Organolanthanoids

XIX [*]. The X-ray crystal structures of di[μ-(acetato-$O,O:O'$)bis(diphenylphosphino-η^5-cyclopentadienyl)ytterbium(III)] and di[μ-(acetato-$O,O:O'$)bis(η^5-cyclopentadienyl)ytterbium(III)] — unexpected examples of formal nine coordination in lanthanoid organometallics

Glen B. Deacon [a], Gary D. Fallon [a], Bryan M. Gatehouse [a], Anna Rabinovich [a],
Brian W. Skelton [b], Allan H. White [b]

[a] *Chemistry Department, Monash University, Clayton, Vic. 3168, Australia*
[b] *Department of Chemistry, University of Western Australia, Nedlands, WA 6907, Australia*

Abstract

Treatment of bis(diphenylphosphinocyclopentadienyl)ytterbium(II) with mercury(II) acetate in tetrahydrofuran (THF) gave $Yb(C_5H_4PPh_2)_2(O_2CCH_3)$ as a fractional (0.75) THF solvate. Crystallization from toluene gave the THF-free dimer $[Yb(\eta^5-C_5H_4PPh_2)_2(\mu-O_2CCH_3)]_2$, the structure of which was determined by X-ray crystallography (monoclinic; $P2_1/n$; $a = 9.615(2)$, $b = 13.665(5)$, and $c = 23.209(9)$Å; $\beta = 91.47(3)°$; $Z = 2$(dimers); $R = 0.034$ for 3996 "observed" data). Unexpectedly, the bridging acetate groups are unsymmetrically chelating to one ytterbium atom and bonded by one oxygen atom to the other, and each ytterbium atom is formally nine coordinate with two $\eta^5-C_5H_4PPh_2$ groups (Ct–Yb–Ct, 130.7°; Ct = centroid), two oxygen atoms from one bridging acetate (Yb–O, 2.454(4), and 2.339(4) Å), and one (Yb–O, 2.282(4) Å) from the other. For comparison, the structure of $YbCp_2(O_2CCH_3)$ (Cp = cyclopentadienyl) was determined (orthorhombic; *Pbam*; $a = 13.16(1)$, $b = 12.98(1)$ and $c = 13.376(4)$ Å; $Z = 4$ (dimers); $R = 0.058$ for 1745 "observed" data) and showed the presence of two crystallographically different acetate-bridged dimers (A and B) with some variation between their geometries. Again, ytterbium is nine coordinated with two η^5-Cp groups (Ct–Yb–Ct, 132.1° (A) or 123.3° (B)), two nearly symmetrically bonded oxygen atoms from one acetate (cf. $Yb(C_5H_4PPh_2)_2(O_2CCH_3)$) (Yb–O 2.38(1) and 2.39(1) Å (A) or 2.42(1) and 2.39(1) Å (B)) and one more tightly bound oxygen atom (Yb–O, 2.25(1) Å (A) or 2.28(1) Å (B)) from the other acetate.

Keywords: Ytterbium; X-ray structure; Cyclopentadienyl; Acetate

1. Introduction

Bis(cyclopentadienyl)lanthanoid halides have been extensively investigated in recent years (for reviews and recent papers see [1–3]), and numerous crystal structures have been determined. There has been considerably less attention directed to bis(cyclopentadienyl)-lanthanoid carboxylates. Although a number have been synthesized [4–11], only a few have been characterized crystallographically [7–11]. Crystal structures of $[Yb(\eta^5-Cp)_2(O_2CC_6F_5)]_2$ [7], $[Yb(\eta^5-Cp)_2(O_2CC_6H_5)]_2$ [8], $[Yb(\eta^5-C_5H_4CH_3)_2(O_2CC_6F_5)]_2$ [9] and the related $[Yb(\eta^5-Cp)_2(O_2S(O)CF_3)]_2$ [12] (Cp = cyclopentadienyl) indicate dimeric structures with bridging carboxylate (or triflate) groups and formal eight coordination for ytterbium. Similar structures have been proposed for other di(cyclopentadienyl)lanthanoid(III) carboxylates on the basis of molecular weight data, mass spectroscopy (MS) and IR measurements [4–6]. By contrast the carboxylates synthesized by CO_2 insertion, $Yb(\eta^5$-

---

[*] Part XVIII, [1]. Dedicated to Professor Herbert Schumann, friend and colleague, on the occasion of his 60th birthday in recognition of his outstanding contribution to organometallic chemistry.

$Cp)_2(\eta^2-O_2C(CH_2)_3N(CH_3)_2)$ [10] and $Sc(\eta^5-Cp)_2(\eta^2-O_2CC_6H_4CH_3)$ [11], are monomers with eight-coordinated metal centres, and there is evidence from MS and IR spectroscopy that some $YbCp_2(O_2CR)$ complexes with bulky organic groups also have similar structures [6]. Structures of di(cyclopentadienyl)lanthanoid(III) acetates do not appear to have been investigated. We now report the synthesis and structure of bis(diphenylphosphinocyclopentadienyl)ytterbium(III) acetate and, for comparison, the structure of the known [4–6] $YbCp_2(O_2CCH_3)$. Surprisingly ytterbium is nine coordinate rather than having the expected eight coordination.

2. Experimental section

All organolanthanoid complexes were extremely air and moisture sensitive. Consequently all manipulations were carried out under purified nitrogen, using standard Schlenk techniques, or under argon in a Miller Howe dry box. The complexes $YbCp_2(O_2CCH_3)$ and $Tl(C_5H_4PPh_2)$ were prepared by the reported methods [6,7,13]. Single crystals of the former were obtained by Dr. T. Feng by crystallization from tetrahydrofuran (THF)–pentane. Commercial $Hg(O_2CCH_3)_2$ (Aldrich) was used without further purification. The solvents used were dried and distilled over sodium benzophenone ketyl under nitrogen. IR spectra ($4000–650$ cm^{-1}) were recorded for Nujol and Fluorolube mulls prepared in a dry box. For ^1H NMR spectroscopy, the sample was dissolved in C_7D_8. Other analytical and spectroscopic methods were as described previously [14]. Light petroleum had a boiling point of $60–70°C$.

2.1. Bis(diphenylphosphino-η^5-cyclopentadienyl)(tetrahydrofuran)ytterbium(II) (1)

A mixture of Yb powder (14.7 mmol), $Tl(C_5H_4PPh_2)$ (4.41 mmol) and Hg (about 0.05 g) was heated under reflux for 16 h. It was then filtered warm through a celite pad to remove Hg, Tl and excess Yb. The dark-red filtrate was evaporated and the resulting solid was dried for 2 h at 80°C. After addition of toluene (10 ml) to the solid and stirring the mixture for 40 min, the dark-green product was isolated, washed with toluene (5 ml) and dried under vacuum for 2 h (yield, 75%). The IR spectrum of the product agreed with the reported data [14].

2.2. Di[μ-acetatobis(diphenylphosphino-η^5-cyclopentadienyl)ytterbium(III)]–tetrahydrofuran (1:1.5) (2. 1.5THF)

A mixture of $Yb(C_5H_4PPh_2)_2(THF)$ (1.78 mmol) and $Hg(O_2CCH_3)_2$ (0.89 mmol) was stirred in THF (50

ml) for 24 h. The resulting red solution was filtered through a Celite pad to remove Hg. The residue was washed with THF (5 ml). The filtrate and washings were evaporated, giving a red–brown solid, which was then dried under vacuum for 1.5 h. On recrystallization from THF (10 ml) – light petroleum (30 ml) and drying under vacuum for 3 h, the product was obtained as orange powder (yield, 64%). Anal. Found: C, 57.6; H, 4.4; Yb, 22.5. $C_{78}H_{74}O_{5.5}P_4Yb_2$ calc.: C, 59.7; H, 4.8; Yb, 22.1%. IR: ν3049w, 2926w, 1569vs, 1477w, 1433s, 1410m, 1338w, 1207w, 1173w, 1156w, 1089w, 1069w, 1037m, 1025m, 998w, 971w, 958w, 939w, 917w, 894w, 850w, 840w, 800w, 788m, 776w, 743m, 722m, 699s, 682m, 668m cm^{-1}. Similar data were obtained when the compound was examined on KBr and AgCl plates. Visible–near IR spectrum [$\lambda_{max}(e)$] (THF): 371(260), 738(1), 781(3), 869(15), 964(13), 986(18), ^1H NMR (C_7D_8): δ-32.4 (v br s, 8H, C_5H_4); -29.5 (v br s, 8H, C_5H_4); 1.9 (br s, 6H, C_4H_8O); 3.8 (br s, 6H, C_4H_8O); 9.0 (br s, 8H, p-H(Ph)); 9.5 (br s, 16H, m-H(Ph)); 12.7 (br s, 16H, o-H(Ph)); 53.0 (br s, 6H, O_2CCH_3) ppm. MS: m/z 731 [0.1, M(monomer)$^+$]; 671 [1, (Yb($C_5H_4PPh_2$)$_2$-H)$^+$]; 482 [40, Yb($C_5H_4PPh_2$)-$O_2CCH_3^+$]; 250 [90, ($C_5H_5PPh_2$)$^+$]; 233 [10, (YbO$_2CCH_3$)$^+$]; 183 [100, ($C_{12}H_8P$)$^+$]. Observed isotope patterns for Yb-containing ions were similar to those calculated for the relevant molecular formulae. Recrystallization from toluene gave single crystals of di[μ-(acetato-$O,O:O'$)bis(diphenylphosphino-η^5-cyclopentadienyl)ytterbium(III)] (2) suitable for crystallographic examination.

2.3. X-ray structure determination

2.3.1. Crystal–refinement data. These were as follows

$C_{72}H_{62}P_4O_4Yb_2$; $M = 1461.3$; monoclinic; space group, $P2_1/n$ (C_{2h}^5; No. 14 variant); $a = 9.615(2)$, $b = 13.665(5)$ and $c = 23.209(9)$ Å; $\beta = 91.47(3)°$; $U = 3048(2)$ Å^3; $D_c = 1.59$ g cm^{-3}; $Z = 2$(dimers); $F(000) = 1452$; $\mu_{Mo} = 32$ cm^{-1}, specimen size, $0.20 \times 0.20 \times 0.06$ mm; the crystal was covered with a heavy oil, was rapidly transferred to a fibre in the goniometer head, and was cooled to 193 K; A^*_{min} 1.20, $A^*_{max} = 1.85$ (analytical correction); N (ω scan mode) $= 6968$, $N_\sigma = 3996$; $R = 0.034$, $R_w = 0.027$; $n_v = 370$; $T = 193$ K. Other specific procedural details: reflection weights, $\omega = [\sigma^2(F_o) + 0.000071\ F_o^2]^{-1}$; SHELXTL PLUS program system [15].

$C_{24}H_{26}O_4Yb_2$, $M = 724.6$; orthorhombic; space group, $Pbam$ (D_{2h}^9; No. 55); $a = 13.16(1)$, $b = 12.98(1)$ and $c = 13.376(4)$ Å; $U = 2285$ Å^3; $D_c = 2.11$ g cm^{-3}; $Z = 4$(dimers); $F(000) = 1368$; $\mu_{Mo} = 82$ cm^{-1}; specimen size, $0.46 \times 0.26 \times 0.16$ mm (capillary); $A^*_{min} = 3.9$, $A^*_{max} = 12.9$ (analytical correction); N ($2\theta–\theta$ scan mode) $= 2224$, N_0 1745; $R = 0.058$ and $R_w = 0.063$; $n_v = 152$; $T = 295$ K. Other specific procedural details:

statistical reflection weights; derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$; XTAL 3.2 program system [16].

2.3.2. Structure determination

Unique diffractometer data sets were measured at the specified temperature within the limit $2\theta_{max} = 55°$; monochromatic Mo Kα radiation ($\lambda = 0.7107$ Å) was employed. N independent reflections were obtained (see above), N_0 with $I > 3\sigma(I)$ being considered "observed" and used in the full matrix least-squares refinement after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at appropriate values. Conventional residuals R, R_w on $|F|$ are quoted at convergence. Neutral atom complex scattering factors were employed [17]. Atomic coordinates are given in Tables 1 and 2, the structures are displayed in Figures 1 and 2, and selected bond distances and angles are in Tables 3 and 4. Complete lists of bond distances and angles, thermal parameters and hydrogen atom coordinates are available from the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Syntheses

The diphenylphosphinoytterbocene $Yb(C_5H_4PPh_2)_2$-(THF) was prepared by reaction of $Tl(C_5H_4PPh_2)$ with ytterbium metal in THF:

$$Yb + 2Tl(C_5H_4PPh_2) \rightarrow Yb(C_5H_4PPh_2)_2 + 2Tl\downarrow \tag{1}$$
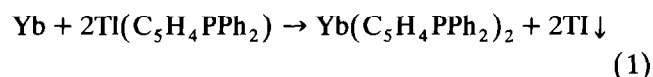
This reaction has previously been used to synthesize the dme complex [14]. The THF complex has hitherto been prepared by other routes, for example

$$Yb(C_6F_5)_2 + 2C_5H_5PPh_2$$
$$\xrightarrow{THF} Yb(C_5H_4PPh_2)_2 + 2C_6F_5H \tag{2}$$
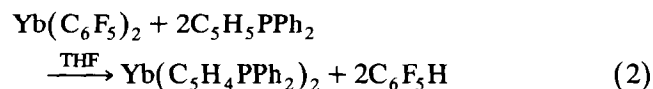
The complex $Yb(C_5H_4PPh_2)_2(THF)$ was oxidized with $Hg(O_2CCH_3)_2$ in THF to give $Yb(C_5H_4PPh_2)_2$-(O_2CCH_3):

$$2Yb(C_5H_4PPh_2)_2 + Hg(O_2CCH_3)_2$$
$$\longrightarrow 2Yb(C_5H_4PPh_2)_2(O_2CCH_3) + Hg\downarrow \tag{3}$$
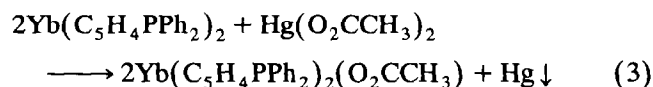
Oxidation of divalent ytterbium compounds with mercury or thallium salts has been used before in the synthesis of Yb(III) carboxylates $YbCp_2(O_2CR)$, where $R = CH_3$, C_6F_5, C_6H_5, CF_3, C_6Br_5 etc [6]. The IR spectrum of the product crystallized from THF–light petroleum contained features associated with the $C_5H_4PPh_2$ group, e.g. a significant $\gamma(CH)$ absorption

Table 1

Atomic coordinates and equivalent isotropic displacement coefficients for $[Yb(\eta^5-C_5H_4PPh_2)_2(\mu-O_2CCH_3)]_2$ (2)

	x	y	z	U_{eq} (Å^2) [a]
Yb	−0.09525(3)	0.07287(2)	0.06041(1)	0.0269(1)
P(1)	−0.21854(15)	0.24571(11)	−0.06506(6)	0.0313(5)
P(2)	0.09344(15)	0.02413(11)	0.21364(6)	0.0281(5)
C(1)	−0.1335(6)	0.2450(4)	0.0066(3)	0.031(2)
C(2)	−0.1915(6)	0.2543(4)	0.0614(3)	0.034(2)
C(3)	−0.0827(6)	0.2477(4)	0.1034(3)	0.037(2)
C(4)	0.0412(6)	0.2330(5)	0.0752(3)	0.042(2)
C(5)	0.0116(6)	0.2304(4)	0.0155(3)	0.035(2)
C(6)	−0.1199(6)	0.3441(4)	−0.0994(3)	0.034(2)
C(7)	−0.0738(6)	0.4283(5)	−0.0705(3)	0.044(2)
C(8)	0.0051(7)	0.4972(5)	−0.0985(3)	0.054(3)
C(9)	0.0377(7)	0.4835(6)	−0.1550(3)	0.059(3)
C(10)	−0.0071(8)	0.4018(5)	−0.1848(3)	0.059(3)
C(11)	−0.0861(7)	0.3317(5)	−0.1568(3)	0.044(2)
C(12)	−0.3891(6)	0.3023(4)	−0.0503(2)	0.031(2)
C(13)	−0.4258(7)	0.3955(5)	−0.0679(3)	0.047(2)
C(14)	−0.5600(7)	0.4301(6)	−0.0597(3)	0.055(3)
C(15)	−0.6550(7)	0.3728(5)	−0.0324(3)	0.049(3)
C(16)	−0.6186(6)	0.2799(5)	−0.0140(3)	0.040(2)
C(17)	−0.4872(6)	0.2441(5)	−0.0238(2)	0.033(2)
C(18)	−0.0556(6)	0.0035(4)	0.1652(2)	0.027(2)
C(19)	−0.0644(6)	−0.0776(5)	0.1279(2)	0.036(2)
C(20)	−0.1996(7)	−0.0848(5)	0.1051(2)	0.047(2)
C(21)	−0.2762(6)	−0.0052(6)	0.1274(3)	0.051(3)
C(22)	−0.1897(6)	0.0472(4)	0.1654(2)	0.038(2)
C(23)	0.0435(6)	0.1389(4)	0.2491(2)	0.029(2)
C(24)	0.1207(7)	0.2224(4)	0.2378(2)	0.038(2)
C(25)	0.0840(8)	0.3109(5)	0.2611(3)	0.051(3)
C(26)	−0.0295(8)	0.3166(5)	0.2964(3)	0.058(3)
C(27)	−0.1048(8)	0.2340(6)	0.3088(3)	0.057(3)
C(28)	−0.0689(7)	0.1453(5)	0.2859(2)	0.043(2)
C(29)	0.0586(5)	−0.0648(5)	0.2709(2)	0.028(2)
C(30)	−0.0485(7)	−0.1345(5)	0.2686(3)	0.042(2)
C(31)	−0.0611(7)	−0.2015(5)	0.3127(3)	0.054(3)
C(32)	0.0301(7)	−0.2007(5)	0.3594(3)	0.048(3)
C(33)	0.1361(7)	−0.1327(5)	0.3625(3)	0.044(2)
C(34)	0.1523(6)	−0.0657(5)	0.3179(2)	0.038(2)
O(1)	−0.1135(4)	−0.0113(3)	−0.0329(2)	0.032(1)
O(2)	−0.2992(4)	0.0489(3)	0.0051(2)	0.034(1)
C(35)	−0.2461(6)	0.0044(4)	−0.0354(2)	0.030(2)
C(36)	−0.3323(6)	−0.0320(5)	−0.0848(2)	0.046(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

at 743 cm^{-1}. The presence of acetate was established by observation of $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ at 1569 cm^{-1} and 1410 cm^{-1} respectively. The separation of 159 cm^{-1} clearly shows that the acetate is not unidentate but does not provide any further information about the nature of the acetate group [18]. It is not clear from the IR spectrum whether THF is present. However, since acetate is not unidentate, the plausible [1] eight-coordinated arrangement $Yb(\eta^5-C_5H_4PPh_2)_2(THF)(OCCH_3)$ can be eliminated. In the ^1H NMR spectrum in C_7D_8 a fractional amount of THF was detected $(THF:C_5H_4PPh_2, 0.75:2)$, and the THF peaks at 3.8

Table 2

Non-hydrogen positional and isotropic displacement parameters for [Yb(η^5-Cp)$_2$(μ-O$_2$CCH$_3$)]$_2$ (3), molecules A and B

Atom	x	y	z	U_{eq} (Å^2)
Yb(A)	0.35174(5)	0.00523(7)	0	0.0361(3)
C(A01)	0.340(1)	−0.084(2)	−0.174(1)	0.069(7)
C(A02)	0.247(2)	−0.096(2)	−0.132(1)	0.083(8)
C(A03)	0.202(1)	0.001(2)	−0.126(1)	0.073(7)
C(A04)	0.274(2)	0.067(2)	−0.169(1)	0.084(9)
C(A05)	0.355(1)	0.023(2)	−0.193(1)	0.082(9)
O(A1)	0.5093(8)	0.096(1)	0	0.054(5)
O(A2)	0.369(1)	0.189(1)	0	0.078(7)
C(A1)	0.463(2)	0.188(3)	0	0.08(1)
C(A2)	0.519(2)	0.291(3)	0	0.11(2)
Yb(B)	0.50939(5)	0.64994(8)	0.5	0.0366(3)
C(B01)	0.422(2)	0.666(2)	0.670(1)	0.10(1)
C(B02)	0.407(1)	0.760(2)	0.622(1)	0.082(9)
C(B03)	0.495(2)	0.808(2)	0.615(1)	0.083(9)
C(B04)	0.569(2)	0.752(3)	0.653(2)	0.11(1)
C(B05)	0.528(3)	0.663(3)	0.692(1)	0.15(2)
O(B1)	0.5989(8)	0.487(1)	0.5	0.046(5)
O(B2)	0.6885(9)	0.620(2)	0.5	0.062(6)
C(B1)	0.688(2)	0.525(2)	0.5	0.049(8)
C(B2)	0.773(2)	0.471(2)	0.5	0.08(1)

and 1.8 ppm were not paramagnetically shifted. In contrast, the resonance due to acetate protons displayed a large paramagnetic shift ($\delta = 53.0$ ppm) which is consistent with coordinated acetate. The C$_5$H$_4$ proton resonances are at −29.5 and −32.4 ppm, which are comparable with the chemical shifts of Cp protons for

Table 3

Selected bond lengths (Å) and angles (°) for [Yb(C$_5$H$_4$PPh$_2$)$_2$-(O$_2$CCH$_3$)]$_2$ (2)

Bond lengths			
Yb–C(1)	2.684(6)	Yb–C(18)	2.628(5)
Yb–C(2)	2.647(6)	Yb–C(19)	2.597(6)
Yb–C(3)	2.590(6)	Yb–C(20)	2.603(7)
Yb–C(4)	2.570(6)	Yb–C(21)	2.593(7)
Yb–C(5)	2.614(6)	Yb–C(22)	2.645(6)
Yb–Ct(1) [a]	2.332	Yb–Ct(2) [a]	2.323
Yb–O(1)	2.454(4)	Yb–O(2)	2.339(4)
Yb–O(1′)	2.282(4)	O(1)–C(35)	1.293(6)
O(2)–C(35)	1.241(7)	C(35)–C(36)	1.483(8)
⟨P–C(Ph)⟩	1.84	⟨P–C(C$_5$H$_4$)⟩	1.83
⟨C$_i$–C$_{i+1}$⟩ [b]	1.41	⟨Yb–C⟩	2.62
Yb ··· Yb′	3.930(2)		
Bond angles			
Ct(1)–Yb–Ct(2)	130.7	O(1)–Yb–O(1′)	67.9(1)
Ct(1)–Yb–O(1)	113.6	Yb–O(1)–Yb′	112.1(1)
Ct(1)–Yb–O(1′)	104.6	C(35)–O(1)–Yb′	157.2(4)
Ct(1)–Yb–O(2)	100.3	O(1)–C(35)–O(2)	118.1(5)
Ct(2)–Yb–O(1)	114.0	Yb–O(1)–C(35)	90.6(3)
Ct(2)–Yb–O(2)	96.8	Yb–O2–C(35)	97.4(3)
Ct(2)–Yb–O(1′)	104.7	O(1)–Yb–O(2)	53.9(1)

[a] Ct(n) is the centroid of the cyclopentadienyl ring defined by the preceding five carbon atoms.

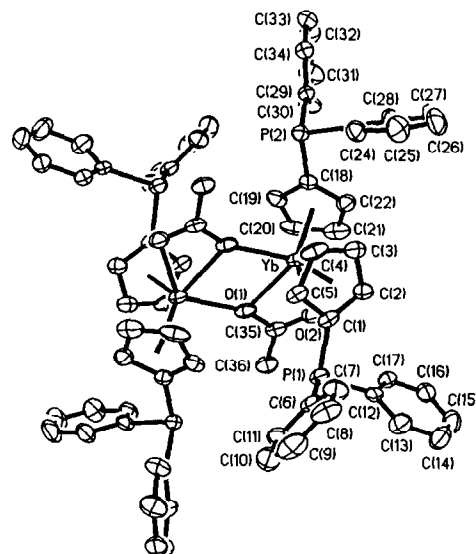[b] C$_i$ and C$_{i+1}$ are adjacent carbon atoms of a cyclopentadienyl ring.

Fig. 1. The X-ray structure of [Yb(η^5-C$_5$H$_4$PPh$_2$)$_2$(μ-O$_2$CCH$_3$)]$_2$ (2).

YbCp$_3$.OPPh$_3$(−35.6 ppm) and YbCp$_3$(THF) (−47.8 ppm) [19]. In addition the peaks due to the phenyl protons are shifted downfield from those of the diamagnetic Yb(C$_5$H$_4$PPh$_2$)$_2$(THF) complex [14]. Accordingly, the broad peaks and very large range of chemical shifts in the ^{1}H NMR spectrum are consistent with the presence of the paramagnetic Yb^{3+} ion. Characteristic Yb(III) absorptions are observed near 1000 cm^{-1} in the near IR spectrum (see Section 2). The mass spectrum of the compound contained a very weak cluster owing to the molecular ion of the monomer as well as ions due to its fragmentation, but no Yb$_2$-containing species were observed by contrast with YbCp$_2$(O$_2$CCH$_3$) [6]. Although the metal analysis of the complex was adequate, the carbon analysis was unsatisfactory, as is often the case with organolanthanoid complexes [20–23]. This may be due to problems in complete combustion of the organolanthanoid [24–27], but slight decomposition during loading of the highly air-sensitive sample into an aluminium capsule in the dry box cannot be ruled out.

Since the THF-containing species crystallizes from toluene as a THF-free acetate bridged dimer (see below) and the THF resonances are not paramagnetically shifted, it is probable that the species obtained from THF–light petroleum is a THF solvate of the acetate-bridged dimer. Indeed, the size of the shift of the acetate methyl resonance may perhaps be attributed to the influence of two paramagnetic Yb^{3+} ions on a bridging acetate.

3.2. X-ray crystal structures of [Yb(η^5-C$_5$H$_4$PPh$_2$)$_2$-(O$_2$CCH$_3$)]$_2$ (2) and [Yb(η^5-Cp)$_2$(O$_2$CCH$_3$)]$_2$ (3)

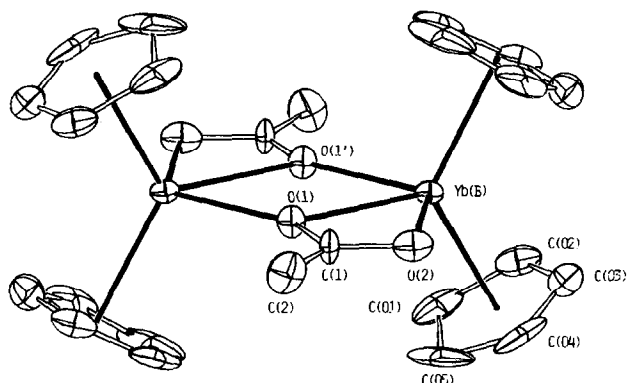Satisfactory single crystals were obtained by crystallization from toluene for **2** and from THF–pentane for

Fig. 2. The X-ray structure of [Yb(η^5-Cp)$_2$(μ-O$_2$CCH$_3$)]$_2$ (3). Dimer B is displayed. Dimer A is essentially the same.

3. Atomic coordinates are given in Tables 1 and 2, the structures are shown in Figs. 1 and 2 and selected bond lengths and angles are in Tables 3 and 4. Data for the structures are compared with each other and with [YbCp$_2$(O$_2$CC$_6$F$_5$)]$_2$ [7] in Table 5.

Both complexes are dimeric with two acetate bridges. However, by contrast with [Yb(C$_5$H$_4$R)$_2$(O$_2$CR')]$_2$ (R = H or Me; R' = C$_6$F$_5$ or Ph) [7–9] (see Section 1), each bridging carboxylate is chelated to one ytterbium atom and bonded through one oxygen atom to the other (bridging tridentate coordination [28]), and each ytterbium atom is formally nine coordinated with two η^5-cyclopentadienyl ligands, two oxygen atoms from one bridging acetate, and one from the other. Although this

Table 4
Selected bond lengths (Å) and angles (°) for [YbCp$_2$(O$_2$CCH$_3$)]$_2$ (3)

	Bond length			Bond angle	
	Dimer A	Dimer B		Dimer A	Dimer B
Yb–C(01)	2.60(2)	2.56(2)	Ct(00) [a]–Yb–Ct(00″) [b]	132.1	123.3
Yb–C(02)	2.60(2)	2.55(3)	Ct(00)–Yb–O(1)	113.5	117.7
Yb–C(03)	2.59(2)	2.57(2)	Ct(00)–Yb–O(1′)	103.8	105.3
Yb–C(04)	2.61(2)	2.56(3)	Ct(00)–Yb–O(2)	99.5	102.4
Yb–C(05)	2.59(2)	2.59(2)	Yb–O(1)–Yb′	114.8(7)	112.2(4)
Yb–Ct(00) [a]	2.324	2.287	O(1)–Yb–O(1′)	65.2(5)	67.8(4)
Yb–O(1)	2.38(1)	2.42(1)	C(2)–C(1)–O(1)	124(2)	126(2)
Yb–O(2)	2.39(2)	2.39(1)	C(2)–C(1)–O(2)	119(3)	122(2)
Yb–O(1′)	2.25(1)	2.28(1)	O(1)–C(1)–O(2)	117(3)	113(2)
O(1)–C(1)	1.34(4)	1.27(2)	C(1)–O(2)–Yb	95(2)	99(1)
O(2)–C(1)	1.24(2)	1.24(3)	C(1)–O(1)–Yb	93(1)	97(1)
C(1)–C(2)	1.53(5)	1.32(3)	C(1)–O(1)–Yb′	152(1)	151(1)
			O(1)–Yb–O(2)	54.9(5)	51.6(5)
$\langle C_i$–$C_{i+1}\rangle$ [c]	1.36	1.37			
$\langle$Yb–C$\rangle$	2.60	2.57			
Yb ⋯ Yb′	3.906(2)	3.899(3)			
O(1) ⋯ O(1′)	2.50(2)	2.62(2)			

[a] Ct(00) is the centroid of the cyclopentadienyl ring.
[b] Doubly primed Ct(00″) is generated by the intradimer reflection operation.
[c] C$_i$ and C$_{i+1}$ are adjacent carbon atoms of a cyclopentadienyl ring.

Table 5
Selected bond lengths (Å) and angles (°) for [Yb(C$_5$H$_4$PPh$_2$)$_2$(O$_2$CCH$_3$)]$_2$, [YbCp$_2$(O$_2$CCH$_3$)]$_2$ and [YbCp$_2$(O$_2$CC$_6$F$_5$)]$_2$

	[Yb(C$_5$H$_4$PPh$_2$)$_2$ (O$_2$CCH$_3$)]$_2$	[YbCp$_2$(O$_2$CCH$_3$)]$_2$		[YbCp$_2$(O$_2$CC$_6$F$_5$)]$_2$ [7]	
		Dimer A	Dimer B	Dimer A	Dimer B
Bond lengths					
Yb ⋯ Yb′	3.930(2)	3.906(2)	3.899(3)	5.06	5.01
$\langle$Yb–C(Cp)$\rangle$ [a]	2.62	2.60	2.57	2.60	2.59
Yb–O(1)	2.454(4)	2.38(1)	2.42(1)	2.178(7)	2.201(7)
Yb–O(2)	2.339(4)	2.39(2)	2.39(1)	—	—
Yb′–O(2)	—	—	—	2.201(8)	2.182(8)
Yb–O(1′)	2.282(4)	2.25(1)	2.28(1)	—	—
Bond angles					
Ct–Yb–Ct′	130.7	132.1	123.3	131.9	132.1
Ct–Yb–O(1)	113.6	113.5	117.7	105.6	104.4
O(1)–Yb–O(n′) [b]	67.9	65.2(5)	67.8(4)	97.4(3)	98.2(3)
O(1)–C–O(2)	118.1(5)	117(3)	113(2)	125(1)	124(1)

[a] $\langle$Yb–C(Cp)$\rangle$ is the average distance between Yb and C atoms of the Cp rings.
[b] O(n′) = O(1′) for [Yb(C$_5$H$_4$PPh$_2$)$_2$(O$_2$CCH$_3$)]$_2$ and [YbCp$_2$(O$_2$CCH$_3$)]$_2$ and O(n′) = O(2′) for [YbCp$_2$(O$_2$CC$_6$F$_5$)]$_2$.

tridentate form of carboxylate bridging [28] is novel in organolanthanoid carboxylates, it is common in simple lanthanoid acetates, e.g. $[Ln(O_2CCH_3)(H_2O)_6]$-$Cl_2.H_2O$ (Ln = La–Sm) [29], $[Ln(O_2CCH_3)_2(H_2O)_3]Cl$ (Ln = Ce–Lu or Y) [29], $[Sm(O_2CCH_3)_3(H_2O)_2]$. CH_3-CO_2H [30], $Pr(O_2CCH_3)_3(H_2O)_{1.5}$ [31], $Ln(O_2CCH_3)_3$ (Ln = Sm–Lu or Y) [32] and $Pr(O_2CCH_3)_3$ [33]. No crystal structure of an organolanthanoid acetate has previously been reported. A conceptually similar nine-coordinated structure has been reported for $[Yb(\eta^5-Cp)_2(\mu_3-H)]_2[Al(\mu_2-H)H_2.N(C_2H_5)_3]_2.C_6H_6$ [34], in which two ytterbium atoms are coordinated by two triethylamine adducts of alane through μ_2- and μ_3-hydrogen atoms.

The crystal structure of 2 contains one dimer (Fig. 1), whereas 3 has two similar independent dimers A and B. Only the latter is displayed (Fig. 2). In A and B, the $Yb(O_2CCH_3)_2Yb$ unit has all the non-hydrogen atoms coplanar in the mirror plane. For each, the inversion centre, through which passes a twofold axis normal to the mirror plane, is located between the pairs of metal and oxygen atoms. The $\eta^5-C_5H_5$ rings are symmetry related with only one being crystallographically independent per dimer. The ring planes of A and B are inclined to the mirror plane by 24.5(11) and 28.3(13)° respectively. There is a significant difference between the centroid–Yb–centroid angle of 2 (132.1°) and dimer A of 3 (130.7°) on the one hand, and dimer B of 3 (123.3°) on the other hand (Table 5). The last value lies within the range expected for nine-coordinated Yb(III) complexes (113–128.9°) [34–39], whereas the angles for 2 and dimer A are within the range for eight-coordinated Yb(III) compounds (126.7–140°) [1,5,7,12,40,41]. The way in which dimer A and 2 compensate for the increased coordination number is not clear, since ⟨Yb–C⟩ and ⟨Yb–O⟩ for 2 and dimer A are similar to those of dimer B. Subtraction of the ionic radius for nine-coordinate Yb^{3+} (1.04 Å) [42] from the average Yb–C distance gives 1.58, 1.56 and 1.53 Å for 2 and dimers A and B of 3 respectively, as effective "ionic radii" [43] of the cyclopentadienide ions. Any possible significance in the 0.05 Å difference between 2 and dimer B is annulled by the smaller difference between A and B.

The structure of 2 shows no evidence for any P–Yb interaction and the P–C distances (Table 3) are similar to those of $[Yb(C_5H_4PPh_2)_2Cl]_2$ [1]. Whereas the latter compound crystallized with two different dimers, one with a *syn* and one with an *anti* arrangement of the PPh_2 groups, complex 2 has only *anti* PPh_2 groups.

A number of interesting relationships emerge from the Yb–O distances (Tables 3–5). In 2, chelation is quite unsymmetrical, with a difference of greater than 0.1 Å between the Yb–O(1) and Yb–O(2) lengths, whereas, in both A and B of 3 chelation is symmetrical. For 2, A and B, the Yb–O(1′) distance is the shortest and is similar to Yb–O of $[YbCp_2(O_2CC_6F_5)]_2$ [7]

(Table 5) and $[YbCp_2(O_2SOCF_3)]_2$ [12], when allowance is made for the 0.06 Å difference in ionic radius between eight- and nine-coordinated Yb^{3+} [42]. By contrast, the Yb–O(1) and Yb–O(2) distances are 0.13–0.17 Å longer, except for Yb–O(2) of 2 which is closer to Yb–O(1′) than to Yb–O(1).

Subtraction of the ionic radius for nine coordinate Yb^{3+} [42] from the Yb–O(1) distances gives 1.41 Å for 2 and 1.34 and 1.38 Å for dimers A and B of 3. Corresponding values from Yb–O(2) are 1.30, 1.35 and 1.35 Å. Both sets are near the value 1.34(5) Å derived from Ln–O of organolanthanoid–ether complexes [44] in which there is not substantial steric crowding. Evidently, any increase in bond strength associated with coordination of a charged ligand is offset by weakening of binding owing to the bridging role. However, subtraction from Yb–O(1′) lengths gives 1.24, 1.24 and 1.21 Å for 2 and A and B of 3 respectively. These shorter values lie between those derived from Ln–O of lanthanoid–phenolate distances (average, 1.27 Å) [45,46] and those from Ln–OPPh₃ distances (1.15–1.19 Å) [47–49]. Subtraction of the ionic radius for eight-coordinated Yb^{3+} [42] from Yb–O of $[YbCp_2(O_2CC_6F_5)]_2$ [7] gives 1.19–1.22 Å. Thus, whilst the smaller size of acetate than pentafluorobenzoate allows a higher coordination number in 2 and 3 than $[YbCp_2(O_2CC_6F_5)]_2$, it is accompanied by an increase in average Yb–O distances that is considerably more (average amount 0.1 Å) than expected for the increase in coordination number. However, this increase is observed essentially in the chelated Yb–O bonds, whilst the Yb–O(1′) distance is close to the value expected simply owing to the coordination number increase. The change from *anti*:*anti* bridging bidentate carboxylates in $[YbCp_2(O_2CC_6F_5)]_2$ to bridging tridentates in (2) and (3) is accompanied by a considerable shortening (more than 1 Å) in the Yb...Yb separation (Table 5), which is approximately equal to the sum (3.88 Å) of two ytterbium metallic radii in 2 and 3. Thus the lengthening of ⟨Yb–O⟩ from the pentafluorobenzoate to 2 and 3 above that expected for the increase in coordination number, may be needed to offset steric repulsion caused by the shorter Yb...Yb distance. Further, the Yb–O(1′) bonds, which resemble the *anti* Yb–O interactions of $[YbCp_2(O_2CC_6F_5)]_2$, do not show this extra lengthening to a significant extent.

By comparison with 2 and 3, the Ln–O bond length relationships for bridging tridentate acetates in $Pr(O_2CCH_3)_3$ [33], $[Sm(O_2CCH_3)_3(H_2O)_2].CH_3CO_2H$ [30], and $Ln(O_2CCH_3)_3$ (Ln = Lu or Ho) [32] show greater variation. However, Ln–O for the bridging unidentate linkage is generally the shortest as in 2 and 3. Where there are also simple bridging bidentate acetates, ⟨Ln–O⟩ is shorter for these than for the tridentate acetates [32,33]. The bridging tridentate ligands of $Ho(O_2CCH_3)_3$ [32] and one of $Pr(O_2CCH_3)_3$ [33] show a pattern similar to that of 2, with a large difference

(about 0.1–0.2 Å) between the chelating Ln–O bond lengths and a smaller difference between the two shortest Ln–O distances. By contrast, the Sm and Lu compounds have a small difference between the chelating Ln–O distances and a marked difference between the two shorter lengths, as observed in **3**. Two of the bridging tridentate acetates of $Pr(O_2CCH_3)_3$ have 0.4–0.5 Å difference between the longer Pr–O distances, and this has no parallel in the organometallic acetates. Subtraction of the appropriate ionic radii from the Ln–O distances of these simple lanthanoid acetates gives values in the range 1.27–1.83 Å, and in each case the average value is significantly higher than for **2** and **3**.

Acknowledgements

References

[1] G.B. Deacon, G.D. Fallon and C.M. Forsyth, *J. Organomet. Chem.*, *462* (1993) 183.

[2] C.J. Shaverien, *Adv. Organomet. Chem.*, *36* (1994) 283; H. Schumann, *Angew. Chem., Int. Ed. Engl.*, *23* (1984) 474; H. Schumann and W. Genthe, in K.A. Gschneidner and L. Eyring (eds.), *Organometallic Compounds of the Rare Earths, Handbook on the Physics and Chemistry of the Rare Earths, Vol. 7*, Elsevier, Amsterdam, 1984, Chapter 53; T.J. Marks and R.D. Ernst, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry, Vol. 3*, Pergamon, Oxford, 1982, p. 173.

[3] C. Qian and D. Zhu, *J. Chem. Soc., Dalton Trans.*, (1994) 1599; C. Sun, G. Wei, Z. Jin and W. Chen, *Polyhedron, 13* (1994) 1483; P. Van de Weghe, C. Bied, J. Collin, J. Marçalo and I. Santos, *J. Organomet. Chem.*, *475* (1994) 121; G. Paolucci, R. D'Ippolito, C. Ye, C. Qian, J. Gräper and R.D. Fischer, *J. Organomet. Chem.*, *471* (1994), 97; C. Qian, X. Zheng, B. Wang, D. Deng and J. Sun, *J. Organomet. Chem.*, *466* (1994) 101.

[4] R.E. Maginn, S. Manastyrskyj and M. Dubeck, *J. Am. Chem. Soc.*, *85* (1963) 672.

[5] R.S.P. Coutts and P.C. Wailes, *J. Organomet. Chem.*, *25* (1970) 117; R.D. Fischer and G. Bielang, *J. Organomet. Chem.*, *191* (1980) 61; Z. Ye, Z. Zhou, S. Yuan and Z. Luo, *Youji Huaxue*, *2* (1984) 119; T.D. Tilley, R.A. Andersen, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, *21* (1982) 2644; C. Qian, C. Ye, H. Lu, Y. Li, J. Zhou and Y. Ge, *Inorg. Chim. Acta*, *94* (1984) 52; J. Zhou, Y. Ge and C. Qian, *Synth. React. Inorg. Met. Org. Chem.*, *14* (1984) 651.

[6] G.B. Deacon and D.L. Wilkinson, *Aust. J. Chem.*, *42* (1989) 845.

[7] G.B. Deacon, G.D. Fallon, P.I. MacKinnon, R.H. Newnham, G.N. Pain, T.D. Tuong and D.L. Wilkinson, *J. Organomet. Chem.*, *277* (1984) C21.

[8] E.C. Baker, *Diss. Abstr. B*, (1978) 730; E.C. Baker, *Ph.D. Thesis*, University of California, 1977.

[9] G.B. Deacon, B.M. Gatehouse, G.D. Fallon and J. Sun, unpublished results.

[10] H. Schumann, J.A. Meese-Marketscheffel, A. Dietrich and F.H. Görlitz, *J. Organomet. Chem.*, *430* (1992) 299.

[11] M.A. St. Clair and B.D. Santarsiero, *Acta Crystallogr. C45* (1989) 850.

[12] J. Stehr and R.D. Fischer, *J. Organomet. Chem.*, *430* (1992) C1.

[13] M.D. Rausch, B.H. Edwards, R.D. Rogers and J.L. Atwood, *J. Am. Chem. Soc.*, *105* (1983) 3882.

[14] G.B. Deacon, C.M. Forsyth, W.C. Patalinghug, A.H. White, A. Dietrich and H. Schumann, *Aust. J. Chem.*, *45* (1992) 567.

[15] G.M. Sheldrick, SHELXTL PLUS, Revision 3.4, Siemens Analytical X-Ray Instruments, Madison, WI, 1988.

[16] S.R. Hall, H.D. Flack and J.M. Stewart (eds.), *The XTAL 3.2 Users Manual*, Universities of Western Australia, Geneva and Maryland, 1992.

[17] J.A. Ibers and W.C. Hamilton (eds.), *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974.

[18] G.B. Deacon, F. Huber and R.J. Phillips, *Inorg. Chim. Acta, 104* (1985) 41; G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, *33* (1980) 227.

[19] P.A. White, *Ph.D. Thesis*, Monash University, 1993.

[20] J. Gräper, R.D. Fischer and G. Paolucci, *J. Organomet. Chem.*, *471* (1994) 87.

[21] D. Deng, X. Zheng, C. Qian, J. Sun, A. Dormond, D. Baudry and M. Visseaux, *J. Chem. Soc., Dalton Trans.*, (1994) 1665.

[22] C. Qian, C. Ye and Y. Li, *J. Organomet. Chem.*, *302* (1986) 171.

[23] H. Schumann, S. Nickel, E. Hahn and M.J. Heeg, *Organometallics, 4* (1985) 800.

[24] R.H. Newnham, *Ph.D Thesis*, Monash University, 1988.

[25] H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, *Organometallics, 1* (1982) 1194.

[26] K.O. Hodgson, F. Mares, D.F. Starks and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, *95* (1973) 8650.

[27] F. Calderazzo, R. Pappalardo and S. Losi, *J. Inorg. Nucl. Chem.*, *28* (1966) 987.

[28] A. Ouchi, Y. Suzuki, Y. Ohki and Y. Koizumi, *Coord. Chem. Rev.*, *92* (1988) 29.

[29] A. Lossin and G. Meyer, *J. Less-Common Met.*, 175 (1991) 301, and references cited therein.

[30] A. Lossin, G. Meyer, R. Fuchs and J. Strähle, *Z. Naturforsch., 47b* (1992) 179.

[31] A. Lossin and G. Meyer, *Z. Naturforsch., 47b* (1992) 1602.

[32] A. Lossin and G. Meyer, *Z. Anorg. Allg. Chem.*, *619* (1993) 1609.

[33] A. Lossin and G. Meyer, *Z. Anorg. Allg. Chem.*, *620* (1994) 438.

[34] S.Ya. Knjazhanskij, B.M. Bulychev, O.K. Kireeva, V.K. Belsky and G.L. Soloveichik, *J. Organomet. Chem.*, *414* (1991) 11.

[35] S.H. Eggers, J. Kopf and R.D. Fischer, *Acta Crystallogr., Sect. C, 43* (1987) 2288.

[36] A. Hammel, W. Schwarz and J. Weidlein, *J. Organomet. Chem.*, *363* (1989) C29.

[37] C. Qian, B. Wang, D. Deng, J. Hu, J. Chen, G. Wu and P. Zheng, *Inorg. Chem.*, *33* (1994) 3382.

[38] D. Deng, C. Qian, F. Song, Z. Wang, G. Wu, P. Zheng, S. Jin and Y. Lin, *J. Organomet. Chem.*, *458* (1993) 83.

[39] P.L. Watson, J.F. Whitney and R.L. Harlow, *Inorg. Chem.*, *20* (1981) 3271.

[40] X.-G. Zhou, Z.-Z. Wu and Z.-S. Jin, *J. Organomet. Chem.*, *431* (1992) 289.

[41] E.C. Baker, L.D. Brown and K.N. Raymond, *Inorg. Chem.*, *14* (1975) 1376.

[42] R.D. Shannon, *Acta Crystallogr., Sect. A, 32* (1976) 751.

[43] K.N. Raymond and C.W. Eigenbrot, Jr., *Acc. Chem. Res.*, *13* (1980) 276.

[44] G.B. Deacon, P.I. MacKinnon, T.W. Hambley and J.C. Taylor, *J. Organomet. Chem.,* *259* (1983) 91.

[45] G.B. Deacon, S. Nickel, P.I. MacKinnon and E.R.T. Tiekink, *Aust. J. Chem.,* *43* (1990) 1245.

[46] G.B. Deacon, T. Feng, S. Nickel, M.I. Ogden and A.H. White, *Aust. J. Chem.,* *45* (1992) 671.

[47] M. Ul-Haque, C.N. Caughlan, F.A. Hart and R. Van Nice, *Inorg. Chem.,* *10* (1971) 115.

[48] G.B. Deacon, B.M. Gatehouse and P.A. White, *Polyhedron, 8* (1989) 1983.

[49] G.B. Deacon, B.M. Gatehouse and P.A. White, *Aust. J. Chem.,* *45* (1992) 1939.