

(Sirigu, Bianchi & Benedetti, 1969). As shown in Figs. 1 and 2, the phosphine acts as a bridging ligand spanning the Ru(1)–Ru(2) edge. Ru(2) has the same regiochemical relationship with respect to the bridging CO ligand [C(7)O(7)] as the first phosphine substitution site adopted in [Ru<sub>6</sub>C(CO)<sub>16</sub>(PPh<sub>2</sub>Et)] (Brown, Evans & Webster, 1981), and the substitution site on Ru(2) is twisted away from the bridging CO side of the molecule to allow coordination of the second P atom to what appears to be the second-preference substitution site [on Ru(1)]. Indeed, in both phosphine- and arene-substituted derivatives, *e.g.* [Ru<sub>6</sub>C(CO)<sub>14</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] (Ansell & Bradley, 1980) and [Ru<sub>6</sub>C(CO)<sub>11</sub>(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>] (Gomez-Sal, Johnson, Lewis, Raithby & Wright, 1985), the non-carbonyl ligands avoid coordination to the Ru atoms involved in the  $\mu$ -CO bridge. The P NMR data at 172 K, with two distinct <sup>31</sup>P environments, are consistent with this structure being maintained in solution.

The shortest Ru–Ru distance is that bridged by the  $\mu$ -CO group, whilst the longest [Ru(1)–Ru(2)] is spanned by the Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> ligand. However, the spread of metal–metal bond lengths in this compound (0.15 Å) is less than that of [Ru<sub>6</sub>C(CO)<sub>17</sub>] (0.20 Å) and [Ru<sub>6</sub>C(CO)<sub>16</sub>(PPh<sub>2</sub>Et)] (0.26 Å), so there is little evidence for the phosphine destabilizing a metal–metal bond. The carbido site [C(16)] is slightly displaced towards Ru(1) and Ru(2), but

the mean Ru–C(carbide) distance is very similar to that of the parent cluster.

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## Structure of Tris( $\eta^5$ -cyclopentadienyl)ytterbium(III)\*

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**Abstract.** [Yb(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>],  $M_r = 368.32$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.988$  (3),  $b = 8.312$  (3),  $c = 18.176$  (6) Å,  $V = 1206.8$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.027$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } \text{K}\alpha) = 0.709261$  Å,  $\mu = 76.97$  cm<sup>-1</sup>,  $F(000) = 700$ ,  $T = 295$  K,  $R = 0.037$  for 2244 unique observed reflections. The structure consists of Yb-centred, strictly mononuclear ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Yb<sup>III</sup> units and is not identical with the structures of the corresponding Tm and Lu complexes. The average Yb–C distance is 2.639 Å, and the Yb atom lies only

0.05 Å above the plane spanned by the centres of the three C<sub>5</sub> pentagons.

**Introduction.** In contrast to the series of strictly isomorphous tetrahydrofuran (THF) adducts ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>M<sup>III</sup>·THF, with M = lanthanoid (La–Lu) and Y (Ni, Deng & Qian, 1985) or U (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983), the parent base-free tris(cyclopentadienyl)lanthanoid(III) complexes, (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Ln<sup>III</sup>, display substantial structural variations with Ln (Eggers, Hinrichs, Kopf, Jahn & Fischer, 1986, and references therein). In view of the unexpectedly drastic structural changes experienced on going from ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Tm<sup>III</sup> to  $[(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_5\text{H}_5)\text{Lu}^{\text{III}}]_{\infty}$

\* Coordination Behaviour in Base-Free Tris(cyclopentadienyl) Complexes of Rare Earth Elements. V. Part IV: Eggers, Hinrichs, Kopf, Jahn & Fischer (1986).

(Eggers, Schultze, Kopf & Fischer, 1986) we report here the structure of the 'missing link',  $(C_5H_5)_3Yb^{III}$  (atomic numbers of Tm, Yb and Lu = 69, 70 and 71, respectively).

**Experimental.** After numerous unsatisfactory attempts to arrive at suitable crystals by sublimation, dark-green single crystals of  $(C_5H_5)_3Yb^{III}$  (Birmingham & Wilkinson, 1956) were obtained from a saturated toluene solution after slow addition of *n*-hexane (room temperature, three days).

Crystals were sealed under  $N_2$  inside Lindemann capillaries because of their sensitivity towards air and moisture; density not measured; crystal size:  $0.11 \times 0.10 \times 0.12$  mm, with six faces; Syntex  $P2_1$  automatic diffractometer, graphite monochromator;  $\theta/2\theta$  scan mode; cell dimensions from 12 reflections,  $10 < 2\theta < 27^\circ$ ; numeric absorption correction with program *SHELX76* (Sheldrick, 1976), transmission factors: 0.4318 (min.), 0.5281 (max.); max.  $(\sin\theta)/\lambda$   $0.75755 \text{ \AA}^{-1}$ ,  $hkl$  range:  $0 \rightarrow 12$ ,  $0 \rightarrow 12$ ,  $0 \rightarrow 27$  (Friedel pairs collected), three standard reflections (200, 020, 004) displaying no significant variation in intensity from average during measurement,  $2\theta$  range:  $4.5 < 2\theta < 65^\circ$ , 5250 data, 2515 unique [including 271,  $F_o < 3\sigma(F_o)$ ],  $R_{\text{int}} = 0.023$ ; structure solved by Patterson (program *SHELXS84*, Sheldrick, 1984) and Fourier (program *SHELX76*) methods, refined on  $F$ , 136 parameters.  $R = 0.037$  for 2244 reflections for which  $F_o > 3\sigma(F_o)$ ,  $wR = 0.041$ , the weighting scheme was based on unit weights, max.  $\Delta/\text{e.s.d.}$ : 0.4, correction for extinction not applied; max. and min. residuals in the final Fourier map 0.7 and  $-1.3 \text{ e \AA}^{-3}$ ; scattering factors for all atoms were taken from program system *SHELX*.

One of the cyclopentadienyl rings (ring 3) was refined as a rigid group with C—C distance of  $1.42 \text{ \AA}$ . The H atoms were placed at calculated positions  $0.96 \text{ \AA}$  from the bonded C atom with a common isotropic temperature factor of  $0.05 \text{ \AA}^2$ .

In an attempt to determine the absolute structure, and in order to avoid systematic errors caused by anomalous-dispersion effects (Flack, 1983), the last two cycles of refinement were repeated with the unaveraged data, using both the original atomic positions and the enantiomeric ones which were obtained by converting the signs of all coordinates into their opposites. The  $R$  values were  $R = 0.041$  ( $wR = 0.046$ ) for the original parameter set, and  $R = 0.037$  ( $wR = 0.041$ ) for the enantiomeric parameter set. Most of the e.s.d.'s were slightly lower for the enantiomeric structure.

The data were merged and both calculations were performed again. The values of several bond lengths and angles were better for the enantiomeric parameter set. Since the max. and min. residuals in the final Fourier map were lower ( $0.7/-1.3$  vs  $0.8/-1.6 \text{ e \AA}^{-3}$ ),

Table 1. *Atomic coordinates and temperature factors  $U_{\text{eq}}$  with e.s.d.'s for the compound  $(C_5H_5)_3Yb^{III}$*

	$x$	$y$	$z$	$U_{\text{eq}}(\text{\AA}^2)$
Yb	0.1741 (1)	-0.4302 (1)	-0.1245 (1)	0.032 (1)
C(11)	-0.1161 (13)	-0.2848 (16)	-0.1244 (9)	0.059 (11)
C(12)	-0.1478 (14)	-0.4388 (17)	-0.0941 (7)	0.058 (12)
C(13)	-0.0748 (15)	-0.4446 (15)	-0.0253 (7)	0.052 (11)
C(14)	0.0090 (16)	-0.2994 (15)	-0.0140 (6)	0.052 (11)
C(15)	-0.0170 (18)	-0.1999 (15)	-0.0765 (6)	0.055 (11)
C(21)	0.3287 (21)	-0.1811 (14)	-0.1827 (7)	0.062 (13)
C(22)	0.1830 (18)	-0.1866 (13)	-0.2234 (6)	0.051 (10)
C(23)	0.1838 (16)	-0.3292 (14)	-0.2645 (6)	0.050 (10)
C(24)	0.3332 (17)	-0.4104 (14)	-0.2496 (6)	0.052 (10)
C(25)	0.4262 (16)	-0.3195 (16)	-0.1975 (7)	0.053 (11)
C(31)	0.4032 (8)	-0.6671 (9)	-0.1337 (4)	0.043 (9)
C(32)	0.4054 (8)	-0.6078 (9)	-0.0604 (4)	0.042 (9)
C(33)	0.2491 (8)	-0.6455 (9)	-0.0274 (4)	0.047 (10)
C(34)	0.1504 (8)	-0.7281 (9)	-0.0803 (4)	0.051 (11)
C(35)	0.2456 (8)	-0.7415 (9)	-0.1460 (4)	0.044 (9)

Table 2. *Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ )*

Cent. = centre of each  $C_5H_5$  ligand.

Yb—C(11)	2.615 (10)	Yb—C(31)	2.693 (7)
Yb—C(12)	2.631 (10)	Yb—C(32)	2.636 (7)
Yb—C(13)	2.687 (12)	Yb—C(33)	2.583 (7)
Yb—C(14)	2.638 (12)	Yb—C(34)	2.610 (7)
Yb—C(15)	2.600 (13)	Yb—C(35)	2.678 (7)
Yb—C(21)	2.633 (13)	Yb—cent. 1	2.351 (12)
Yb—C(22)	2.709 (11)	Yb—cent. 2	2.359 (12)
Yb—C(23)	2.682 (11)	Yb—cent. 3	2.348 (7)
Yb—C(24)	2.610 (12)	Yb...Yb'	6.739
Yb—C(25)	2.581 (12)	Yb...Yb''	7.988
$C_p$ —Yb— $C_p$	119.5	Yb—Yb'—Yb''	72.7
$C_p$ —Yb— $C_p$	120.5	Yb— $C_p$ —Yb'	150.5
$C_p$ —Yb— $C_p$	119.8	Yb— $C(14)'$ —Yb'	167.5

and the  $R$  values were slightly better ( $R = 0.0367$ ,  $wR = 0.0412$  vs  $R = 0.0371$ ,  $wR = 0.0415$ ), we decided to take these atomic positions, and all bond lengths and angles given here refer to them.

**Discussion.** Atomic parameters are listed in Table 1,\* selected bond distances and angles in Table 2.

Unlike its polymeric Lu congener,  $[(\eta^5C_5H_5)_2(\mu-\eta^1:\eta^1-C_5H_5)Lu^{III}]_\infty$ , and in spite of the very similar ionic radii of Lu<sup>III</sup> and Yb<sup>III</sup> ( $0.977$  and  $0.985 \text{ \AA}$ , respectively; Shannon, 1976), the Yb compound is strictly mononuclear (Fig. 1). Each Yb<sup>III</sup> ion is, like each Tm<sup>III</sup> (and Er<sup>III</sup>) ion, surrounded by three  $\eta^5$ - $C_5H_5$  ligands; however, the particularly long *intermolecular* distances,  $(Yb \cdots C')_{\text{min}}$  and  $(Yb \cdots Yb')_{\text{min}}$  (Table 3), strongly advocate the existence of quasi-free  $(\eta^5C_5H_5)_3Yb^{III}$  molecules in the lattice. The data of Table 3 lend, on the

\* Lists of structure factors, anisotropic thermal and H-atom positional parameters, deviations from least-squares planes and distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44265 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

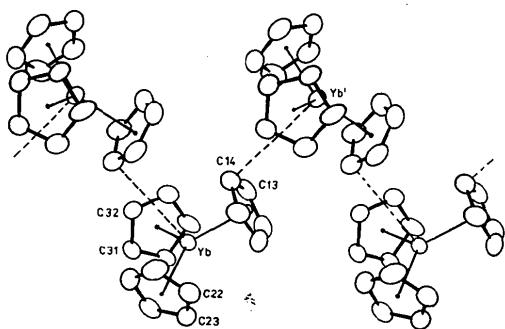


Fig. 1. ORTEP drawing (Johnson, 1976) of  $(C_5H_5)_3Yb^{III}$ . Dashed line: trace of closest-packed zigzag chain in the lattice.

other hand, further support for the assumption of weak 'chemical' interactions between each  $Tm^{III}$  (or  $Er^{III}$ ) ion and one distinct ring C atom of an adjacent  $(C_5H_5)_3Ln$  molecule.

The structural non-equivalence of (solution-) crystallized  $(C_5H_5)_3Yb^{III}$  and (vacuum-) sublimed  $(C_5H_5)_3Tm^{III}$  may be compared with the recently reported (Lamberts, Lueken & Elsenhans, 1986) dimorphism of  $[(C_5H_5)_2Gd^{III}(\mu_2-Br)]_2$  which consists either of isolated molecules (sublimation temperature  $\sim 403$  K;  $D_x = 2.289$  g cm $^{-3}$ ) or of infinite chains of  $\mu_2$ -Br-bridged dimers (sublimation temperature  $\sim 423$  K;  $D_x = 2.392$  g cm $^{-3}$ ).

The displacement of the  $Yb^{III}$  ion from the plane of the three  $C_5H_5$  ring centres (0.050 Å) is notably smaller than the corresponding quantity for  $Ln = Tm$  or  $Er$  ( $ca$  0.3 Å) and also that in  $[(CH_3)_3Si]_2N\}_3Yb^{III}$  ( $ca$  0.4 Å; Eller, Bradley, Hursthouse & Meek, 1977). Hence,  $(C_5H_5)_3Yb^{III}$  belongs to the still-rare group of condensed  $LnX_3$  systems of almost ideal pseudo- $D_{3h}$  microsymmetry. Expectedly (Fischer & Li, 1985), the mean  $Yb-C$  distance of 2.639 Å in the base-free molecule is slightly shorter than the corresponding distance in the pseudotetrahedral molecules  $(C_5H_5)_3-$

Table 3. Parameters indicative of variable packing of  $(C_5H_5)_3Ln^{III}$  molecules

Ln	$(Ln \cdots C')_{min}^*$ (Å)	$(Ln \cdots Ln')_{min}^*$ (Å)	$Ln \cdots Ln' \cdots Ln''$ (°)	$D_x$ (g cm $^{-3}$ )
Er	3.137	3.190	5.934	114.3
Tm	3.243	3.334	5.891	114.5
Yb	4.139		6.739	72.7
Lu	2.519 (2.654)		6.163	107.7
				2.038
				2.045
				2.027
				2.100

\* Shortest possible intermolecular distance.

$Yb^{III}(N_2C_4H_4)_{1/2}$  [2.68(1) Å; Baker & Raymond (1977)] and  $(C_5H_5)_3Lu^{III} \cdot THF$  [2.69(4) Å; Ni *et al.* (1985)].

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## Structure of Thermochromic Crystals of Benzimidazolium Tetrachlorocuprate(II) Hydrate

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**Abstract.**  $2C_6H_7N^+ \cdot CuCl_4^{2-} \cdot H_2O$ ,  $M_r = 461.7$ , monoclinic,  $P2_1/c$ ,  $a = 16.040$  (3),  $b = 4.243$  (1),  $c = 27.501$  (6) Å,  $\beta = 104.78$  (4)°,  $V = 1809.7$  (8) Å $^3$ ,  $Z =$

= 4,  $D_x = 1.690$  (1) Mg m $^{-3}$ ,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.85$  mm $^{-1}$ ,  $F(000) = 932$ ,  $T = 293$  K, final  $R = 0.038$ ,  $wR = 0.042$  for 2806 reflections [ $I > 3\sigma(I)$ ]. The