The synthesis and X-ray structures of ytterbocene(II) complexes containing pendant pyridyl groups, $[Yb(Cp^x)_2]$ $\{Cp^x = \eta^5\text{-}C_5H_3(R)[CMe_2(CH_2)_nC_5H_4N\text{-}2]\text{-}1,3;$ $R = H$ or $SiMe_3$ and $n = 0$ or $1\}$ *

Johannes R. van den Hende, Peter B. Hitchcock and Michael F. Lappert
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)

Terence A. Nile
Department of Chemistry, University of North Carolina, Greensboro, NC (USA)

(Received January 27, 1994)

Abstract

Metallation of $C_5H_5[C(Me)_2CH_2C_5H_4N\text{-}2]$ ($\equiv Cp^{py}H$), $C_5H_4(SiMe_3)\{C(Me)_2CH_2C_5H_4N\text{-}2\}\text{-}3]$ ($\equiv Cp'^{py}H$), $C_5H_5\text{-}[C(Me)_2C_5H_4N\text{-}2]$ ($\equiv Cp^{py(s)}H$), and $C_5H_4[(SiMe_3)\{C(Me)_2C_5H_4N\text{-}2\}\text{-}3]$ [$\equiv Cp'^{py(s)}H$] with KH in THF yielded the potassium complexes KCp^{py} (**1**), KCp'^{py} (**2**), $KCp^{py(s)}$ (**3**), or $KCp'^{py(s)}$ (**4**). Compounds **1–4** were readily converted into their homoleptic solvent-free ytterbium(II) complexes $[Yb(Cp^{py})_2]$ (**5**), $[Yb(Cp'^{py})_2]$ (**6**), $[Yb(Cp^{py(s)})_2]$ (**7**) and $[Yb(Cp'^{py(s)})_2]$ (**8**). The crystal structures of **5** and **8** show that both of the pyridyl groups in each complex are coordinated to the ytterbium. Some angles in **5** are Cp(1)–Yb–Cp(2) 137.7° and N(1)–Yb–N(2) 100.8(2)°, and the corresponding angles in **8** are Cp(1)–Yb–Cp(2) 136.9° and N(1)–Yb–N(2) 84.0(4)° (where Cp refers to the centroid of the cyclopentadienyl ring).

Key words: Ytterbium; Ytterbocene; Lanthanides; Functionalized cyclopentadienyls; Crystal structure

1. Introduction

Almost all the known lanthanide (Ln) complexes containing two cyclopentadienyl rings (lanthanocene complexes) have one to three additional ligands in the Ln^{n+} coordination sphere. This is consistent with the large size of the Ln^{2+} or Ln^{3+} radius. For many years no structurally characterized homoleptic lanthanocene(II) complex analogous to ferrocene was known.

The first monomeric unsolvated complexes of this type characterized by X-ray crystallography were those containing the pentamethylcyclopentadienyl ($\equiv \overline{C}p^*$) ligand. The solvent-free decamethyllanthanocene(II) complexes $LnCp^*_2$ (Ln = Sm, Eu, or Yb) were obtained by desolvation during sublimation of the corresponding tetrahydrofuran (THF) [1,2] or diethyl ether (OEt_2) [3] solvates. Other lipophilic, homoleptic lanthanocene(II) complexes to have been isolated were $Yb(\eta\text{-}C_5H_4R)_2$ ($R = SiMe_3$ [4] or ^tBu [5]) and $[(LnCp''_2)_\infty]$ $\{Cp'' = C_5H_3(SiMe_3)_2\text{-}1,3$ and Ln = Sm [6], Eu [7], or Yb [7]$\}$. X-Ray diffraction data on the latter two compounds showed that they (like the $LnCp^*_2$ analogues) were polymeric by virtue of weak intermolecular interactions, resulting in Ln^{2+} being three-coordinate; *e.g.* each $YbCp''_2$ unit and the methyl group of a neighbour had a close Yb $\cdots$ CH_3 contact [7].

An alternative means of obtaining homoleptic lanthanocene(II) complexes, which is central to the present paper, is to use an appropriate Lewis base-functionalized cyclopentadienyl ligand. In the literature compounds containing such ligands have been reported previously, namely $Sm[\eta\text{-}C_5Me_4(CH_2CH_2NMe_2)]_2$ [8] and $Ln[\eta\text{-}C_5H_4(CH_2CH_2OMe)]_2$ (Ln = Sm or Yb) [9],

Correspondence to: Professor M.F. Lappert.
* Dedicated to Professor H. Werner, as a mark of esteem and friendship on the occasion of his 60th birthday.

0022-328X/94/$7.00
SSDI 0022-328X(94)24590-F

but the crystal structures of these complexes are yet unknown. Ligands of this type already have a role in the chemistry of Ln^{III} complexes; the most recent examples relate to the X-ray characterized crystalline complexes $[Ln(\mu\text{-}L)L_2]$ [L = $C_5H_4(CH_2CH_2NMe_2)$ and Ln = La or Nd] [10].

We report below an approach to homoleptic lanthanocene(II) complexes using the following potentially bidentate cyclopentadienyl ligands containing a pendant pyridyl substituent: $[C_5H_4(CMe_2CH_2C_5H_4N\text{-}2)]^-$ (≡ $^-Cp^{py}$), $[C_5H_3(SiMe_3)(CMe_2CH_2C_5H_4N\text{-}2)\text{-}3]^-$ (≡ $^-Cp'^{py}$), $[C_5H_4(CMe_2C_5H_4N\text{-}2)]^-$ [≡ $^-Cp^{py(s)}$], and $[C_5H_3(SiMe_3)(CMe_2C_5H_4N\text{-}2)\text{-}3]^-$ [≡ $^-Cp'^{py(s)}$]. As a class, these ligands are not totally new, one of them having been employed in titanium(IV) chemistry [11].

2. Experimental details

2.1. Materials and procedures

All manipulations were carried out under vacuum or 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 [12], $Cp^{py}H$ [13], $Cp'^{py}H$ [13] and $Cp'^{py(s)}H$ [13], and $Cp'^{py(s)}H$ [13]. Microanalyses were carried out by Medac Ltd (Brunel University) or in the micro-analytical department of the University of Sussex. NMR Spectra were recorded using Bruker WM250, Bruker WM360 or Bruker WM500 spectrometers.

2.2. Synthesis of KCp^{py} (1)

A solution of $Cp^{py}H$ (4.50 g, 22.6 mmol) in THF (80 ml) was slowly added to a stirred suspension of KH (0.90 g, 22.4 mmol) in THF (40 ml) at −50°C. The suspension was stirred for 16 h while warming slowly to room temperature. Volatiles were removed *in vacuo* and the residue was washed with hexane (100 ml). After drying *in vacuo*, the white solid was shown to be **1** (4.15 g, 17.5 mmol, 80%). Anal. Found: C, 72.1; H, 7.04; N, 6.17. $C_{14}H_{16}KN$ calc.: C, 70.8; H, 6.79; N, 5.90%. NMR: ^1H (C_5D_5N, 20°C): δ 1.60 (s, 6H, CMe_2); 3.24 (s, 2H, CH_2); 6.00 (t, 2H, Cp-ring); 6.24 (t, 2H, Cp-ring); 6.97 (t, 1H, C_5H_4N); 7.21 (d, 1H, C_5H_4N); 7.49 (t, 1H, C_5H_4N); 8.45 (d, 1H, C_5H_4N). ^{13}C (C_5D_5N, 20°C); δ 31.86 (q, CMe_2); 37.01 (s, CMe_2); 55.70 (t, CH_2); 102.74 (d, CH); 103.89 (d, CH); 120.81 (d, CH); 125.79 (d, CH); 128.99 (s, C); 135.52 (d, CH); 148.22 (d, CH), 162.47 (s, C).

2.3. Synthesis of KCp'^{py} (2)

A solution of $Cp'^{py}H$ (17.9 g, 65.9 mmol) in THF (70 ml) was added to a stirred solution of KH (2.6 g, 64.8 mmol) in THF (30 ml) at −78°C. After 2 h stirring at −78°C, the suspension was allowed to warm to room temperature with stirring, stirred at that temperature for 60 h and then refluxed for 1.5 h. The solvent was removed *in vacuo*, yielding a white solid, which was washed with hexane (50 ml) and dried *in vacuo* to afford **2** (17.85 g, 57.7 mmol, 89%) as a white powder. Anal. Found: C, 66.0; H, 7.61; N, 4.65. $C_{17}H_{24}KNSi$ calc.: C, 66.0; H, 7.81; N, 4.52%. NMR: ^1H (C_4D_8O, 25°C): δ 0.02 (s, 9H, $SiMe_3$); 1.20 (s, 6H, CMe_2); 2.77 (s, 2H, CH_2); 5.1–5.7 (m, 3H, Cp-ring); 7.0–7.1 (m, 2H, C_5H_4N); 7.5–7.6 (m, 1H, C_5H_4N); 8.2–8.3 (m, 1H, C_5H_4N). ^{13}C (C_4D_8O, 25°C): δ 0.97 (q, $SiMe_3$); 30.95 (q, CMe_2); 35.94 (s, CMe_2); 54.57 (t, CH_2); 101.94 (d, CH); 102.87 (d, CH); 105.97 (d, CH); 108.43 (d, CH); 109.19 (s, C); 110.99 (d, CH); 120.34 (d, CH); 125.18 (d, CH); 128.19 (s, C); 131.52 (s, C); 135.01 (d, CH); 147.83 (d, CH); 161.38 (s, C). $^{29}Si\{^1H\}$ (C_5D_5N, 25°C); δ −14.63 ($SiMe_3$).

2.4. Synthesis of $KCp^{py(s)}$ (3)

A brown solution of $Cp^{py(s)}H$ (6.55 g, 35.3 mmol) in THF (100 ml) was added to a suspension of KH (1.37 g, 34.2 mmol) in THF (100 ml) at −78°C. After 0.5 h at −78°C, the suspension was slowly warmed to room temperature and stirred for 60 h. Volatiles were removed *in vacuo* and the residue was washed with pentane (70 ml). After drying *in vacuo*, the beige solid **3** (6.60 g, 29.5 mmol, 86%) was isolated. Anal. Found: C, 70.1; H, 6.37; N, 6.14. $C_{13}H_{14}KN$ calc.: C, 69.9; H, 6.32; N, 6.27%. NMR: ^1H (C_5D_5N, 20°C): δ 2.00 (s, 6H, CMe_2); 6.08 (t, 2H, Cp-ring); 6.28 (t, 2H, Cp-ring); 6.86 (dd, 1H, C_5H_4N); 7.50 (t, 2H, C_5H_4N); 8.46 (d, 1H, C_5H_4N). ^{13}C (C_5D_5N, 20°C): δ 31.95 (q, CMe_2); 43.28 (s, CMe); 103.07 (d, CH); 104.16 (d, CH); 119.95 (d, CH); 123.07 (s, C); 130.43 (d, CH); 136.16 (d, CH); 148.59 (d, CH); 174.26 (s, C).

2.5. Synthesis of $KCp'^{py(s)}$ (4)

A solution of $Cp'^{py(s)}H$ (9.45 g, 36.7 mmol) in THF (50 ml) was added to a stirred suspension of KH (1.40 g, 34.9 mmol) in THF (120 ml) at −78°C. The suspension was stirred for 70 h, while it slowly warmed to room temperature, yielding a brown solution. The solvent was removed *in vacuo* and the oily residue was washed with pentane (2 × 50 ml). After drying *in vacuo*, the beige solid **4** (8.50 g, 28.8 mmol, 78%) was obtained. Anal. Found: C, 65.0; H, 7.39; N, 4.74. $C_{16}H_{22}KNSi$ calc.: C, 65.0; H, 7.50; N, 4.74%. NMR: ^1H (C_5D_5N, 20°C): δ 0.37 (s, 9H, $SiMe_3$); 1.91 (s, 6H, CMe_2); 5.9–6.4 (m, 3H, Cp-ring); 6.85–6.95 (m, 1H, C_5H_4N); 7.45–7.6 (m, 2H, C_5H_4N); 8.50 (m, 1H, C_5H_4N). ^{13}C (C_5D_5N, 25°C): δ 2.03 (q, $SiMe_3$); 31.81 (q, CMe_2); 43.07 (s, CMe_2); 103.05 (d, CH); 104.11 (d, CH); 107.03 (d, CH); 109.29 (s, C); 109.73 (d, CH);

112.32 (d, CH); 119.44 (d, CH); 120.15 (d, CH); 130.73 (s, C); 133.86 (d, CH); 148.87 (d, CH); 173.64 (s, C). $^{29}Si\{^1H\}$ (C_5D_5N, 25°C); δ −14.43 ($SiMe_3$).

2.6. Synthesis of $[Yb(Cp^{py})_2]$ (5)

A dark green suspension of YbI_2 (1.9 g, 4.45 mmol) and **1** (2.09 g, 8.80 mmol) in THF (100 ml) was stirred at room temperature for 18 h. The solid was allowed to settle and the supernatant liquid was decanted and filtered. The filtrate was concentrated and cooled to −30°C, yielding dark green crystals of **5** (1.08 g, 1.90 mmol, 43%). Anal. Found: C, 59.1; H, 6.03; N, 5.15. $C_{28}H_{32}N_2Yb$ calc.: C, 59.0; H, 5.66; N, 4.92%. NMR: ^1H (C_5D_5N, 20°C): δ 1.29 (s, 12H, CMe_2); 3.01 (s, 4H, CH_2); 5.81 (s, 4H, Cp-ring); 6.00 (s, 4H, Cp-ring); 7.15 (t, 2H, C_5H_4N); 7.30 (d, 2H, C_5H_4N); 7.93 (t, 2H, C_5H_4N); 8.38 (d, 2H, C_5H_4N). ^{13}C (C_4D_8O, 25°C): δ 30.71 (q, CMe_2); 35.52 (s, CMe_2); 55.47 (t, CH_2); 102.93 (d, CH); 105.41 (d, CH); 122.43 (d, CH); 128.59 (d, CH); 130.87 (s, C); 137.82 (d, CH); 147.57 (d, CH); 162.18 (s, C). $^{171}Yb\{^1H\}$ (C_6D_6/THF, 31°C): δ 456.9 ($w_{1/2} \approx 35$ Hz).

2.7. Synthesis of $[Yb(Cp'^{py})_2]$ (6)

A solution of **2** (1.80 g, 5.81 mmol) in THF (50 ml) was added to YbI_2 (1.66 g, 3.90 mmol) at room temperature. The dark green suspension was stirred for 16 h, the solvent then removed *in vacuo*, and the residue extracted with toluene. The dark green extract was concentrated and cooled to −30°C to afford dark green, crystalline **6** (1.55 g, 2.20 mmol, 75%). Recrystallization from hexane gave cubic crystals. Anal. Found: C, 57.1; H, 6.77; N, 3.93. $C_{34}H_{48}N_2Si_2Yb$ calc.: C, 57.2; H, 6.78; N, 3.92%. NMR: ^1H (C_7D_8, 40°C): δ 0.07 (s, 18H, $SiMe_3$); 1.04 (s, 6H, CMe); 1.30 (s, 6H, CMe); 2.61 (d, 2H, CH); 3.12 (d, 2H, CH); 5.60 (s, 2H, Cp-ring); 6.18 (s, 2H, Cp-ring); 6.31 (m, 2H, Cp-ring); 6.64 (m, 4H, C_5H_4N); 7.13 (t, 2H, C_5H_4N); 8.13 (s, 2H, C_5H_4N). ^{13}C (C_6D_6/THF, 25°C): δ 0.58 (q, $SiMe_3$); 27.09 (q, CMe_2); 35.41 (s, CMe_2); 54.97 (t, CH_2); 111.16 (s, C); 112.63 (d, CH); 115.47 (d, CH); 121.60 (d, CH); 128.39 (d, CH); 134.80 (s, C); 137.80 (d, CH); 138.07 (d, CH); 148.38 (d, CH); 161.95 (s, C). $^{29}Si\{^1H\}$ (C_6D_6/C_6H_6, 20°C); δ −12.71 ($SiMe_3$). $^{171}Yb\{^1H\}$ (C_4D_8O/THF, 31°C): δ 543.7 ($w_{1/2} \approx 25$ Hz).

2.8. Synthesis of $[Yb(Cp^{py(s)})_2]$ (7)

A dark green suspension of YbI_2 (1.25 g, 2.93 mmol) and **3** (1.30 g, 5.82 mmol) in THF (80 ml) was stirred at room temperature for 24 h. The solid material was allowed to settle. The supernatant liquid was decanted and filtered. The filtrate was concentrated and cooled to −30°C to yield the dark green solid **7** (1.70 g, 3.14 mmol, 54%). Recrystallization from a toluene/pentane mixture gave dark green crystals. Anal. Found: C, 57.8; H, 5.26; N, 4.95. $C_{26}H_{28}N_2Yb$ calc.: C, 57.7; H, 5.21; N, 5.17%. NMR: ^1H (C_5D_5N, 20°C): δ 1.85 (s, 12H, CMe_2); 5.95 (s, 4H, Cp-ring); 6.20 (s, 4H, Cp-ring); 6.80 (t, 2H, C_5H_4N); 7.56 (d, 2H, C_5H_4N); 7.70 (t, 2H, C_5H_4N); 8.14 (br. s, 2H, C_5H_4N). ^{13}C (C_5D_5N, 25°C); δ 31.95 (q, CMe_2); 43.40 (s, CMe_2); 104.47 (d, CH); 106.11 (d, CH); 120.38 (d, CH); 121.70 (d, CH); 128.67 (s, C); 136.56 (d, CH); 148.47 (d, CH); 175.39 (s, C). $^{171}Yb\{^1H\}$ (C_5D_5N/C_5H_5N, 31°C): δ 594.6 ($w_{1/2} \approx 150$ Hz).

2.9. Synthesis of $[Yb(Cp'^{py(s)})_2]$ (8)

A dark green suspension of YbI_2 (1.35 g, 3.16 mmol) and **4** (1.80 g, 6.09 mmol) in THF (100 ml) was stirred at room temperature for 17 h. Volatiles were removed *in vacuo* and the residue was extracted with toluene (50 ml). The dark green solution was layered with pentane and cooled to −30°C, yielding the dark green solid **8** (1.8 g, 2.62 mmol, 86%). Anal. Found: C, 56.5; H, 6.51; N, 4.02. $C_{32}H_{44}N_2Si_2Yb$ calc.: C, 56.0; H, 6.47; N, 4.08%. NMR: ^1H (C_6D_6, 25°C): δ 0.27 (s, 18H, $SiMe_3$); 1.64 (s, 12H, CMe_2); 6.01 (t, 2H, Cp-ring); 6.20 (m, 2H, Cp-ring); 6.40 (t, 2H, Cp-ring); 6.84 (t, 2H, C_5H_4N); 6.93 (d, 4H, C_5H_4N); 8.19 (d, 2H, C_5H_4N). ^{13}C (C_6D_6/C_6H_6, 25°C): δ 0.96 (q, $SiMe_3$); 31.45 (q, CMe_2), 43.24 (s, CMe_2); 108.46 (d, CH); 112.60 (d, CH); 114.36 (d, CH); 114.57 (s, C); 120.63 (d, CH); 122.12 (d, CH); 134.03 (s, C); 136.85 (d, CH); 147.44 (d, CH); 177.75 (s, C). $^{29}Si\{^1H\}$ (C_6D_6/C_6H_6, 25°C): δ −12.50 ($SiMe_3$). $^{171}Yb\{^1H\}$ (C_6D_6/C_6H_6, 31°C): δ 851.0 ($w_{1/2} \approx 30$ Hz).

2.10. X-Ray structure determination for $[Yb(Cp^{py})_2]$ (5) and $[Yb(Cp'^{py(s)})_2]$ (8)

In each case, unique data sets were collected from a crystal sealed in a capillary under argon on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarization effects (Lp) and also for absorption using DIFABS [14] after isotropic refinement. Reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/\mathrm{Lp}$ were considered observed.

Each structure was solved using the heavy atom routines of SHELXS-86 [15]. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares using programs from the Enraf-Nonius MOLEN package. The hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. For each structure, the absolute

TABLE 1. X-Ray crystal structure details

	$[Yb(Cp^{py})_2]$ (5)	$[Yb(Cp'^{py(s)})_2]$ (8)
Formula	$C_{28}H_{32}N_2Yb$	$C_{32}H_{44}N_2Si_2Yb$
M	569.6	685.9
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $Fdd2$
a, b, c (Å)	7.713(8), 17.486(4), 17.734(4)	23.189(4), 46.209(6), 13.141(2)
U (Å^3), Z, D_c (g cm^{-3})	2391.7, 4, 1.58	14080.9, 16, 1.29
$F(000)$	1136	5568
μ (Mo-Kα) (cm^{-1})	39.1	27.3
Crystal size (mm^3)	0.4 × 0.3 × 0.03	0.4 × 0.4 × 0.1
Total unique reflections, (θ_{max} = 25°)	2424	3374
Significant reflections, $\|F^2\| > 2\sigma\|F^2\|$	2048	2661
Number of variables	280	334
R, R' [a]	0.029, 0.034	0.058, 0.061

[a] $R = \Sigma w(|F_o| - |F_c|)/(\Sigma w(|F_o|)$; $R' = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma w(|F_o|^2)]^{1/2}$.

structure was checked by refinement of both alternatives and the results quoted are for the prefered absolute structure.

TABLE 2. Fractional atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2 ×10^3) for $[Yb(Cp^{py})_2]$ (5)

	x	y	z	U_{eq} [a]
Yb1	1367.9(5)	569.5(2)	1187.6(2)	30.3(1)
N(1)	−696(10)	664(4)	2266(4)	36(4)
N(2)	3314(9)	−453(4)	1639(4)	33(4)
C(1)	−771(14)	89(6)	2779(6)	47(6)
C(2)	−1641(13)	152(6)	3461(6)	47(6)
C(3)	−2461(14)	814(7)	3612(5)	54(7)
C(4)	−2470(14)	1390(6)	3101(5)	44(6)
C(5)	−1589(12)	1313(5)	2419(5)	35(5)
C(6)	−1540(14)	1911(6)	1821(5)	42(5)
C(7)	−19(13)	2468(6)	1790(5)	38(5)
C(8)	1669(12)	2068(5)	1582(4)	30(5)
C(9)	2391(13)	1993(6)	857(5)	40(5)
C(10)	3885(14)	1567(7)	893(6)	52(6)
C(11)	4096(13)	1363(6)	1651(6)	45(6)
C(12)	2769(13)	1646(6)	2069(5)	37(5)
C(13)	−474(4)	3067(6)	1195(7)	57(6)
C(14)	159(15)	2870(6)	2552(6)	48(6)
C(15)	3583(15)	−453(6)	2392(5)	49(6)
C(16)	4476(15)	−1016(7)	2768(5)	51(6)
C(17)	5157(15)	−1617(7)	2378(6)	55(6)
C(18)	4988(15)	−1604(7)	1608(6)	54(7)
C(19)	4109(11)	−1018(5)	1238(5)	39(5)
C(20)	3946(14)	−986(6)	382(5)	46(6)
C(21)	2195(14)	−1185(6)	39(5)	38(5)
C(22)	883(12)	−530(6)	121(4)	40(5)
C(23)	936(17)	170(7)	−250(5)	59(7)
C(24)	−461(16)	584(9)	−68(6)	74(7)
C(25)	−1453(16)	156(8)	419(6)	77(7)
C(26)	−625(13)	−540(7)	541(5)	51(5)
C(27)	2506(17)	−1341(7)	−813(6)	63(7)
C(28)	1530(17)	−1929(7)	378(6)	63(7)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Fractional atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2 ×10^3) for $[Yb(Cp'^{py(s)})_2]$ (8)

	x	y	z	U_{eq} [a]
Yb	2436.1(2)	614.9(1)	0.0	56(1)
Si(1)	3827.8(21)	112.6(12)	27.6(65)	98(4)
Si(2)	1820.9(29)	1123.3(14)	2211.3(49)	108(4)
N(1)	2572(5)	735(3)	−1809(11)	71(8)
N(2)	1437(6)	507(2)	−528(10)	66(8)
C(1)	2345(7)	1093(3)	1165(13)	66(9)
C(2)	2289(6)	1189(3)	205(12)	57(8)
C(3)	2842(7)	1148(3)	−342(14)	72(10)
C(4)	3220(6)	1029(3)	305(12)	68(10)
C(5)	2936(8)	996(3)	1242(14)	86(11)
C(6)	2924(7)	1234(3)	−1471(12)	70(10)
C(7)	2589(11)	1517(4)	−1725(19)	127(17)
C(8)	3562(8)	1282(5)	−1637(21)	149(17)
C(9)	2730(6)	996(3)	−2220(11)	63(9)
C(10)	2711(9)	1042(4)	−3224(14)	97(13)
C(11)	2540(9)	826(5)	−3918(16)	118(16)
C(12)	2382(8)	564(3)	−3489(15)	88(12)
C(13)	2425(7)	536(4)	−2509(16)	91(12)
C(14)	2033(16)	885(6)	3294(20)	237(26)
C(15)	1826(19)	1486(6)	2788(30)	349(34)
C(16)	1138(12)	988(12)	1897(31)	443(43)
C(17)	3064(6)	145(3)	322(12)	68(10)
C(18)	2595(8)	46(3)	−198(17)	85(13)
C(19)	2068(6)	74(2)	334(10)	47(7)
C(20)	2244(8)	176(4)	1272(12)	77(11)
C(21)	2837(8)	221(3)	1287(14)	82(11)
C(22)	1476(7)	−1(3)	−21(12)	65(9)
C(23)	1504(9)	−253(4)	−765(20)	129(16)
C(24)	1097(9)	−97(5)	876(20)	130(16)
C(25)	1165(7)	257(4)	−543(14)	75(11)
C(26)	661(8)	223(4)	−1071(23)	156(17)
C(27)	388(9)	444(4)	−1502(24)	140(17)
C(28)	651(8)	715(3)	−1422(19)	105(13)
C(29)	1133(7)	738(3)	−929(14)	71(10)
C(30)	4032(9)	−268(5)	−160(43)	273(32)
C(31)	4253(10)	257(6)	1086(22)	155(22)
C(32)	4005(12)	336(6)	−1114(21)	171(23)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[Yb(Cp^{py})_2]$ (5) [a]

Bonds			
Yb–Cp(1)	2.401	Yb–Cp(2)	2.415
Yb–N(1)	2.494(7)	Yb–N(2)	2.469(7)
Yb–C(8)	2.723(9)	Yb–C(22)	2.722(9)
Yb–C(9)	2.677(9)	Yb–C(23)	2.664(9)
Yb–C(10)	2.661(11)	Yb–C(24)	2.635(11)
Yb–C(11)	2.651(10)	Yb–C(25)	2.667(12)
Yb–C(12)	2.674(10)	Yb–C(26)	2.728(11)
C(8)–C(9)	1.406(12)	C(22)–C(23)	1.39(2)
C(8)–C(12)	1.419(13)	C(22)–C(26)	1.381(13)
C(9)–C(10)	1.37(2)	C(23)–C(24)	1.34(2)
C(10)–C(11)	1.399(14)	C(24)–C(25)	1.37(2)
C(11)–C(12)	1.357(14)	C(25)–C(26)	1.39(2)
Angles			
Cp(1)–Yb–Cp(2)	137.7	Cp(1)–Yb–N(1)	98.3
Cp(1)–Yb–N(2)	104.2	Cp(2)–Yb–N(1)	107.7
Cp(2)–Yb–N(2)	103.0	N(1)–Yb–N(2)	100.8(2)

[a] Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings C(8) to C(12) and C(22) to C(26), respectively.

TABLE 5. Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[Yb(Cp'^{py(s)})_2]$ (8) [a]

Bonds			
Yb–Cp(1)	2.40	Yb–Cp(2)	2.39
Yb–N(1)	2.462(15)	Yb–N(2)	2.470(13)
Yb–C(1)	2.698(15)	Yb–C(17)	2.65(2)
Yb–C(2)	2.687(13)	Yb–C(18)	2.670(14)
Yb–C(3)	2.676(14)	Yb–C(19)	2.678(11)
Yb–C(4)	2.671(14)	Yb–C(20)	2.67(2)
Yb–C(5)	2.67(2)	Yb–C(21)	2.65(2)
C(1)–C(2)	1.34(2)	C(17)–C(18)	1.37(2)
C(1)–C(5)	1.45(2)	C(17)–C(21)	1.42(2)
C(2)–C(3)	1.48(2)	C(18)–C(19)	1.41(2)
C(3)–C(4)	1.34(2)	C(19)–C(20)	1.38(2)
C(4)–C(5)	1.40(2)	C(20)–C(21)	1.39(3)
Angles			
Cp(1)–Yb–Cp(2)	136.9	Cp(1)–Yb–N(1)	91.7
Cp(1)–Yb–N(2)	121.9	Cp(2)–Yb–N(1)	121.0
Cp(2)–Yb–N(2)	91.1	N(1)–Yb–N(2)	84.0(4)

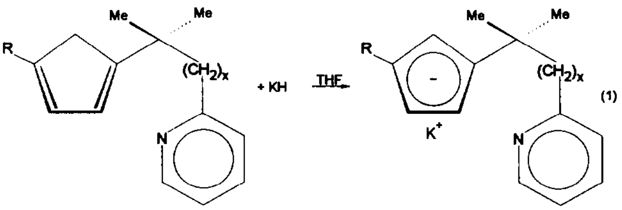
[a] Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings C(1) to C(5) and C(17) to C(21), respectively.

Further details are given in Table 1. Atom positions are listed in Tables 2 and 3, and selected bond lengths and angles are given in Tables 4 and 5. Complete lists of bond lengths and angles and tables of H atom positions and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. The potassium cyclopentadienyl complexes 1–4

The potassium cyclopentadienyl complexes KCp^{py} (1), KCp'^{py} (2), $KCp^{py(s)}$ (3), and $KCp'^{py(s)}$ (4) were



1: R = H, x = 1

2: R = $SiMe_3$, x = 1

3: R = H, x = 0

4: R = $SiMe_3$, x = 0

synthesized by treating KH with $Cp^{py}H$, $Cp'^{py}H$, $Cp^{py(s)}H$, or $Cp'^{py(s)}H$, respectively (eqn. (1)). Compounds 1–4 were isolated as off-white or beige powders in good yields (1, 80%; 2, 89%; 3, 86%; 4, 78%).

The potassium cyclopentadienyls 1–4 were shown to have varying solubilities: KCp^{py} (1) and $KCp^{py(s)}$ (3) were insoluble in aromatic solvents and only slightly soluble in pyridine, whereas the $SiMe_3$-substituted cyclopentadienyls KCp'^{py} (2) and $KCp'^{py(s)}$ (4) were very soluble in THF or pyridine and even slightly soluble in aromatic hydrocarbon solvents. Characterization of 1–4 by ^1H, ^{13}C, and ^{29}Si (2 and 4 only) NMR spectroscopy showed that no solvent molecules were coordinated to the potassium in 1–4, and this was confirmed by elemental (C, H, N) analysis.

3.2. The synthesis, characterization, and X-ray structure of $[Yb(Cp^{py})_2]$ (5)

The reaction of ytterbium(II) iodide with two equivalents of KCp^{py} (1) in THF afforded a dark green solution. After filtration, cooling of the filtrate gave $[Yb(Cp^{py})_2]$ (5) as dark green prisms (eqn. (2)).

$$2\,KCp^{py} + YbI_2 \xrightarrow{THF} \underset{(5)}{[Yb(\eta\text{-}Cp^{py})_2]} \qquad (2)$$

The ytterbocene(II) complex (5) was highly soluble in THF or pyridine, but insoluble in aromatic hydrocarbon solvents. The ^1H NMR spectrum in C_5D_5N showed that there was no THF coordinated to the ytterbium centre. Elemental (C, H, N) analyses were also consistent with 5 being unsolvated. Compound 5 was further characterized by ^{13}C and $^{171}Yb\{^1H\}$ [16] NMR spectroscopy, and a single crystal X-ray diffraction study.

The molecular structure and atom numbering scheme for crystalline $[Yb(Cp^{py})_2]$ (5) are shown in Fig. 1; selected bond lengths and angles are listed in Table 4.

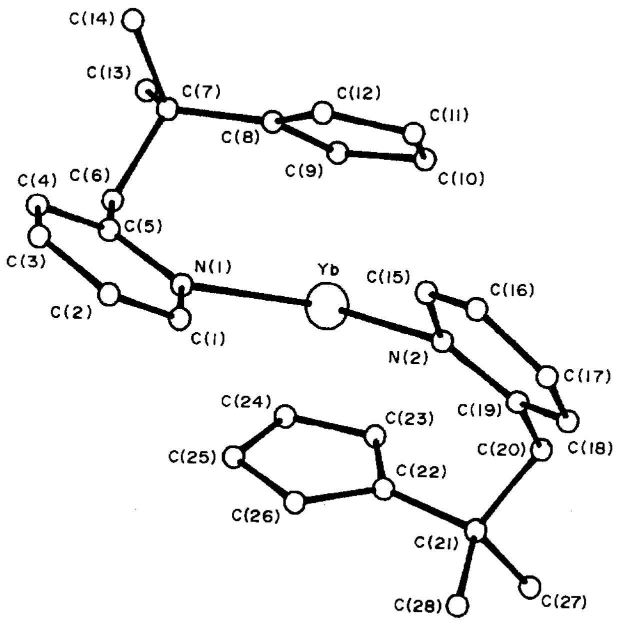


Fig. 1. X-Ray molecular structure and atom labelling for [Yb{η-$C_5H_4(CMe_2CH_2C_5H_4N$-2)}$_2$] (5).

The structure of **5** involves a distorted tetrahedral arrangement of the ligands around the metal with Cp(1)–Yb–Cp(2) 137.7° and N(1)–Yb–N(2) 100.8° [Cp(1) is the centroid of C(8)–C(12), Cp(2) of C(22)–C(26)]. The Cp(1)–Yb–Cp(2) angle is similar to those found in [$YbCp^*_2(py)_2$] (136.3°) [17], [Yb(η-$C_5H_4SiMe_3)_2(THF)_2$] (133°) [4], or [Yb($Cp''_2)_\infty$] (138°) [7]. The linking of the pyridyl rings to the cyclopentadienyl ligands results in: (i) a substantially wider N(1)–Yb–N(2) angle in **5** than in [$YbCp^*_2(py)_2$] (82.5°) [17] and (ii) slightly longer Yb–C distances on the side of the pyridyl link (see Table 4). The mean Yb–C bond length of 2.68 Å in **5** may be compared with 2.74 Å in [$YbCp^*_2(py)_2$] [17] and 2.75 Å in [Yb(η-$C_5H_4SiMe_3)_2$-$(THF)_2$] [4], while the mean Yb–N distance of 2.48 Å in **5** is shorter than the 2.57 Å in [$YbCp^*_2(py)_2$] [17] and 2.55 Å in [$YbCp^*_2(THF)(NH_3)$] [18]; see also Table 6.

To a first approximation, the crystalline complex **5** seems to be symmetrical, but closer examination of the conformation of the two pyridyl groups shows that they are bonded differently. For one pyridyl ring, the Cp–Yb–N angles are 98.3 and 107.7° while for the other they are 104.2 and 103.0°.

The ^1H NMR spectrum of **5** in C_4D_8O at 25°C showed a singlet for the CMe_2 group (δ 1.29), a singlet for the CH_2 group (δ 3.01) and two singlets for the Cp-ring protons (δ 5.81 and 6.00). At −75°C, the two sets of methyl, CH_2, and the Cp-ring protons were found to be inequivalent. Thus, a doublet was observed for the CMe_2 and CH_2 groups, and two doublets for the Cp-ring protons. The positions of the signals from the pyridyl groups remained unchanged over this temperature range and only one set of resonances was observed for both pyridyl groups. In solution, as in the solid state, both pyridyl groups are evidently coordinated to the ytterbium centre. However, it appears that a low Yb–N rotational barrier allows the pyridyl groups to become equivalent even at low temperature.

3.3. *The synthesis and characterization of [Yb($Cp'^{py})_2$] (6), [Yb($Cp^{py(s)})_2$] (7) and [Yb($Cp'^{py(s)})_2$] (8)*

The ytterbocene(II) complexes **6–8** were each made in the way used for **5** (eqn. (3)). The reaction of YbI_2 with two equivalents of **2**, **3**, or **4** afforded a dark green suspension in each case. Crystallization from toluene yielded **6–8** as crystalline powders. Recrystallizing from petroleum ether (**6**) or a toluene/petroleum ether mixture (**7** or **8**) yielded the ytterbocene(II) complexes **6–8** as dark green crystals.

Compounds **6–8** were characterized by ^1H, ^{13}C, $^{29}Si\{^1H\}$ (**6** and **8**), and $^{171}Yb\{^1H\}$ NMR spectroscopy. These data and elemental (C, H, N) analyses were consistent with their formulation as unsolvated complexes.

$$2\ KCp^x + YbI_2 \xrightarrow{THF} [Yb(Cp^x)_2] \qquad (3)$$

6: $Cp^x = Cp'^{py}$

7: $Cp^x = Cp^{py(s)}$

8: $Cp^x = Cp'^{py(s)}$

3.4. *The X-ray structure of [Yb($Cp'^{py(s)})_2$] (8)*

The molecular structure and atom numbering scheme for [Yb($Cp'^{py(s)})_2$] (**8**) are shown in Fig. 2; selected bond lengths and angles are listed in Table 5,

TABLE 6. Selected geometric parameters in some crystalline four-coordinate ytterbocene(II) complexes

Complex	⟨Yb–C⟩ (Å)	⟨Yb–N⟩ (Å)	Cp(1)–Yb–Cp(2) (°)	N(1)–Yb–N(2) (°)	Ref.
[Yb($Cp^{py})_2$] (**5**)	2.68(1)	2.48(1)	137.7	100.8(2)	This work
[Yb($Cp'^{py(s)})_2$] (**8**)	2.68(2)	2.47(1)	136.9	84.0(4)	This work
[$YbCp^*_2(py)_2$]	2.74(4)	2.56(1)	136.3(3)	82.5(2)	17
[Yb(η-$C_5H_4SiMe_3)_2(THF)_2$]	2.75	–	133	–	4
[$YbCp^*_2(THF)(NH_3)$]	2.77(4)	2.55(3)	139.31	87.5(9) [a]	18

[a] N–Yb–O.

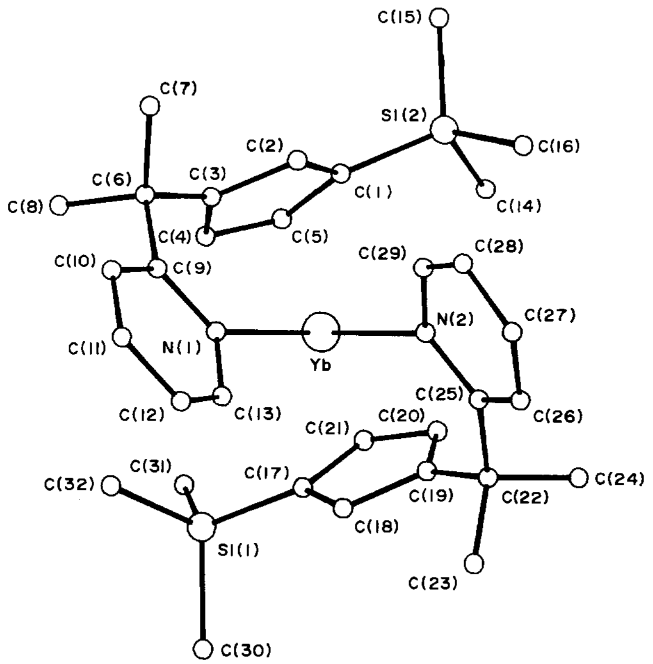


Fig. 2. X-Ray molecular structure and atom labelling for [Yb{η-$C_5H_3(SiMe_3)(CMe_2C_5H_4N$-2)-1,3}$_2$] (**8**).

with some comparative data on **5** and three other four-coordinate ytterbocene(II) complexes in Table 6.

The molecular structure of crystalline **8** resembles that of **5** in having a distorted tetrahedral arrangement of the ligands around the metal with Cp(1)–Yb–Cp(2) 136.9° and N(1)–Yb–N(2) 84.0° [Cp(1) is the centroid of C(1)–C(5), Cp(2) or C(17)–C(21)]. The Cp(1)–Yb–Cp(2) angle is similar to those found in **5**, [$YbCp_2^*(py)_2$] (136.3°) [17] and [$(YbCp_2'')_\infty$] (138°) [7], while the magnitude of the angle N(1)–Yb–N(2) is similar to that in [$YbCp_2^*(py)_2$] (82.5°) [17], but significantly narrower than that in **5** (100.8°).

Compared with **5**, complex **8** has two different features in its ligand system: (i) an $SiMe_3$-substituent and (ii) only one carbon atom linking the pyridyl rings with the cyclopentadienyl ligands. Feature (i) has no significant effect on Cp(1)–Yb–Cp(2), but the shorter link between the pyridyl rings to the cyclopentadienyl ligands in **8** results in a substantially smaller N(1)–Yb–N(2) angle (84.0°) than in **5** (100.8°).

Feature (ii) also has a pronounced effect on the orientation of the pyridyl rings with respect to the cyclopentadienyls (*cf.* Figs. 1 and 2). For one pyridyl ring, in **8** the Cp–Yb–N angles are 91.7° and 121.0° (**5** 98.3 and 107.1°), compared with 91.7° and 121.9° (**5** 104.2 and 103.0°) for the other ring.

Acknowledgements

We thank Shell Research BV (Koninklijke/Shell-Laboratorium, Amsterdam) for providing a studentship to J.R.v.d.H. (and Dr. R.W. Chorley for his support and interest) and the SERC for other support.

References

1 W.J. Evans, L.A. Hughes and T.P. Hanusa, *J. Am. Chem. Soc.*, *106* (1984) 4270.
2 W.J. Evans, L.A. Hughes and T.P. Hanusa, *Organometallics*, *5* (1986) 1285.
3 C.J. Burns, Ph.D. Thesis, University of California, Berkeley, 1987.
4 M.F. Lappert, P.I.W. Yarrow, J.L. Atwood, R. Shakir and J. Holton, *J. Chem. Soc., Chem. Commun.*, (1980) 987.
5 Q. Shen, D. Zheng, L. Lin and Y. Lin, *J. Organomet. Chem.*, *391* (1990) 321.
6 W.J. Evans, R.A. Keyer and J.W. Ziller, *J. Organomet. Chem.*, *394* (1990) 87.
7 P.B. Hitchcock, J.A.K. Howard, M.F. Lappert and S. Prashar, *J. Organomet. Chem.*, *437* (1992) 177.
8 P. Jutzi, J. Dahlhus and M.O. Kirsten, *J. Organomet. Chem.*, *450* (1993) C1.
9 D. Deng, C. Qian, F. Song, Z. Wang, G. Wu and P. Zheng, *J. Organomet. Chem.*, *443* (1993) 79.
10 R. Anwander, W.A. Herrmann, W. Scherer and F.C. Munk, *J. Organomet. Chem.*, *462* (1993) 163.
11 T.J. Clark, T.A. Nile, D. McPhail and A.T. McPhail, *Polyhedron*, *8* (1989) 1804.
12 T.D. Tilley, J.M. Boncella, D.J. Berg, C.J. Burns and R.A. Andersen, *Inorg. Synth.*, *27* (1990) 146.
13 T.A. Nile, unpublished work.
14 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, *39* (1983) 158.
15 G.M. Sheldrick, in G.M. Sheldrick, C. Krüger and R. Goddard (eds.), Crystallographic Computing 3, Oxford University Press, 1985, pp. 175–189.
16 A.G. Avent, M.A. Edelman, M.F. Lappert and G.A. Lawless, *J. Am. Chem. Soc.*, *111* (1989) 3423.
17 T.D. Tilley, R.A. Andersen, B. Spencer and A. Zalkin, *Inorg. Chem.*, *21* (1982) 2647.
18 A.L. Wayda, J.L. Dye and R.D. Rogers, *Organometallics*, *3* (1984) 1605.