$_2$ | 298 | 764 | — | — | 11(*a*) |
| **6** [Yb(CHR$_2$)(OR′)(OEt$_2$)$_2$] | C$_6$H$_5$Me | 293 | 744 | Doublet | 30 | 11(*a*) |
| **7** [Yb(CHR$_2$)$_2$(tmen)] | C$_6$H$_6$ | 304 | 1068 | 25 | — | This work |
| **8** [{Yb(CHR$_2$)(OEt$_2$)}$_2$C$_6$H$_4$(NR)$_2$-1,4] | OEt$_2$ | 298 | 596 | — | — | This work |
| **9** [Yb(NR$_2$)$_2${NC$_5$H$_4$(CH$_2$R)-2}$_3$] | C$_6$H$_6$ | 304 | 880 | 450 | — | This work |
| **10** [Yb(NR$_2$)$_2${NC$_5$H$_4$(CHR$_2$)-2}$_2$] | C$_6$H$_6$ | 304 | 819 | 550 | — | This work |
| **11** [Yb{NC$_5$H$_4$(CHR)-2}$_2$(dme)] | thf | 304 | 770 | 80 | — | This work |
| **12** [K{Yb[NC$_5$H$_4$(CHR)-2]$_3$}(dme)$_2$] | dme | 223 | 690 | 30 | — | This work |
| **I** [{Yb(NR$_2$)(μ-NR$_2$)}$_2$] | C$_6$H$_6$ | 304 | 779 | 200 | — | 1 |
| **VIII** [Yb(NR$_2$)$_2$(py)$_2$] | py | 213 | 919 | 60 | — | 1 |

[a] Spectra were recorded at 43.77 (for complexes **7**, **9**–**12**, **I** and **VIII**), 63.01 (for **1**, **3**, **4** and **6**) or 87.5 MHz (for **5** and **8**) relative to [Yb(η-C$_5$Me$_5$)$_2$(thf)$_2$] in 10% C$_6$D$_5$CD$_3$ at 273 K.[15] [b] 10–20% v/v C$_6$D$_6$ or C$_6$D$_5$CD$_3$ was used as lock.

(C, H) analysis. Complex **2** may be isostructural with its isoelectronic X-ray characterised amide [(R$_2$N)Yb(μ-NR$_2$)$_2$Na] **II**.[16] Compound **2** was stable at −30 °C but slowly decomposed at room temperature. The $^{29}$Si-{$^1$H} NMR spectrum of freshly prepared **2** showed a signal at δ 0.1. After 1 month it had partially decomposed; the $^{29}$Si-{$^1$H} NMR spectrum showed two signals at δ 0.08 and δ −10.77. The latter was broad, which is attributed to the paramagnetic effect of the decomposition products, as is the failure to observe the $^{171}$Yb-{$^1$H} NMR signal of **2**.

The compound [Yb(OR′)$_2$(OEt$_2$)$_2$] **III** (R′ = C$_6$H$_2$Bu$^t_2$-2,6-Me-4)[17] was treated with 2 equivalents of K(CHR$_2$) in diethyl ether; the reaction was monitored by $^{171}$Yb-{$^1$H} NMR spectroscopy (Table 1). The proton-coupled spectrum indicated that there were two ytterbium(II) species present in solution, a doublet and triplet pattern being observed at δ 744 and 1035, respectively. These multiplicities are assigned to $^2J$($^{171}$Yb–$^1$H) = 30 Hz. The signals are assigned to the bis(alkyl) [Yb(CHR$_2$)$_2$(OEt$_2$)$_2$] **1** (triplet) and the mixed alkyl–phenoxide [Yb(CHR$_2$)(OR′)(OEt$_2$)$_2$] **6** (doublet). It is assumed that in **6**, as in the case of **III**, there are two diethyl ether ligands, equation (3).

$$\underset{\textbf{III}}{[\mathrm{Yb(OR')_2(OEt_2)_2}]} + 2\mathrm{K(CHR_2)} \xrightarrow{\mathrm{OEt_2}} \underset{\textbf{1}}{[\mathrm{Yb(CHR_2)_2(OEt_2)_2}]} + \underset{\textbf{6}}{[\mathrm{Yb(CHR_2)(OR')(OEt_2)_2}]} + \mathrm{KOR'} \quad (3)$$

The $^2J$($^{171}$Yb–$^1$H) and reduced ($^2k$) spin–spin coupling constant of 30 Hz may be compared with such data for other $^2J$($^x$M–$^1$H) couples (obtained for MPr$^n_n$),[18] $^2J$($^x$M–$^1$H)[$^2k$ ($^x$M–$^1$H)(× 10$^{19}$ N m$^3$A$^{-2}$)]: $^x$M = $^{171}$Yb 30 [14.1], $^{113}$Cd 52 [20.7], $^{119}$Sn 49 [10.9], $^{199}$Hg 95 [44.2] and $^{207}$Pb 40 Hz [15.8].

The mixed ytterbium(II) alkyl–phenoxide [Yb(CHR$_2$)(OR′)(thf)$_3$] **3** was obtained when [Yb(OR′)$_2$(thf)$_3$][17] was treated with 1 equivalent of K(CHR$_2$) in thf. The formulation is consistent with the analytical data. A singlet was observed at δ 725 in its $^{171}$Yb-{$^1$H} NMR spectrum (Table 1).

The reaction of [Yb(η-C$_5$Me$_5$)$_2$(OEt$_2$)][14] with 2 equivalents of Li(CHR$_2$) in diethyl ether afforded a red oil, which was dissolved in toluene and excess of tmen; the isolated product was [Yb(CHR$_2$)$_2$(tmen)] **7**, equation (4). Attempts to obtain crystalline material were unsuccessful. The $^{171}$Yb-{$^1$H} NMR signal of **7** was observed at a slightly higher frequency (δ 1068) than that for [Yb(CHR$_2$)$_2$(OEt$_2$)$_2$] **1** (Table 1). A similar route had previously been employed in the preparation of the alkaline-earth-metal complexes [M(CHR$_2$)$_2$(thf)$_3$] complexes (M = Ca or Sr).[19]

$$[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})_2(\mathrm{OEt_2})] + 2\mathrm{Li(CHR_2)} + \mathrm{tmen} \xrightarrow{\mathrm{OEt_2}} \underset{\textbf{7}}{[\mathrm{Yb(CHR_2)_2(tmen)}]} + 2\mathrm{Li(C_5Me_5)} \quad (4)$$

*Reactions of* [Yb(CHR$_2$)$_2$(OEt$_2$)$_2$] **1**.—The substitution lability of the ether ligands in complex **1** was demonstrated by their displacement by the chelating 1,2-bis(dimethylphosphino)ethane. One equivalent of dmpe with **1** in toluene yielded [Yb(CHR$_2$)$_2$(dmpe)] **4**, equation (5). Compound **4** was characterised by NMR [$^{13}$C-{$^1$H}, $^{31}$P-{$^1$H}, $^{171}$Yb-{$^1$H}] spectroscopy. The $^{171}$Yb-{$^1$H} NMR resonance was observed at somewhat higher frequency (δ 1231) than that of **1** or **7** (Table 1). The broad signal ($w_{\frac{1}{2}}$ = 260 Hz) indicates that the dmpe ligand in **4** was undergoing rapid dissociation–association.

$$\underset{\textbf{1}}{[\mathrm{Yb(CHR_2)_2(OEt_2)_2}]} + \mathrm{dmpe} \longrightarrow \underset{\textbf{4}}{[\mathrm{Yb(CHR_2)_2(dmpe)}]} + 2\mathrm{OEt_2} \quad (5)$$

The reaction of two molar portions of complex **1** with one of C$_6$H$_4$(NHR)$_2$-1,4 in diethyl ether afforded [{Yb(CHR$_2$)(OEt$_2$)}$_2$C$_6$H$_4$(NR)$_2$-1,4] **8** as a brown solid, equation (6).

$$2\underset{\textbf{1}}{[\mathrm{Yb(CHR_2)_2(OEt_2)_2}]} + \mathrm{C_6H_4(NHR)_2\text{-}1,4} \xrightarrow{\mathrm{OEt_2}} \underset{\textbf{8}}{[\{\mathrm{Yb(CHR_2)(OEt_2)}\}_2\mathrm{C_6H_4(NR)_2\text{-}1,4}]} + 2\mathrm{CH_2R_2} \quad (6)$$

Compound **8** was characterised by NMR [$^1$H, $^{29}$Si-{$^1$H}, $^{171}$Yb-{$^1$H} (Table 1)] spectroscopy. There were two equal-intensity $^{29}$Si-{$^1$H} NMR signals at δ −22.01 and −17.05, confirming that there are two different SiMe$_3$ groups in the molecule.

*Synthesis and Characterisation of* [{Yb(CR$_3$)(μ-OEt)(OEt$_2$)}$_2$] **5**.—The reaction of YbI$_2$ with 2 equivalents of K(CR$_3$) in diethyl ether at room temperature yielded orange-red crystals of [{Yb(CR$_3$)(μ-OEt)(OEt$_2$)}$_2$] **5** rather than the expected [Yb(CR$_3$)$_2$] or [Yb(CR$_3$)$_2$(OEt$_2$)$_n$]. The $^-$OEt moiety may have resulted from the cleavage of OEt$_2$ by either K(CR$_3$) or [Yb(CR$_3$)$_2$], equations (7)–(10). Dialkyl ethers are known readily to be cleaved by the heavier boron trihalides, *e.g.* BCl$_3$. It may be that K(CR$_3$) or [Yb(CR$_3$)$_2$] has sufficient ionic

**Table 2** Selected intramolecular distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for [{Yb($CR_3$)(μ-OEt)($OEt_2$)}$_2$] **5**

| | | | |
|---|---|---|---|
| Yb···Yb | 3.531(1) | Yb–O(1) | 2.267(10) |
| Yb–O(1′) | 2.276(10) | Yb–O(2) | 2.479(13) |
| Yb–C(1) | 2.573(13) | O(1)–C(11) | 1.33(2) |
| O(2)–C(13) | 1.80(4) | O(2)–C(15) | 1.58(4) |
| C(11)–C(12) | 1.44(3) | C(13)–C(14) | 1.06(6) |
| C(15)–C(16) | 1.11(5) | | |
| O(1)–Yb–O(1′) | 78.0(4) | O(1)–Yb–O(2) | 105.4(4) |
| O(1)–Yb–C(1) | 120.7(4) | O(1′)–Yb–O(2) | 106.7(4) |
| O(1′)–Yb–C(1) | 123.4(4) | O(2)–Yb–C(1) | 116.1(4) |
| Yb–O(1)–Yb′ | 102.0(4) | Yb–O(1)–C(11) | 120.9(8) |
| Yb′–O(1)–C(11) | 137.1(9) | Yb–O(2)–C(13) | 121(1) |
| Yb–O(2)–C(15) | 120(1) | C(13)–O(2)–C(15) | 104(2) |
| Yb–C(1)–Si(1) | 108.8(6) | Yb–C(1)–Si(2) | 102.5(6) |
| Yb–C(1)–Si(3) | 107.6(6) | Si(1)–C(1)–Si(2) | 111.9(8) |
| Si(1)–C(1)–Si(3) | 114.0(8) | Si(2)–C(1)–Si(3) | 111.4(8) |
| O(1)–C(11)–C(12) | 119(1) | O(2)–C(13)–C(14) | 91(3) |
| O(2)–C(15)–C(16) | 123(3) | | |

Primed atoms are related by $-x$, $-y$, $-z$.

**Table 3** Fractional atomic coordinates with e.s.d.s in parentheses for [{Yb($CR_3$)(μ-OEt)($OEt_2$)}$_2$] **5**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Yb | 0.003 47(8) | 0.063 43(4) | 0.087 15(4) |
| Si(1)[a] | 0.013 2(8) | −0.073 4(4) | 0.258 8(3) |
| Si(2)[a] | −0.234 2(6) | 0.050 6(4) | 0.247 2(4) |
| Si(3)[a] | 0.066 2(7) | 0.110 5(4) | 0.296 6(4) |
| O(1) | 0.147 6(11) | −0.019 4(6) | 0.013 5(6) |
| O(2) | 0.073 5(14) | 0.207 8(8) | 0.053 1(7) |
| C(1) | −0.036 7(15) | 0.033 5(8) | 0.237 8(8) |
| C(2) | −0.080 6(24) | −0.120 8(14) | 0.353 3(13) |
| C(3) | −0.029 4(22) | −0.144 9(13) | 0.176 6(12) |
| C(4) | 0.215 5(25) | −0.081 3(14) | 0.279 5(14) |
| C(5) | −0.297 3(26) | 0.142 0(15) | 0.181 2(14) |
| C(6) | −0.301 3(27) | 0.070 5(15) | 0.350 9(15) |
| C(7) | −0.337 7(26) | −0.044 5(15) | 0.203 9(14) |
| C(8) | 0.252 0(24) | 0.126 7(15) | 0.255 5(13) |
| C(9) | −0.014 1(26) | 0.220 1(15) | 0.291 7(14) |
| C(10) | 0.107 4(26) | 0.083 9(14) | 0.395 9(14) |
| C(11) | 0.284 4(16) | −0.029 8(9) | 0.034 4(8) |
| C(12) | 0.336 5(26) | −0.112 3(16) | 0.052 0(14) |
| C(13) | −0.054 1(41) | 0.280 1(24) | 0.009 9(24) |
| C(14) | −0.034 4(45) | 0.322 5(28) | 0.057 6(27) |
| C(15) | 0.214 4(37) | 0.223 7(22) | 0.004 0(22) |
| C(16) | 0.322 8(36) | 0.216 7(21) | 0.031 5(20) |
| Si(1a)[b] | −0.117 9(36) | −0.069 5(21) | 0.242 7(18) |
| Si(2a)[b] | −0.151 1(39) | 0.116 3(21) | 0.267 6(19) |
| Si(3a)[b] | 0.151 5(40) | 0.040 2(21) | 0.295 6(20) |

[a] Occupancy 0.9. [b] Occupancy 0.1.

**Table 4** Crystal data for [{Yb($CR_3$)(μ-OEt)($OEt_2$)}$_2$] **5**

| | |
|---|---|
| Formula | $C_{32}H_{84}O_4Si_6Yb_2$ |
| *M* | 1047.6 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ (no. 14) |
| *a*/Å | 9.358(8) |
| *b*/Å | 16.069(11) |
| *c*/Å | 16.547(12) |
| β/° | 91.12(6) |
| *Z* | 2 |
| $U$/Å$^3$ | 2487.6 |
| $D_c$/g cm$^{-3}$ | 1.40 |
| *F*(000) | 4825 |
| *N* (total unique) | 4551 |
| $N_o$ (observed) | 2655 |
| $\mu_{Mo}$/cm$^{-1}$ | 38.9 |
| Specimen/mm | 0.3 × 0.3 × 0.2 |
| *R* | 0.072 |
| *R*′ | 0.080 |
| *S* | 2.1 |
| Absorption corrections, maximum, minimum | 1.24, 0.64 |
| Weighting scheme employed (*w*) | $1/\sigma^2(F)$ |

$$YbI_2 + 2K(CR_3) \longrightarrow [Yb(CR_3)_2] + 2KI \qquad (7)$$

$$[Yb(CR_3)_2] \xrightarrow{OEt_2} \tfrac{1}{2}[\{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)\}_2] + CHR_3 + CH_2CH_2 \qquad (8)$$

5

$$K(CR_3) + OEt_2 \longrightarrow CHR_3 + CH_2CH_2 + KOEt \qquad (9)$$

$$YbI_2 + K(CR_3) + KOEt \xrightarrow{OEt_2} \tfrac{1}{2}[\{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)\}_2] + 2KI \qquad (10)$$

5

character for $K^+$ or $Yb^{2+}$ to behave as such a Lewis acid. Alternatively $OEt_2$ cleavage by $YbI_2$ or Yb($CR_3$)I cannot be ruled out.

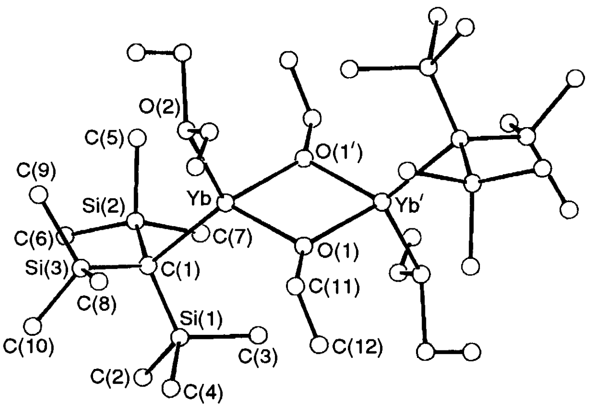


**Fig. 1** Molecular structure of [{Yb($CR_3$)(μ-OEt)($OEt_2$)}$_2$] **5** and atom numbering scheme

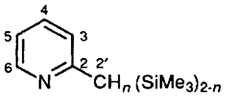
Compound **5** was characterised by elemental (C, H) analysis, NMR [$^1$H, $^{13}$C-{$^1$H}, $^{171}$Yb-{$^1$H} (Table 1)] spectroscopy and X-ray crystallography. Reaction of $YbI_2$ with an equimolar portion of K($CR_3$) in diethyl ether at room temperature also afforded **5**, rather than the expected [{Yb($CR_3$)(μ-I)($OEt_2$)}$_2$].

Subsequently, our colleagues have prepared and characterised crystallographically [Yb($CR_3$)$_2$] **IV** [from $YbI_2$ + 2 K($CR_3$) in $C_6H_6$] and [{Yb($CR_3$)(μ-I)($OEt_2$)}$_2$] **V** (from **IV** and an excess of MeI or $ICH_2CH_2I$ in $OEt_2$), and shown that **V** reacts with $OEt_2$ to yield **5**.[11c]

*Crystal Structure of* [{Yb($CR_3$)(μ-OEt)($OEt_2$)}$_2$] **5**.—The molecular structure and atom numbering scheme for compound **5** are shown in Fig. 1; selected bond lengths and angles are in Table 2, fractional atomic coordinates in Table 3 and the crystal data and refinement parameters in Table 4.

The structure reveals an ethoxo-bridged dimer, with each ytterbium atom in a distorted-tetrahedral geometry. The molecule lies across a crystallographic inversion centre. The central YbOYbO ring is planar, as in [{Yb(OR′)(μ-OR′)}$_2$] **VI**, but unlike that in [{Yb($NR_2$)(μ-OCBu$^t_3$)}$_2$] **VII**.[20] The Yb–C distance, 2.573(13) Å, is slightly longer than in **IV** [2.490(8) and 2.501(9) Å] or **V** [2.47(2) Å].[11c] The Yb–OEt bond lengths in **5** [average 2.27(1) Å] are comparable to those for Yb–OR′$_{br}$ in **VI** [average 2.28(2) Å] and Yb–O in **VII** [average 2.31(1) Å]. The endocyclic angles are O–Yb–O 78.0(4)° in **5**, average 79.6(6)° in **VI** and 84.1(7)° in **VII**, and Yb–O–Yb 102.0(4)° in **5**, average 100.4(7) in **VI** and 93.3(2)° in **VII**.

**Table 5** Proton NMR spectral chemical shifts (δ)



$n = 1$ or 0

| Compound | $SiMe_3$ | 2′ | 3 | 4 | 5 | 6 | Ref. |
|---|---|---|---|---|---|---|---|
| $NC_5H_4(CH_2R)$[a] | −0.05 | 2.10 | 6.80 | 7.25 | 6.80 | 8.35 | 12(*i*) |
| $NC_5H_4(CHR_2)$[a] | −0.07 | 2.20 | 6.70 | 7.38 | 6.70 | 8.25 | 12(*i*) |
| **9**[b] | 0.00 ($NR_2$)<br>0.32 ($CH_2R$) | 1.57 | 6.45 | 7.4 | 6.45 | 8.3 | This work |
| **10**[b] | 0.06 ($NR_2$)<br>0.13 ($CHR_2$) | 1.67 | 6.49 | 6.98 | 6.54 | 8.40 | This work |
| **11**[b] | 0.28 | 2.30 | 6.55 | 7.02 | 6.62 | 8.46 | This work |
| **12**[b] | 0.31 | 2.20 | 5.55 | 6.57 | 6.30 | 7.32 | This work |

[a] Recorded in $CDCl_3$; δ calibrated with respect to $SiMe_4$. [b] Recorded in $C_6D_6$ at 250.13 MHz (**9**) at 304 K, in $C_6D_6$ at 360.13 MHz (**10** and **11**) at 293 K or in $C_6D_5CD_3$ at 360.13 MHz (**12**) at 293 K; δ calibrated with respect to internal solvent.

**Table 6** The $^{13}C$ NMR spectral chemical shifts (δ) (for atom numbering see Table 5)

| Compound | $SiMe_3$ | 2′ | 2 | 3 | 4 | 5 | 6 | Ref. |
|---|---|---|---|---|---|---|---|---|
| $NC_5H_4(CH_2R)$-2[a] | −1.8 | 30.0 | 161.3 | 121.9 | 135.6 | 119.0 | 148.9 | 12(*i*) |
| $NC_5H_4(CHR_2)$-2[a] | 0.0 | 33.4 | 164.4 | 122.8 | 135.5 | 118.0 | 149.2 | 12(*i*) |
| **9**[b] | 0.38 ($NR_2$)<br>6.07 ($CH_2R$) | 22.64 | 164.64 | 123.05 | 135.01 | 118.31 | 149.16 | This work |
| **10**[b] | 0.44 ($NR_2$)<br>5.80 ($CHR_2$) | 33.51 | 164.69 | 123.21 | 135.59 | 118.46 | 149.05 | This work |
| **11**[b] | 1.03 | 41.30 | 161.84 | 122.32 | 135.68 | 119.36 | 149.52 | This work |
| **12**[b] | 1.92 | 61.39 | 167.96 | 119.55 | 132.59 | 114.98 | 149.59 | This work |

[a] Recorded in $CDCl_3$; δ calibrated with respect to $SiMe_4$. [b] Recorded in $C_6D_6$ at 62.90 MHz (**9**) at 304 K, in $C_6D_6$ at 125.76 MHz (**10** and **11**) at 293 K or in $C_6D_5CD_3$ at 125.76 MHz (**12**) at 293 K; δ calibrated with respect to internal solvent.

*Lewis-base Adducts of* $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I**.—Four equivalents of $NC_5H_4(CH_2R)$-2 or $NC_5H_4(CHR_2)$-2 with $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I**[13] in hexane at ambient temperature afforded $[Yb(NR_2)_2\{NC_5H_4(CH_2R)\text{-}2\}_2]$ **9** or $[Yb(NR_2)_2\{NC_5H_4(CHR_2)\text{-}2\}_2]$ **10**, respectively, in an almost quantitative yield, equation (11). It was evident from the NMR

$$\underset{\mathbf{I}}{[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]} + 4NC_5H_4(CHXR)\text{-}2 \xrightarrow{\text{hexane}} 2[Yb(NR_2)_2\{NC_5H_4(CHXR)\text{-}2\}_2] \quad (11)$$

$$X = H\ \mathbf{9} \text{ or } R\ \mathbf{10}$$

[$^1H$ (Table 5), $^{13}C\text{-}\{^1H\}$ (Table 6) and $^{29}Si\text{-}\{^1H\}$ (see Experimental section), $^{171}Yb\text{-}\{^1H\}$ (Table 1)] spectra that **9** and **10** were the Lewis-base adducts of the ytterbium(II) amide. There was no evidence for protolytic ligand exchange, indicating that $NC_5H_4(CH_2R)$-2 and $NC_5H_4(CHR_2)$-2 are weaker Brønsted acids than $NH(SiMe_3)_2$. Complex **10** was also obtained when 2 equivalents of the pyridine derivative were allowed to react with **I** in toluene under reflux for 8 h.

The signals in the $^1H$ and $^{13}C\text{-}\{^1H\}$ NMR spectra of complexes **9** and **10** corresponding to the carbon atoms bearing the $Me_3Si$ groups were shifted to lower frequency compared with those of the free pyridine derivatives; the signals for the pyridyl protons remained largely unshifted (Tables 5 and 6). The $^{171}Yb$ NMR spectral data (Table 1) showed high-frequency shifts for **9** and **10** compared with **I**, due to the co-ordination of two pyridyl groups at the ytterbium centre. A similar $^{171}Yb$ shift was observed for $[Yb(NR_2)_2(py)_2]$ **VIII** (py = pyridine) compared with **I** (Table 1).[15]

*Synthesis and Characterisation of* $[\overline{Yb\{NC_5H_4(C}HR)\text{-}2\}_2(dme)]$ **11** *and* $[K\{\overline{Yb[NC_5H_4(C}HR)\text{-}2]_3\}(dme)_2]$ **12**.—The reaction of $YbI_2$ with 2 equivalents of $[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]$ in diethyl ether, followed by crystallisation from dme, afforded maroon crystals of $[\overline{Yb\{NC_5H_4(C}HR)\text{-}2\}_2(dme)]$ **11** equation (12). When $YbI_2$ was treated with 3 equivalents of $[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]$ in dme maroon crystals of $[K\{\overline{Yb[NC_5H_4(C}HR)\text{-}2]_3\}(dme)_2]$ **12** were obtained from diethyl ether, equation (13). Complexes **11** and

$$YbI_2 + 2[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)] \xrightarrow{OEt_2} \underset{\mathbf{11}}{[\overline{Yb\{NC_5H_4(C}HR)\text{-}2\}_2(dme)]} + 2KI \quad (12)$$

$$YbI_2 + 3[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)] \xrightarrow{dme} \underset{\mathbf{12}}{[K\{\overline{Yb[NC_5H_4(C}HR)\text{-}2]_3\}(dme)_2]} + 2KI \quad (13)$$

**12** were characterised by NMR [$^1H$ (Table 5), $^{13}C\text{-}\{^1H\}$ (Table 6) and $^{29}Si\text{-}\{^1H\}$ (see Experimental section), $^{171}Yb\text{-}\{^1H\}$ (Table 1)] spectroscopy and elemental (C, H, N) analysis. The $^1H$ NMR spectra at ambient temperature showed a low-frequency shift for the pyridyl ring protons relative to $NC_5H_4(CH_2R)$-2 (Table 5). The signals corresponding to the carbon atoms bearing the $Me_3Si$ groups showed little deviation from those observed for the free pyridine derivative (Table 5). The $^1H$ NMR spectra showed the presence of one molecule of dme in **11** and two in **12**. A variable-temperature $^1H$ NMR spectral study showed that the $Me_3Si$ groups became inequivalent at low temperature. The $^1H$ NMR (250.13 MHz) spectrum of **12** in $C_6D_5CD_3$ showed that the $Me_3Si$ groups coalesced at $T_c = 238 \pm 1$ K. Determination of the corresponding $\Delta G^\ddagger$ was hampered by the insolubility of **12** in $C_6D_5CD_3$ at low temperature, making it impracticable to measure δ(ν). The fluxional behaviour is believed to arise from terminal–bridging $NC_5H_4(CHR)$ site exchange. The signals for the $Me_3Si$ groups shifted to higher frequency at lower temperature. This is attributed to a second fluxional process, believed to arise from site exchange of co-ordinating and non-co-ordinating pyridyl groups.

The $^{13}C$-{$^1H$} NMR spectra of complexes **11** and **12** were unexceptional. The signals for the carbon atoms ($C\alpha$) bearing the $Me_3Si$ group were shifted to higher frequency compared with those for $NC_5H_4(CH_2R)$-2 (Table 6). This is consistent with data for a number of deprotonated methyl-substituted pyridines,[21] which were attributed to delocalisation of the negative charge and increased p character of the α-carbon atom. The $^{13}C$ NMR spectrum of **11** showed a doublet at δ 41.30 with $^1J_{CH}$ = 122.49 Hz. This value is unexceptional for an $sp^3$-hybridised carbon atom. The pyridyl ring resonances remained largely unshifted in the $^{13}C$-{$^1H$} NMR spectra of **11** and **12** (Table 6).

The $^{171}Yb$-{$^1H$} NMR resonances of complexes **11** (at 304 K) and **12** (at 223 K) were observed at relatively low frequency compared with those for $[Yb(CHR_2)_2(OEt_2)_2]$ **1** and $[Yb(CHR_2)_2(dmpe)]$ **4** (Table 1). No $^{171}Yb$-{$^1H$} NMR signal for **12** was observed at 304 K. This may be due to the fluxional behaviour of the $NC_5H_4(CHR)$-2 ligands at ambient temperature.

Other previously reported heterobimetallic ytterbium(II) complexes include $[(R_2N)Yb(\mu\text{-}NR_2)_2Na]$ **II**,[16] $[Li\{Yb(NR_2)_3\}(tmen)]$[1] and $[Yb(CHR_2)_3Na]$ **2**. Complex **12** may be isostructural with that of the crystallographically characterised amide **II**.[16]

## Experimental

*General.*—All manipulations were carried out under vacuum or in a stream of argon by Schlenk techniques. Solvents were dried and distilled over potassium–sodium alloy under argon prior to use. The following compounds were prepared by known procedures: $YbI_2$,[14] $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I**,[13] $[Yb(OR')_2(OEt_2)_2]$ **III**,[17] $[Yb(OR')_2(thf)_3]$,[17] $[Yb(\eta\text{-}C_5Me_5)_2(OEt_2)]$,[14] $Li(CHR_2)$,[22] $Na(CHR_2)$,[23] $K(CHR_2)$,[23] $K(CR_3)$,[24] $NC_5H_4(CH_2R)$-2[12i] and $NC_5H_4(CHR_2)$-2.[12i] *N,N,N′,N′*-Tetramethylethylenediamine (tmen) was obtained from Aldrich and distilled from KOH.

Microanalyses were carried out by Medac Ltd., Uxbridge, Middlesex. The NMR spectra were recorded using Bruker WP-80, AC-250, WM-360 or AMX-500 spectrometers and mass spectra using a VG Autospec instrument. Melting points are uncorrected and were determined under argon in sealed capillary tubes using an Electrothermal apparatus.

*Syntheses.*—$[Yb(CHR_2)_2(OEt_2)_2]$ **1**. A colourless solution of $Na(CHR_2)$ (1.14 g, 6.28 mmol) in $OEt_2$ (50 $cm^3$) was added to a yellow suspension of $YbI_2$ (1.34 g, 3.14 mmol) in $OEt_2$ (100 $cm^3$) at 25 °C. The mixture was stirred for 24 h, leaving a red-orange solution and a white precipitate. After filtration, the filtrate was concentrated to *ca.* 5 $cm^3$ and cooled to −30 °C, affording red-orange crystals of complex **1** (1.0 g, 1.6 mmol, 50%). NMR: $^1H$ ($C_6D_6$, 360.13 MHz, 20 °C), δ −1.55 (s, 1 H, C*H*SiMe$_3$), 0.34 (s, 18 H, $SiMe_3$), 0.95 (br s, 6 H, $OCH_2$*Me*) and 3.36 (br s, 4 H, OC*H*$_2$Me); $^{13}C$ ($C_6D_6$, 62.90 MHz, 25 °C), δ 6.15 (q, $^1J_{CH}$ = 116.3, $SiMe_3$), 14.11 (q, $^1J_{CH}$ = 126.5, $OCH_2$*Me*), 27.34 (d, $^1J_{CH}$ = 94.3, *C*HSiMe$_3$) and 64.64 (t, $^1J_{CH}$ = 148.8 Hz, O*C*H$_2$Me); $^{29}Si$-{$^1H$} ($OEt_2$–$C_6D_6$, 49.70 MHz, 25 °C), δ −7.8 ($SiMe_3$).

$[Yb(CHR_2)_3Na]$ **2**. Hexane (100 $cm^3$) was added to a mixture of solid $YbI_2$ (0.87 g, 2.03 mmol) and $Na(CHR_2)$ (1.15 g, 6.1 mmol). The suspension was stirred at room temperature for 2 d, leaving a red-brown solution and a pale yellow precipitate. After filtration, the filtrate was concentrated to *ca.* 5 $cm^3$. Cooling to −30 °C afforded red-brown crystals of complex **2** (0.65 g, 0.97 mmol, 48%) (Found: C, 37.1; H, 8.40. $C_{21}H_{57}NaSi_6Yb$ requires C, 37.4; H, 8.50%). NMR: $^1H$ ($C_6D_6$, 360.13 MHz, 20 °C), δ −1.78 (s, C*H*SiMe$_3$) and 0.29 (s, $SiMe_3$); $^{29}Si$-{$^1H$} ($C_6H_{14}$–$C_6D_6$, 49.70 MHz, 25 °C), δ 0.1 ($SiMe_3$).

*Mixture of* $[Yb(CHR_2)_2(OEt_2)_2]$ **1** *and* $[Yb(CHR_2)(OR')(OEt_2)_2]$ **6**. Solid $K(CHR_2)$ (1.1 g, 5.5 mmol) was added to a stirring solution of $[Yb(OR')_2(OEt_2)_2]$ **III** (2.1 g, 2.75 mmol) in $OEt_2$ (30 $cm^3$) at 0 °C. An immediate change from red-orange to brown was noted as the $K(CHR_2)$ was added. The reaction mixture was stirred for 30 min at 0 °C and then allowed to warm to room temperature. The solvent volume was reduced to *ca.* 15 $cm^3$ and a white solid was isolated at −30 °C. A portion of the reaction mixture was placed in a NMR spectral tube and its $^{171}Yb$ NMR spectrum recorded. The latter showed a triplet and doublet pattern, assigned to complexes **1** and **6**, respectively.

$[Yb(CHR_2)(OR')(thf)_3]$ **3**. Solid $K(CHR_2)$ (0.51 g, 2.6 mmol) was added to a stirring solution of $[Yb(OR')_2(thf)_3]$ (2.12 g, 2.6 mmol) in toluene (20 $cm^3$) at 0 °C. A change from yellow-orange to brown was noted. The toluene was removed *in vacuo*, the residue was taken up in hexane and a white precipitate was filtered off. The hexane was removed from the filtrate *in vacuo*. The residue of crude **3** was redissolved in the minimum of toluene (5 $cm^3$) and cooled (−30 °C). This yielded brown, microcrystalline **3** (0.49 g, 0.64 mmol, 25%) (Found: C, 51.2; H, 7.4. $C_{34}H_{66}O_4Si_2Yb$ requires C, 53.2, H, 8.65%).

$[Yb(CHR_2)_2(tmen)]$ **7**. A solution of $Li(CHR_2)$ (0.55 g, 3.30 mmol) in $OEt_2$ (5 $cm^3$) was added to $[Yb(\eta\text{-}C_5Me_5)_2(OEt_2)]$ (0.85 g, 1.65 mmol) in $OEt_2$ (40 $cm^3$) at −70 °C. The green suspension was stirred and slowly warmed to room temperature; a colour change to red was noted at *ca.* −70 °C. After stirring for 4 h at room temperature the solid was allowed to settle. The supernatant layer was decanted off and filtered. The volatiles were removed from the filtrate *in vacuo* to afford a red oil, which was dissolved in a mixture of toluene (20 $cm^3$) and tmen (1 $cm^3$) to give a red solution. Attempts to obtain crystalline material were unsuccessful. The volatiles were removed *in vacuo*, the residue was taken up in benzene (2.5 $cm^3$) and the solution transferred to a NMR spectral tube. $^{29}Si$-{$^1H$} NMR ($C_6H_6$–$C_6D_6$, 99.36 MHz, 25 °C): δ −8.16 ($SiMe_3$).

$[Yb(CHR_2)_2(dmpe)]$ **4**. The diphosphine dmpe (0.4 g, 2.7 mmol) was added to a toluene solution of $[Yb(CHR_2)_2(OEt_2)_2]$ **1** (1.9 g, 3.0 mmol) with stirring at −30 °C. An immediate change from brown to purple was noted. The solvent was removed *in vacuo* to yield a purple waxy solid. Recrystallisation from hexane afforded purple needles of complex **4** (0.43 g, 0.67 mmol, 25%). NMR ($C_6D_5CD_3$, 20 °C): $^{13}C$-{$^1H$} (62.90 MHz), δ 5.6 ($SiMe_3$), 13.3 [(*Me*$_2$PCH$_2$)$_2$] and 27.6 [(Me$_2$P*C*H$_2$)$_2$]; $^{31}P$-{$^1H$} (101.2 MHz), δ −42.6.

$[\{Yb(CHR_2)(OEt_2)\}_2C_6H_4(NR)_2\text{-}1,4]$ **8**. A solution of $C_6H_4(NHR)_2$-1,4 (0.25 g, 0.81 mmol) in $OEt_2$ (20 $cm^3$) was added to an orange solution of complex **1** (1.07 g, 1.67 mmol) in $OEt_2$ (50 $cm^3$). The mixture was stirred at room temperature for 24 h, changing to brown. The solvent was removed *in vacuo* to yield a brown solid, which was recrystallised from benzene to give dark brown microcrystalline complex **8** (0.65 g, 0.61 mmol, 75%). NMR: $^1H$ ($C_6D_6$, 360.13 MHz, 25 °C), δ 0.43 (s, 36 H, $SiMe_3$), 0.55 (s, 18 H, $SiMe_3$), 1.39 (br s, 24 H, $OCH_2$*Me*), 1.78 (s, 2 H, C*H*SiMe$_3$), 3.71 (br s, 16 H, OC*H*$_2$Me) and 6.85–7.12 (m, 4 H, $C_6H_4$); $^{29}Si$-{$^1H$} ($OEt_2$–$C_6D_6$, 49.70 MHz, 25 °C), δ −22.0 ($SiMe_3$) and −17.1 ($SiMe_3$).

$[\{Yb(CR_3)(\mu\text{-}OEt)(OEt_2)\}_2]$ **5**. A solution of $K(CR_3)$ (0.83 g, 3.07 mmol) in $OEt_2$ (20 $cm^3$) was added to a suspension of $YbI_2$ (0.65 g, 1.5 mmol) in $OEt_2$ (100 $cm^3$). The mixture was stirred at room temperature for 24 h, leaving an orange solution and a white precipitate which was filtered off. The filtrate was concentrated to *ca.* 10 $cm^3$ and cooled to −30 °C to yield orange crystals of complex **5** (0.5 g, 0.48 mmol, 63%) (Found: C, 35.1; H, 7.75. $C_{32}H_{84}O_4Si_6Yb_2$ requires C, 36.7; H, 8.10%). NMR: $^1H$ ($C_5D_5N$, 360.13 MHz, 25 °C), δ 0.11 (s, 27 H, $SiMe_3$), 1.10 (t, 6 H, $OCH_2$*Me*), 1.58 (br s, 3 H, μ-$OCH_2$*Me*), 3.33 (q, 4 H, OC*H*$_2$Me) and 3.36 (br s, 2 H, μ-C*H*$_2$Me); $^{29}Si$-{$^1H$} ($OEt_2$–$C_6D_6$, 49.70 MHz, 25 °C), δ −11.2 ($SiMe_3$).

$\mathrm{[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]}$. A yellow solution of $\mathrm{NC_5H_4(CH_2R)\text{-}2}$ (5.89 g, 35.6 mmol) in dme (20 cm$^3$) was added to a suspension of KH (1.36 g, 33.9 mmol) in dme (100 cm$^3$) at room temperature, yielding a brown suspension. The latter was stirred for 16 h, refluxed for 6 h and again stirred at room temperature for 14 h to give a dark red-brown solution. The mixture was filtered and the volatiles were removed from the filtrate *in vacuo*. The residual dark red oil was washed with pentane to give a dark red, impure (by $^1$H NMR spectroscopy) solid (9.5 g), which was dried *in vacuo* and recrystallised from $\mathrm{OEt_2}$ to yield orange crystals of $\mathrm{[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]}$ (4.0 g, 10.9 mmol, 32%). Mass spectrum (electron impact, EI): *m/z* 422 (4%). NMR: $^1$H ($\mathrm{C_5D_5N}$, 360.13 MHz, 20 °C), δ 0.23 (s, 9 H, $\mathrm{SiMe_3}$), 1.12 (t, 6 H, $\mathrm{OCH_2}\mathit{Me}$), 3.25 (s, 6 H, $\mathrm{CH_2O}\mathit{Me}$), 3.35 (q, 4 H, $\mathrm{OC}\mathit{H}_2\mathrm{Me}$), 3.48 (s, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{OMe}$), 6.25 (s, 1 H, $\mathrm{C}\mathit{H}\mathrm{SiMe_3}$), 6.61 (t, 1 H, $\mathrm{C_5H_4N}$), 7.10 (d, 1 H, $\mathrm{C_5H_4N}$), 7.30 (t, 1 H, $\mathrm{C_5H_4N}$) and 8.50 (d, 1 H, $\mathrm{C_5H_4N}$); $^{13}$C ($\mathrm{C_5D_5N}$, 62.90 MHz, 25 °C), δ 1.24 (q, $^1J_{\mathrm{CH}}$ = 117.2, $\mathrm{SiMe_3}$), 15.57 (q, $^1J_{\mathrm{CH}}$ = 125.47, $\mathrm{OCH_2}\mathit{Me}$), 58.74 (q, $^1J_{\mathrm{CH}}$ = 140.68, $\mathrm{CH_2O}\mathit{Me}$), 65.86 (t, $^1J_{\mathrm{CH}}$ = 137.55, $\mathrm{O}\mathit{C}\mathrm{H_2Me}$), 72.08 (t, $^1J_{\mathrm{CH}}$ = 141.66, $\mathit{C}\mathrm{H_2OMe}$), 110.95 (d, $^1J_{\mathrm{CH}}$ = 150.5, $\mathit{C}\mathrm{HSiMe_3}$), 115.98 (d, $^1J_{\mathrm{CH}}$ = 170.3, CH), 118.68 (d, $^1J_{\mathrm{CH}}$ = 163.2, CH), 123.86 (d, $^1J_{\mathrm{CH}}$ = 163.0, CH), 135.48 (d, $^1J_{\mathrm{CH}}$ = 159.0 Hz, CH) and 160.88 (s, C); $^{29}$Si-{$^1$H} ($\mathrm{C_6D_6}$, 49.70 MHz, 25 °C), δ − 5.36 ($\mathrm{SiMe_3}$).

$\mathrm{[Yb(NR_2)_2\{NC_5H_4(CH_2R)\text{-}2\}_2]}$ **9**. A hexane solution of $\mathrm{NC_5H_4(CH_2R)\text{-}2}$ (41.5 cm$^3$, 0.06 mol dm$^{-3}$, 2.5 mmol) was added to $\mathrm{[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]}$ **I** (0.60 g, 0.61 mmol) at room temperature. The resulting dark red suspension was stirred for 15 h. The volatiles were removed *in vacuo* and the dark brown, oily residue was extracted into pentane (30 cm$^3$). The extract was filtered and the pentane removed from the filtrate *in vacuo* to afford dark brown, sticky solid complex **9** (0.95 g, 1.15 mmol, 94%). NMR: $^1$H ($\mathrm{C_6D_6}$, 250.13 MHz, 31 °C), δ 0.00 [s, 36 H, $\mathrm{N(SiMe_3)_2}$], 0.32 (s, 18 H, $\mathrm{CH_2Si}\mathit{Me}_3$), 1.57 (br s, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 6.45 (br s, 4 H, $\mathrm{C_5H_4N}$), 7.4 (br s, 2 H, $\mathrm{C_5H_4N}$) and 8.3 (br s, 2 H, $\mathrm{C_5H_4N}$); $^{13}$C-{$^1$H} ($\mathrm{C_6H_6}$–$\mathrm{C_6D_6}$, 62.90 MHz, 25 °C), δ 0.38 (q, $\mathrm{SiMe_3}$), 6.07 (q, $\mathrm{SiMe_3}$), 22.64 (t, $\mathit{CH}_2\mathrm{SiMe_3}$), 118.31 (d, CH), 123.05 (d, CH), 135.01 (d, CH), 149.16 (d, CH) and 164.64 (s, C); $^{29}$Si-{$^1$H} ($\mathrm{C_6H_6}$–$\mathrm{C_6D_6}$, 49.70 MHz, 25 °C), δ −9.07 [$\mathrm{N(SiMe_3)_2}$] and 7.57 ($\mathrm{CH_2SiMe_3}$).

$\mathrm{[Yb(NR_2)_2\{NC_5H_4(CHR_2)\text{-}2\}_2]}$ **10**. A hexane solution (50 cm$^3$) of $\mathrm{NC_5H_4(CHR_2)\text{-}2}$ (0.55 g, 2.9 mmol) was added to complex **I** (0.55 g, 0.56 mmol) at room temperature. The resulting dark red suspension was stirred for 17 h. The volatiles were removed *in vacuo* and the dark brown, oily residue was extracted into pentane (20 cm$^3$). The extract was filtered and the pentane removed from the filtrate *in vacuo* to afford complex **10** as a red-brown oil (0.95 g, 1.09 mmol, 97%). NMR: $^1$H ($\mathrm{C_6D_6}$, 360.13 MHz, 20 °C), δ 0.06 [s, 36 H, $\mathrm{N(SiMe_3)_2}$], 0.13 [s, 36 H, $\mathrm{CH(Si}\mathit{Me}_3)_2$], 1.67 [br s, 2 H, $\mathrm{C}\mathit{H}\mathrm{(SiMe_3)_2}$], 6.49 (t, 2 H, $\mathrm{C_5H_4N}$) 6.54 (d, 2 H, $\mathrm{C_5H_4N}$), 6.98 (t, 2 H, $\mathrm{C_5H_4N}$) and 8.40 (br s, 2 H, $\mathrm{C_5H_4N}$); $^{13}$C-{$^1$H} ($\mathrm{C_6H_6}$–$\mathrm{C_6D_6}$, 125.76 MHz, 25 °C), δ 0.44 (q, $\mathrm{SiMe_3}$), 5.80 (q, $\mathrm{SiMe_3}$), 33.51 [d, $\mathit{C}\mathrm{H(SiMe_3)_2}$], 118.46 (d, CH), 123.21 (d, CH), 135.59 (d, CH), 149.05 (d, CH) and 164.69 (s, C); $^{29}$Si-{$^1$H} ($\mathrm{C_6H_6}$–$\mathrm{C_6D_6}$, 49.70 MHz, 25 °C), δ −11.94 [$\mathrm{N(SiMe_3)_2}$] and 5.21 [$\mathrm{CH(SiMe_3)_2}$].

$\mathrm{[Yb\{NC_5H_4(CHR)\text{-}2\}_2(dme)]}$ **11**. Diethyl ether (100 cm$^3$) was added to $\mathrm{[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]}$ (0.70 g, 2.05 mmol) and $\mathrm{YbI_2}$ (0.50 g, 1.17 mmol) at room temperature, yielding a red-brown suspension, which was stirred for 24 h. The volatiles were removed *in vacuo*. The brown solid residue was recrystallised from dme to yield maroon, crystalline complex **11** (0.45 g, 0.90 mmol, 88%) (Found: C, 42.1; H, 6.20; N, 4.30. $\mathrm{C_{22}H_{38}N_2O_2Si_2Yb}$ requires C, 44.6; H, 6.45; N, 4.75%). Mass spectrum (EI): *m/z* 816 (1%). NMR: $^1$H ($\mathrm{C_6D_6}$, 360.13 MHz, 20 °C), δ 0.28 (s, 18 H, $\mathrm{SiMe_3}$), 2.30 (s, 2 H, $\mathrm{C}\mathit{H}\mathrm{SiMe_3}$), 3.12 (s, 6 H, $\mathrm{CH_2O}\mathit{Me}$), 3.32 (s, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{OMe}$), 6.55 (t, 2 H, $\mathrm{C_5H_4N}$), 6.62 (d, 2 H, $\mathrm{C_5H_4N}$), 7.02 (t, 2 H, $\mathrm{C_5H_4N}$) and 8.46 (d, 2 H, $\mathrm{C_5H_4N}$); $^{13}$C ($\mathrm{C_4H_8O}$–$\mathrm{C_6D_5CD_3}$, 125.76 MHz, 25 °C), δ 1.03 (q, $^1J_{\mathrm{CH}}$ = 118.19, $\mathrm{SiMe_3}$), 41.30 (d, $^1J_{\mathrm{CH}}$ = 122.49, $\mathit{C}\mathrm{HSiMe_3}$), 58.55 (q, $^1J_{\mathrm{CH}}$ = 133.28, $\mathrm{CH_2O}\mathit{Me}$), 72.17 (t, $^1J_{\mathrm{CH}}$ = 128.14, $\mathit{C}\mathrm{H_2OMe}$), 119.36 (d, $^1J_{\mathrm{CH}}$ = 162.99, CH), 122.32 (d, $^1J_{\mathrm{CH}}$ = 162.51, CH), 135.68 (d, $^1J_{\mathrm{CH}}$ = 154.43, CH), 149.52 (d, $^1J_{\mathrm{CH}}$ = 174.46 Hz, CH) and 161.84 (s, C); $^{29}$Si-{$^1$H} ($\mathrm{C_4H_8O}$–$\mathrm{C_6D_5CD_3}$, 99.36 MHz, 25 °C), δ −18.64 ($\mathrm{CHSiMe_3}$).

$\mathrm{[K\{Yb[NC_5H_4(CHR)\text{-}2]_3\}(dme)_2]}$ **12**. 1,2-Dimethoxyethane (100 cm$^3$) was added to $\mathrm{[K\{NC_5H_4(CHR)\text{-}2\}(dme)(OEt_2)]}$ (2.0 g, 5.9 mmol) and $\mathrm{YbI_2}$ (0.75 g, 1.8 mmol) at room temperature, yielding a red-brown suspension. The latter was stirred for 64 h. The volatiles were removed *in vacuo* to afford a brown solid. Recrystallisation from diethyl ether yielded maroon, crystalline complex **12** (0.95 g, 1.07 mmol, 59%) (Found: C, 49.1; H, 7.15; N, 5.25. $\mathrm{C_{35}H_{62}KN_3O_4Si_3Yb}$ requires C, 47.5; H, 7.05; N, 4.75%), m.p. *ca.* 100 °C (decomp.). Mass spectrum (EI): *m/z* 497 (7%). NMR: $^1$H ($\mathrm{C_6D_5CD_3}$, 360.13 MHz, 20 °C), δ 0.31 (s, 27 H, $\mathrm{SiMe_3}$), 2.20 (s, 3 H, $\mathrm{C}\mathit{H}\mathrm{SiMe_3}$), 2.99 (s, 12 H, $\mathrm{CH_2O}\mathit{Me}$), 3.01 (s, 8 H, $\mathrm{C}\mathit{H}_2\mathrm{OMe}$), 5.55 (br s, 3 H, $\mathrm{C_5H_4N}$), 6.30 (d, 3 H, $\mathrm{C_5H_4N}$), 6.57 (m, 3 H, $\mathrm{C_5H_4N}$) and 7.32 (br s, 3 H, $\mathrm{C_5H_4N}$); $^{13}$C-{$^1$H} (dme–$\mathrm{C_6D_5CD_3}$, 125.76 MHz, 25 °C), δ 1.92 (q, $\mathrm{SiMe_3}$), 61.39 (d, $\mathit{C}\mathrm{HSiMe_3}$), 114.98 (d, CH), 119.55 (d, CH), 132.59 (d, CH), 149.59 (d, CH) and 167.96 (s, C); $^{29}$Si-{$^1$H} (dme–$\mathrm{C_6D_5CD_3}$, 99.36 MHz, 25 °C), δ −13.72 ($\mathrm{CHSiMe_3}$).

*X-Ray Crystallography for Compound* **5**.—Details are given in Table 4. An unique data set was collected, using a single crystal on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with monochromated Mo-Kα radiation (λ = 0.710 69 Å). Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarisation effects ($L_\mathrm{p}$) and also for absorption using DIFABS[25] after isotropic refinement. Reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_\mathrm{p}$ were considered to be observed. The structure was solved by the heavy-atom method using SHELXS 86[26] and refined by full-matrix least squares with Yb and Si atoms anisotropic, C and O atoms isotropic and H atoms at fixed positions. The $\mathrm{CR_3}$ group is disordered such that there are two sets of silicon positions in a ratio of 0.9 : 0.1; only the major sites are shown in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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