Preparation and Properties of Some Bis(cyclopentadienyl)ytterbium(II) Complexes and the *X*-Ray Crystal and Molecular Structures of [Yb(η-$C_5H_4SiMe_3)_2$(thf)$_2$]

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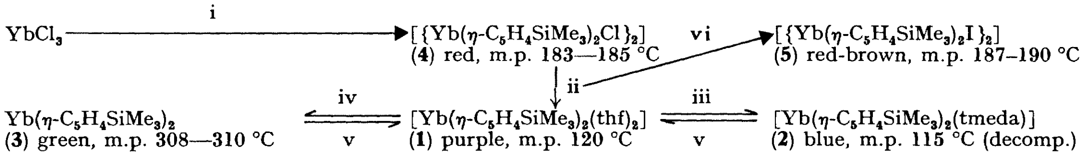
Summary Reduction of [{Yb(η-$C_5H_4SiMe_3)_2$Cl}$_2$] by Na–Hg in tetrahydrofuran (thf) yields the purple, diamagnetic, toluene-soluble Yb^{II} title complex, from which similarly highly reactive, but thermally stable, Yb^{II} complexes [Yb(η-$C_5H_4SiMe_3)_2$(tmeda)] (tmeda = $Me_2NCH_2CH_2NMe_2$) and Yb(η-$C_5H_4SiMe_3)_2$ are obtained, or [{Yb(η-$C_5H_4SiMe_3)_2$I}$_2$] from oxidation by I_2; *X*-ray analysis of the title compound to R = 0·077 shows a roughly tetrahedral disposition of valencies around Yb, with Yb–O_{av} = 2·41 Å and Yb–C(η)$_{av}$ = 2·75 Å.

WE report (a) some well defined, thermally stable, divalent lanthanoid(II) complexes [Yb(η-$C_5H_4SiMe_3)_2L_2$] [L_2 = (thf)$_2$ or tmeda], (**1**) and (**2**) (see Scheme); (b) their reversible interconversion (reactions iii and v in Scheme); (c) the formation from (**1**) of the solvate-free ytterbocene, (**3**), and the converse process (reactions iv and v in Scheme); (d) the preparation and properties of a Yb^{III} precursor (**4**) of complex (**1**), and the iodo-analogue (**5**), [{Yb(η-$C_5H_4SiMe_3)_2$X}$_2$][X = Cl, (**4**); X = I, (**5**)]; and (e) crystallographic data on complex (**1**), the first lanthanoid(II) organometallic compound to be so characterised.†

There are previous accounts[1] of lanthanoid(II) cyclopentadienyls, M(η-$C_5H_5)_2$ (M = Sm, Eu, or Yb), M(η-$C_5H_5)_2$-$(NH_3)_x$, or M(η-$C_5H_5)_2$(thf)$_x$ (M = Sm or Yb), but the compounds were unstable or ill-defined.[1]† We have previously used the trimethylsilyl-substituted cyclopentadienyl ligand to confer good hydrocarbon solubility on its derived complexes;[2] it is interesting that in the present instance this technique also provides for enhanced thermal stability.

The crystal structure of the title compound was solved from 1226 independent observed reflections and refined to R = 0·077.



SCHEME. *Reagents and conditions:* i, 2Li($C_5H_4SiMe_3$) in thf, followed by precipitation from *n*-C_6H_{14}, at −30 °C, and sublimation (*ca.* 250 °C/10^{-3} Torr); ii, Na–Hg in thf for 1 h, followed by filtration, concentration, addition of n-C_6H_{14}, and cooling to −30 °C; iii, addition of tmeda, and recrystallisation (PhMe); iv, warm to 30 °C/10^{-3} Torr and then sublimation (*ca.* 300 °C/10^{-3} Torr); v, thf; vi, I_2 in thf. *Characterisation.* The new compounds (**1**)—(**5**) have been characterised by analytical and spectral data [the mass spectra of (**1**)—(**3**) each have a prominent peak at *m/e* corresponding to (**3**)$^+$, while (**4**) and (**5**) show parent molecular ions; compounds (**1**) and (**2**) are diamagnetic and show appropriate ^1H n.m.r. spectra in C_6D_6].

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† *Added in proof.* Since the submission of this manuscript, the following relevant publications have appeared: P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1980, 652 {dealing with [Yb(η-$C_5Me_5)_2$(thf)$_2$]}, and H. A. Zinnen, J. J. Pluth, and W. J. Evans, *J. Chem. Soc., Chem. Commun.*, 1980, 810 {dealing with [Yb(η-$C_5H_4Me)_2$(thf)], including its structure determination by *X*-ray diffraction}.

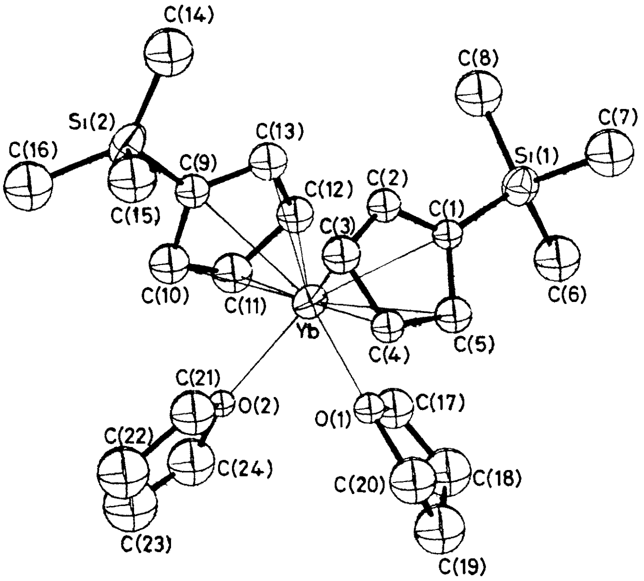

FIGURE Molecular structure and atom numbering scheme for [Yb(η $C_5H_4SiMe_3)_2(thf)_2$] (**1**)

Crystal data $C_{24}H_{42}YbO_2Si_2$, M = 591 8 monoclinic, space group $P2_1/n$, a = 13 439(7) b = 10 322(7), c = 21 340(9) Å β = 105 57(3)° U = 2851 6 Å^3, Z = 4 D_c = 1 38 g cm^{-3} and μ(Mo-K_α) = 35 5 cm^{-1}

The molecule with our atom numbering scheme is shown in the Figure ‡ The Yb–C(η) bond lengths range from 2 64(4) to 2 84(4) Å and average 2 75 Å This compares favourably with the 2 61 Å value[3] found for compounds of Yb^{3+} after two factors are taken into account First the 2+ ionic radius, 0 93 Å,[4] is 0 07 Å larger than that of the 3+ ion Second, the influence of the trimethylsilyl appendage has been found in $[Zr(\eta\text{-}C_5H_4SiMe_3)_2\{CH(SiMe_3)_2\}Cl]$[5] to produce a 0 03 Å elongation of the Zr–C(η) bond length over the normal Zr–C(η) distance (2 54 *vs* [6] 2 51 Å) Thus the Yb-C(η) bond length is expected to approach 2 71 Å based on known structural data

The size of the 2+ ion is also apparent in the Yb–O bond lengths, 2 42(2) and 2 39(3) Å This compares well with the Gd–O distance, 2 494(7) Å in $[Gd(\eta\text{-}C_5H_5)_3(thf)]$[7] since Gd^{3+} is *ca* 0 01 Å larger in radius than Yb^{2+}

The ligands are disposed about the ytterbium atom in a roughly tetrahedral fashion as evidenced by angles centroid-(1)–Yb–centroid(2) = 133° centroid(1)–Yb–O(1) = 107° centroid(1)–Yb–O(2) = 109°, centroid(2)–Yb–O(1) = 107° centroid(2)–Yb–O(2) = 106° and O(1)–Yb–O(2) = 85°

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‡ The atomic co ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory Lensfield Road Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

[1] *cf* T J Marks *Prog Inorg Chem* 1978 **24** 51 and references cited therein
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[4] *cf* F A Cotton and G Wilkinson Advanced Inorganic Chemistry 4th edn Interscience New York 1980 pp 982 1002
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[7] R D Rogers R V Bynum and J L Atwood *J Organomet Chem* 1980 **192** 65