Organolanthanoids.
XIII*. Bis(pentadeuterocyclopentadienyl)ytterbium(II)

G. B. DEACON, D. L. WILKINSON
Chemistry Department, Monash University, Clayton, Vic. 3168, Australia
and R. L. DAVIS
Australian Institute of Nuclear Science and Engineering, Lucas Heights, N.S.W. 2234, Australia

(Received June 16, 1987)

Abstract

The complex $(C_5D_5)_2Yb(dme)$ (dme = 1,2-dimethoxyethane) has been prepared by reaction of $Tl(C_5D_5)$ with ytterbium metal in dme and is isostructural with $(C_5H_5)_2Yb(dme)$. Thermal desolvation under vacuum yields $(C_5D_5)_2Yb$, for which essentially identical high resolution neutron powder diffraction data were obtained at 294 K and 77 K, but the structure could not be determined.

Introduction

The recent discovery that uncomplexed bis(pentamethylcyclopentadienyl)lanthanoid(II) compounds $(C_5Me_5)_2M$ (M = Sm, Eu or Yb) have structures with inclined pentamethylcyclopentadienyl ligands rather than the expected parallel ring ('ferrocene-type') structure [2, 3] has created considerable interest in the structures of the unsubstituted cyclopentadienyl analogues, $(C_5H_5)_2M$. Quasi-relativistic Xα-SW calculations for $(C_5H_5)_2M$ (M = Eu or Yb) in the tilted ring (C_{2v}) and parallel ring (D_{5d}) arrangements did not reveal a significant preference for either structure [3]. These compounds are soluble only in polar solvents with which they form complexes [4, 5], and desolvation gives powders in the case of ytterbium derivatives [6]. The compounds have low volatility [4] inhibiting preparation of single crystals by sublimation. (Although $(C_5H_5)_2Yb$ is reported to sublime with decomposition at 360 °C under high vacuum [7], the reported colour of the compound before and after volatilisation is at variance with other reports [6, 8, 9].) The number of atoms in $(C_5H_5)_2Yb$ is sufficiently low for investigation by neutron powder diffraction. However, an unsatisfactory powder pattern was observed with high background owing to spin incoherent scattering from the hydrogen atoms. In an attempt to overcome this, the first perdeuterocyclopentadienyllanthanoid, $(C_5D_5)_2Yb$, has been prepared and its neutron powder diffraction behaviour investigated.

Experimental

Analytical and spectroscopic methods, solvent purification and handling of air-sensitive compounds were largely as given previously [6, 10–13]. The ^2H NMR spectrum of $(C_5D_5)_2Yb(dme)$ (dme = 1,2-dimethoxyethane) in purified dme under purified (BASF 3/11 oxygen-removal catalyst and grade 4A molecular sieves) nitrogen in a screw-capped NMR tube was recorded with a Brüker AM-300 spectrometer. Infrared spectra (4000–650 cm^{-1}) are of compounds as mulls in dried Nujol and Fluorolube.

Ytterbium metal was from Research Chemicals (Nucor) or Rare Earth Products, U.K. Deuterium oxide (98%) was from the Australian Atomic Energy Commission. $Tl(C_5D_5)$ was prepared by the reported method from cyclopentadiene, thallium(I) sulfate, deuterium oxide and sodium [14–16], sublimed under vacuum and stored under nitrogen. Mass spectroscopic analysis indicated 93% $Tl(C_5D_5)$ and 7% $Tl(C_5HD_4)$ (lit. [14], 90:10%).

1,2-Dimethoxyethanebis(pentadeuterocyclopentadienyl)ytterbium(II)

Dry purified 1,2-dimethoxyethane (30 ml) was added by syringe under purified nitrogen to ytterbium powder (9.14 mmol) and thallium(I) pentadeuterocyclopentadienide (7.57 mmol) in a greaseless Schlenk flask, to which a Schlenk filter (covered with a glass fibre filter paper, a thin (0.5 cm) layer of dried diatomaceous earth and another glass filter paper) and a further Schlenk flask were attached. The reaction mixture was heated under reflux under nitrogen for 72 h, giving an emerald–green solution, which was filtered and the filter washed with 1,2-dimethoxyethane (20 ml). Evapora-

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*Part XII is ref. 1.

0020-1693/88/$3.50

tion of the solvent under vacuum gave emerald–green crystals of the title compound (97%). *Anal.* Found: C, 42.0; $H_2O + D_2O$, 2.13 mg from 4.495 mg of complex. Calc. for $C_{14}H_{10}D_{10}O_2Yb$: C, 41.7; $H_2O + D_2O$, 2.12 mg. IR absorption: 2985w, 2930w, 2882w, 2736w, 2715w, 2328w and 2282w [ν(CD)], 1325w, 1282w, 1242w, 1195m, 1162w, 1105m, 1090m, 1062s, 1022w, 1005w, 850s, 825m, 765s, 725w, 662w cm^{-1}. ^{2}H NMR (dme): 7.11, s, ppm downfield from deuterated Me_4Si.

X-ray Data (Table I)

A crystal (from dme) was sealed under purified (BASF 3/11 catalyst and molecular sieves) argon in a recirculating atmosphere dry box. Data were collected with a Philips PW1100 automatic four-circle diffractometer equipped with a graphite monochromator [17].

Bis(pentadeuterocyclopentadienyl)ytterbium(II)

Heating $(C_5D_5)_2$Yb(dme) at 150 °C under vacuum (10^{-3} mm) for 3 h gave the orange–brown title compound. *Anal.* Found: Yb, 54.6. Calc. for $C_{10}D_{10}Yb$: Yb, 55.3%. IR absorption: 2300w [ν(CD)], 1335w, 1322w, 1280sh, 1060m, 924w, 875w, 850w, 785w, 738m, 710w, 690w, 670w cm^{-1}.

Neutron powder diffraction

Samples of $(C_5D_5)_2$Yb and $(C_5H_5)_2$Yb [6] (*ca.* 3g) were inserted into standard vanadium canisters under nitrogen in a dry box. The canisters were sealed with teflon tape and a teflon O-ring coated with vacuum grease. On exposure to the atmosphere, the canisters showed no weight change over 7 d, indicating that they were fully sealed. The samples were mounted on the Australian Atomic Energy Commission high resolution powder diffractometer [18] (now with eight detectors). Data were collected for samples at room temperature and cooled in liquid nitrogen. For $(C_5H_5)_2$Yb, no meaningful results were obtained. *d* spacings (main lines only) for $(C_5D_5)_2$Yb: 7.25, 5.56, 5.32, 4.26, 3.98, 3.82, 3.55 Å at −196 °C (e.s.d.s, 0.05 Å). 7.25, 5.80, 5.42, 4.41, 4.29, 4.03, 3.95, 3.82, 3.62 Å at room temperature (e.s.d.s 0.05 Å).

Results and Discussion

We have recently shown that the redox transmetallation reaction of thallium(I) cyclopentadienide with lanthanoid metals in tetrahydrofuran [6, 19], 1,2-dimethoxyethane [6, 19], pyridine and acetonitrile [10] provides a simple preparation of tris- and some bis-(cyclopentadienyl)lanthanoids, and of $(C_5H_5)_2YbL_n$ (L = thf, dme, py or MeCN; $n = 1$ or 2) in particular. An analogous synthesis of bis(pentadeuterocyclopentadienyl)ytterbium(II) appears attractive because there is a convenient route from D_2O (as the deuterium source) to thallium(I) pentadeuterocyclopentadienide. Thus, reaction of this compound with an excess of ytterbium was carried out in dme and gave a near quantitative yield of $(C_5D_5)_2$Yb(dme).

$$2Tl(C_5D_5) + Yb \xrightarrow{dme} (C_5D_5)_2Yb + 2Tl\downarrow \qquad (1)$$

Carbon–deuterium stretching of the C_5D_5 group is observed at 2328 and 2282 cm^{-1} compared with $\nu(CH_{arom})$ of $(C_5H_5)_2$Yb(dme) [6] at 3080 cm^{-1} [$\nu(CH)/\nu(CD)_{ave} = 1.33$], whilst bands of $(C_5H_5)_2$Yb(dme) at 1002 and 750/738 cm^{-1} [6] attributable [14, 20] to CH in-plane and out-of-plane deformation, respectively, are shifted to 765 and <650 cm^{-1} in $(C_5D_5)_2$Yb(dme). The compound was also characterized by ^{2}H NMR spectroscopy (see Experimental). Unit cell data for $(C_5D_5)_2$Yb(dme) are very similar to those [21] of $(C_5H_5)_2$Yb(dme) (Table I), indicating that the complexes are isostructural. Thus, $(C_5D_5)_2$Yb(dme) has the pseudo-tetrahedral stereochemistry and 8-coordination of ytterbium, established [21] for the hydrocarbon analogue.

The solvent-free $(C_5D_5)_2$Yb was obtained by heating the dme complex under vacuum. Infrared bands at 2300 cm^{-1} [ν(CD)] and 785 cm^{-1} [CD in-plane bending] show the expected shifts from the corresponding bands (3086 and 1006 cm^{-1}) [8] of $(C_5H_5)_2$Yb. Neutron powder diffraction for $(C_5D_5)_2$Yb (see Experimental for *d* spacings) showed that spin coherent scattering was no longer a problem, but a low signal precluded the possibility of a satisfactory structural refinement from the

TABLE I. Unit Cell Data for $(C_5D_5)_2$Yb(dme)[a] and $(C_5H_5)_2$Yb(dme)[b]

Compound	*M* (g mol^{-1})	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å^3)
$(C_5D_5)_2$Yb(dme) [$C_{14}H_{10}D_{10}O_2Yb$]	403.26	9.206(5)	23.115(11)	8.267(4)	123.92(12)	1459.81
$(C_5H_5)_2$Yb(dme) [$C_{14}H_{20}O_2Yb$]	393.26	9.25(2)	23.49(5)	8.23(2)	123.59(4)	1489.63

[a] This work. [b] From ref. 21.

powder data. Moreover, cooling the compound with liquid nitrogen did not give an improved pattern. It would appear that there is a problem with disorder, as observed for single crystals of $(C_5H_5)_2Yb(dme)$ [21]. This effectively would double the number of atomic positions that have to be refined.

In view of the widespread scope of transmetallation between lanthanoid metals and thallous cyclopentadienide in ethers, pyridine and acetonitrile [6, 10, 19], the successful synthesis of $(C_5D_5)_2Yb$ by reaction (1) suggests that $Tl(C_5D_5)$ should be an equally versatile source of $(C_5D_5)_nM$ ($n = 2$ or 3) derivatives by redox transmetallation.

Acknowledgements

We are grateful to the Australian Research Grants Scheme and the Australian Institute of Nuclear Science and Engineering for support, to Rare Earth Products, U.K., for a gift of REACTON ytterbium and for a Commonwealth Postgraduate Research Award (to D.L.W.).

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