JOM 23642

Organolanthanoids

XVIII *. The synthesis and X-ray crystal structure of di[μ-chlorobis(diphenylphosphino-η⁵-cyclopentadienyl)ytterbium(III)] **

G.B. Deacon, G.D. Fallon and C.M. Forsyth [1]

Chemistry Department, Monash University, Clayton, Vic. 3168 (Australia)

(Received February 10, 1993)

Abstract

Reaction of the divalent phosphinoytterbocene $Yb(C_5H_4PPh_2)_2(THF)$ (THF = tetrahydrofuran) with mercuric chloride in THF or toluene yields mercury metal and the lanthanoid(III) complex $Yb(C_5H_4PPh_2)_2Cl$. An X-ray crystal structure of the compound revealed the presence of two independent chloride-bridged dimers (one centrosymmetric, one non-centrosymmetric, in a ratio of 1:2) with uncoordinated Ph_2P groups and pseudo-tetrahedral eight coordination (two η^5-$C_5H_4PPh_2$ and two μ-Cl ligands) at ytterbium. The dimers differ in the arrangement (*syn, anti*) of the Ph_2P groups. Solution spectroscopic data suggest that there is P–Yb bonding in toluene.

1. Introduction

Organo-f-element chemistry is dominated by species containing the η^5-bound cyclopentadienyl ligand or its substituted derivatives, which yield stable and isolable complexes [1]. Recently synthesis of lanthanoid and actinoid complexes of the heterodifunctional diphenylphosphinocyclopentadienide ligand $(C_5H_4PPh_2)^-$ have been developed as precursors to novel f-block/d-block heterobimetallics [2–6]. For example, the organoytterbium ligand $Yb(C_5H_4PPh_2)_2$ has been prepared [2,3] and shown to give the bimetallics $Yb(THF)_n(C_5H_4PPh_2)_2Z$ ($n = 1$ or 2, $Z = PtMe_2$ [2,3], $Ni(CO)_2$ or $Mo(CO)_4$ [3]). The free phosphines in f-block compounds, $ML_n(\eta^5$-$C_5H_4PPh_2)_m$, may potentially coordinate to another f-block atom to give either homo- or hetero-bimetallics. Up to now no such interactions have been

observed, possibly owing to the unfavourable combination of a hard oxophilic metal and a soft donor ligand. We now report the synthesis of $Yb(C_5H_4PPh_2)_2Cl$, and an investigation of the structure in the solid state, and (by spectroscopy) in solution.

2. Experimental section

The organolanthanoid complexes described in this paper decompose rapidly in air. Consequently all manipulations were carried out under purified nitrogen or argon in a Vacuum Atmospheres or Miller-Howe dry box or by use of standard Schlenk techniques. Solvents were dried and distilled over sodium benzophenone ketyl under nitrogen. The complex $Yb(C_5H_4PPh_2)_2$-(THF) was prepared by a published procedure [3], whilst commercial $HgCl_2$ (Aldrich) was used as received. Analytical and spectroscopic methods and instrumentation were as described previously [3].

2.1. Di[μ-chlorobis(diphenylphosphino-η⁵-cyclopentadienyl)ytterbium(III)]

A mixture of $Yb(C_5H_4PPh_2)_2(THF)$ (2.0 mmol) and $HgCl_2$ (1.0 mmol) was stirred in THF (25 cm³) for 12 h at room temperature. The resulting bright orange solu-

---

Correspondence to: Dr. G.B. Deacon.

* Part XVII, see ref. 3.

** Dedicated to Professor Michael F. Lappert in recognition of his outstanding and creative contribution to organometallic chemistry, and particularly to organometallic synthesis, across the whole Periodic Table.

[1] Present address: CSIRO Division of Forest Products, Clayton, Vic. 3168, Australia.

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Yb(1)	3590(1)	4377(1)	7099(1)	37(1)
Yb(2)	5588(1)	3578(1)	6448(1)	39(1)
Yb(3)	366(1)	1129(1)	603(1)	35(1)
Cl(1)	3794(3)	2862(3)	6723(2)	45(2)
Cl(2)	5405(3)	5098(3)	6859(2)	49(2)
Cl(3)	1320(3)	298(3)	13(2)	40(2)
P(1)	872(4)	2621(3)	5994(2)	48(2)
P(2)	5586(4)	6415(4)	8374(2)	49(2)
P(3)	4845(4)	1458(3)	5223(2)	49(2)
P(4)	8302(4)	5266(4)	7635(3)	55(2)
P(5)	−753(4)	1528(4)	1996(2)	54(2)
P(6)	−2059(4)	1961(3)	−88(2)	46(2)
C(1)	1688(14)	3825(12)	6232(8)	44(5)
C(2)	2452(14)	4274(12)	5942(8)	49(5)
C(3)	2863(16)	5189(14)	6196(9)	64(6)
C(4)	2414(15)	5321(14)	6656(9)	61(6)
C(5)	1682(14)	4488(12)	6675(9)	51(5)
C(6)	521(13)	2345(11)	6698(8)	40(4)
C(7)	1096(16)	1922(13)	7102(9)	61(6)
C(8)	919(17)	1729(14)	7655(10)	66(6)
C(9)	109(16)	1926(14)	7790(10)	66(6)
C(10)	−499(18)	2334(15)	7397(10)	75(7)
C(11)	−254(14)	2543(12)	6864(8)	48(5)
C(12)	−398(13)	2706(12)	5483(8)	42(4)
C(13)	−1286(16)	1894(14)	5256(9)	63(6)
C(14)	−2260(19)	1889(16)	4833(10)	78(7)
C(15)	−2331(18)	2645(14)	4646(10)	68(6)
C(16)	−1485(17)	3461(15)	4858(10)	72(6)
C(17)	−507(16)	3457(13)	5296(9)	57(5)
C(18)	4573(13)	5286(11)	8230(8)	40(4)
C(19)	4855(15)	4475(12)	8221(8)	51(5)
C(20)	3906(16)	3751(14)	8140(9)	60(5)
C(21)	3077(16)	4080(14)	8073(9)	59(5)
C(22)	3452(14)	4997(12)	8140(8)	44(5)
C(23)	5810(13)	6742(12)	9212(8)	42(4)
C(24)	5770(15)	6130(14)	9618(9)	57(5)
C(25)	6081(16)	6396(15)	10260(10)	67(6)
C(26)	6344(16)	7285(14)	10475(11)	69(6)
C(27)	6389(16)	7921(14)	10100(9)	63(6)
C(28)	6143(14)	7651(13)	9469(9)	51(5)
C(29)	4780(14)	7074(12)	7980(8)	50(5)
C(30)	4001(15)	7281(13)	8182(9)	56(5)
C(31)	3404(17)	7775(14)	7850(10)	71(6)
C(32)	3579(18)	8006(15)	7312(11)	77(7)
C(33)	4323(18)	7800(15)	7109(11)	80(7)
C(34)	4933(15)	7344(12)	7422(9)	53(5)
C(35)	4992(13)	2639(11)	5362(8)	40(4)
C(36)	4224(13)	3057(11)	5318(7)	38(4)
C(37)	4698(14)	3984(12)	5373(8)	48(5)
C(38)	5787(15)	4132(14)	5439(9)	56(5)
C(39)	5973(15)	3337(12)	5403(8)	51(5)
C(40)	3953(15)	1067(13)	4420(9)	53(5)
C(41)	3801(17)	1648(16)	3992(10)	72(6)
C(42)	3122(19)	1293(17)	3373(11)	84(7)
C(43)	2638(19)	395(17)	3190(12)	86(7)
C(44)	2767(19)	−201(17)	3593(11)	86(7)
(C45)	3472(17)	171(15)	4221(10)	70(6)

TABLE 1 (*continued*)

	x	y	z	U_{eq} [a]
C(46)	3892(15)	941(12)	5636(9)	51(5)
C(47)	4293(17)	619(14)	6175(9)	66(6)
C(48)	3657(19)	276(15)	6545(11)	80(7)
C(49)	2610(20)	233(16)	6338(11)	85(7)
C(50)	2182(20)	532(15)	5812(11)	82(7)
C(51)	2828(15)	887(13)	5458(9)	56(5)
C(52)	7472(14)	4093(13)	7316(9)	49(5)
C(53)	7491(15)	3512(13)	6839(9)	53(5)
C(54)	6794(15)	2661(13)	6782(9)	54(5)
C(55)	6300(16)	2648(14)	7241(9)	57(5)
C(56)	6712(16)	3533(13)	7569(10)	62(6)
C(57)	9590(15)	5144(13)	8077(9)	52(5)
C(58)	10524(17)	5918(15)	8247(10)	72(6)
C(59)	11490(20)	5899(17)	8652(11)	87(7)
C(60)	11520(18)	5130(15)	8875(10)	74(6)
C(61)	10627(18)	4346(16)	8697(10)	76(7)
C(62)	9660(18)	4376(15)	8282(10)	73(6)
C(63)	8553(17)	5662(14)	6923(10)	66(6)
C(64)	7979(18)	6164(15)	6643(11)	77(7)
C(65)	8120(18)	6411(16)	6053(11)	80(7)
C(66)	8727(20)	6130(17)	5829(13)	94(8)
C(67)	9338(20)	5680(17)	6101(12)	92(8)
C(68)	9268(19)	5430(16)	6670(11)	86(7)
C(69)	182(13)	1149(11)	1728(7)	37(4)
C(70)	174(14)	263(12)	1533(8)	42(4)
C(71)	1174(15)	353(13)	1483(8)	54(5)
C(72)	1852(15)	1257(12)	1644(8)	50(5)
C(73)	1268(14)	1751(13)	1797(8)	49(5)
C(74)	−294(14)	1432(12)	2841(8)	50(5)
C(75)	303(16)	941(14)	3084(10)	70(6)
C(76)	597(18)	892(15)	3740(10)	78(7)
C(77)	187(18)	1373(15)	4087(11)	77(7)
C(78)	−429(17)	1815(15)	3840(10)	74(6)
C(79)	−668(15)	1913(13)	3212(9)	60(5)
C(80)	−2010(14)	567(12)	1718(8)	47(5)
C(81)	−2323(17)	−107(14)	2062(10)	65(6)
C(82)	−3366(19)	−784(16)	1854(11)	83(7)
C(83)	−4075(20)	−746(17)	1315(11)	86(7)
C(84)	−3804(21)	−132(17)	952(12)	92(8)
C(85)	−2813(19)	560(17)	1164(11)	83(7)
C(86)	−627(14)	2179(12)	47(8)	44(5)
C(87)	−75(13)	1994(11)	−328(8)	42(4)
C(88)	1042(15)	2383(12)	−9(9)	53(5)
C(89)	1193(16)	2825(13)	581(9)	55(5)
C(90)	159(15)	2681(13)	633(9)	54(5)
C(91)	−2174(13)	3038(11)	−286(8)	38(4)
C(92)	−3159(15)	3147(13)	−350(8)	54(5)
C(93)	−3326(17)	3924(14)	−501(9)	68(6)
C(94)	−2519(16)	4608(15)	−580(9)	65(6)
C(95)	−1518(16)	4569(14)	−507(9)	62(6)
C(96)	−1388(15)	3744(13)	−374(8)	54(5)
C(97)	−2700(13)	1247(11)	−876(8)	38(4)
C(98)	−2547(14)	1550(13)	−1401(8)	52(5)
C(99)	−3039(17)	999(14)	−1983(10)	70(6)
C(100)	−3739(16)	126(14)	−2014(10)	60(5)
C(101)	−3876(16)	−186(14)	−1490(9)	63(6)
C(102)	−3373(16)	353(14)	−901(10)	63(6)

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

tion was filtered through a Celite pad to remove the metallic mercury and the filtrate was evaporated to leave an orange oil, which solidified on standing. Recrystallization from THF/petrol (1:4 v/v) and drying under vacuum gave the title compound as an orange crystalline solid (yield 85%) (Anal. found: C, 57.1; H, 4.8; Yb, 25.0; $C_{68}H_{56}Cl_2P_4Yb_2$ calc.: C, 57.8; H, 4.0; Yb, 24.5%). IR (Nujol): 3040w, 1585w, 1435s, 1305w, 1210m, 1175m, 1160m, 1095m, 1080m, 1040s, 1035m, 1010m, 1000m, 860m(br), 805s, 795vs, 745vs, 725s, 700vs, cm^{-1}. Vis/near IR spectrum [$\lambda_{max}(\epsilon)$](THF): 390(216), 873(1), 896(1), 923(7), 947(16), 981(10), 988(25), 998(3), 1024(1); (toluene): 407(284), 510(sh)(127), 839(1), 876(3), 908(7), 944(28), 982(19), 990(16), 995(14), 1006(2), 1032(1) nm. The ^1H NMR spectrum of a hydrolysed sample showed only resonances attributable to $Ph_2PC_5H_5$ and indicated the absence of THF. $^{31}P\{^1H\}$ NMR spectrum (THF): +9.3, br s ($\Delta\nu_{1/2}$ 50 Hz); (toluene): +10.9, br s ($\Delta\nu_{1/2}$ 200 Hz); +45.5 br s ($\Delta\nu_{1/2}$ 200 Hz) (relative area 10:7) ppm. Mass spectrum: m/z 706 [3, M(monomer)$^+$ $-$H], 671 [12, M(monomer)$^+$ $-$HCl], 522 [6, M(monomer)$^+$ $-$PPh$_2$], 487 [7, Yb(C$_5$H$_4$PPh$_2$)(C$_5$H$_4$)$^+$], 458 [7, Yb(C$_5$H$_4$P-Ph$_2$)Cl$^+$], 209 [12, YbCl$^+$]. Each observed isotope pattern for Yb or YbCl containing ions was similar to that calculated for the relevant molecular formula. Some extremely weak ions with indistinct isotope patterns were also observed at m/z 980 [Yb$_2$Cl$_2$(C$_5$H$_4$P-Ph$_2$)$_2$(C$_5$H$_4$)$^+$, calc. m/z 980] 838, 796, 736 and 722, which possibly result from fragmentation of a dimeric species. μ_{eff} (291 K) = 3.87 μB. An identical preparation in toluene gave the same product (IR, vis/near IR, ^{31}P NMR and m.s. identification) (yield 80%) after evaporation of the solvent from the filtered reaction mixture, but was impure (Anal. found: C, 61.9; H, 4.1%, $C_{82}H_{72}Cl_2P_4Yb_2$ ([Yb(C$_5$H$_4$PPh$_2$)$_2$Cl]$_2$ · 2PhMe) calc.: C, 61.6; H, 4.5%).

2.2. X-ray structure determination

Single crystals, suitable for X-ray structure analysis, were obtained by slow cooling of a hot, saturated toluene solution and were mounted under argon in Lindemann glass capillaries. A representative clear orange-red tabular crystal of approximate dimensions 0.22 × 0.21 × 0.11 mm was used for data collection.

2.2.1. Crystal data

$C_{68}H_{56}Cl_2P_4Yb_2$, M = 1414.0, triclinic, space group $P\bar{1}$, a 13.779(4), b 15.817(6), c 22.674(3) Å, α 93.20(2), β 106.61(2), γ 108.57(2)°, U 4436(2) Å^3, D_c 1.59 g cm^{-3}, Z 3, μ 33.7 cm^{-1} for Mo Kα radiation (λ0.71073 Å), F(000) 2094, T = 20(1)°C. Cell parameters were derived by least-squares calculations from angular set-

tings of 29 reflections measured between $5° < 2\theta < 23°$.

### 2.3. Structure determination

Intensity measurements were made on a Nicolet R3m/V diffractometer using graphite monochromated Mo Kα radiation with $3.5° < 2\theta < 45.0°$, and operating in ω scan mode with a scan range of 1.20° at a scan rate of between 4.51° and 26.04° min^{-1}. A total of 11593 unique data were collected ($\pm$h, $\pm$k, $+$l), 6546 of which were considered to be observed [$F \geq 6\sigma(F)$]. Three standard reflections monitored every 197 reflections showed no significant variation over the data collection period. Intensity data were corrected for Lorentz and polarization effects and a face indexed numerical absorption correction was applied [7], maximum and minimum transmission factors being 0.972 and 0.931 respectively. Atomic scattering factors for neutral atoms were corrected for anomalous dispersion [8]. The structure was solved by Patterson and Fourier methods. Full matrix least-squares refinement [7] employing anisotropic thermal parameters for Yb, Cl and P and isotropic parameters for all other atoms (single fixed isotropic thermal parameter for hydrogen in geometrically idealised positions, C–H 0.96 Å) reduced R to 0.058 and wR to 0.070 at convergence, where $wR = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega(|F_o|^2)^{1/2}$ and $\omega = [\sigma^2(F_o) + 0.0019F^2]^{-1}$. The goodness of fit value ([$\Sigma\omega(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$) was 1.12. The largest peak in the difference Fourier synthesis was 1.93 eÅ^{-3}. All calculations were performed on a Micro VAX 2000 computer. Final atomic parameters are listed in Table 1. 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. Synthesis

The oxidation of Yb(C$_5$H$_4$PPh$_2$)$_2$(THF) with HgCl$_2$ in THF or toluene readily afforded Yb(C$_5$H$_4$PPh$_2$)$_2$Cl and mercury (eqn. (1)). This reaction parallels the synthesis of Yb(C$_5$H$_5$)$_2$Cl from Yb(C$_5$H$_5$)$_2$(DME) (DME = MeOCH$_2$CH$_2$OMe) [9], and is in contrast with the usual preparations of bis(cyclopentadienyl) lanthanoid chlorides [10] by metathesis between LnCl$_3$ and an alkali metal or thallium(I) cyclopentadienide and cleavage of tris(cyclopentadienyl) derivatives.

$$2Yb(C_5H_4PPh_2)_2 + HgCl_2 \longrightarrow$$
$$2Yb(C_5H_4PPh_2)_2Cl + Hg\downarrow \quad (1)$$
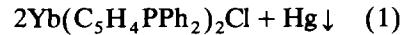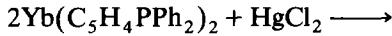
Spectroscopically identical products were obtained from the two different solvents. That obtained from

THF (and recrystallized from THF/petrol) had the THF-free composition, $Yb(C_5H_4PPh_2)_2Cl$. The room temperature magnetic moment (Experimental section) lies at one end of the range (3.9–4.9 μB) for ytterbium(III) organometallics [11]. Features associated with the $C_5H_4PPh_2$ group [3] were observed in the infrared spectrum, which was too complex to provide clear evidence as to the presence or absence of THF. However, the ^{1}H NMR spectrum of the hydrolysis products (reaction (2)) indicated that no THF was present.

$$Yb(C_5H_4PPh_2)_2Cl + 3H_2O \longrightarrow$$

$$Yb(OH)_3 + HCl + 2C_5H_5PPh_2 \quad (2)$$
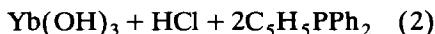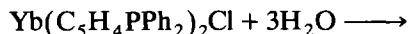
Likewise, no THF$^+$ ion was observed in the mass spectrum. Ions from fragmentation of $Yb(C_5H_4PPh_2)_2$ Cl^+ were the main feature (see Experimental section), but there was no monomer parent ion. Some very weak high mass ions were also detected and may arise from breakdown of a dimer parent ion. Analytical data for the product from toluene are consistent with the composition, $Yb(C_5H_4PPh_2)_2Cl \cdot PhMe$. However, the product may simply have been impure, since single crystals grown from this solvent did not contain toluene of crystallization.

3.2. X-ray crystal structure of $[Yb(\eta^5\text{-}C_5H_4PPh_2)_2Cl]_2$

Atomic coordinates for $[Yb(C_5H_4PPh_2)_2Cl]_2$ are given in Table 1, the structure is shown in Fig. 1, and selected bond distances and angles are listed in Table 2. The structure consists of two different chloride-bridged dimers, one non-centrosymmetric (A) and one centrosymmetric (B) in a ratio of 2:1. Each ytterbium in each dimer is coordinated by two $\eta^5\text{-}C_5H_4PPh_2$ groups and two μ-Cl ligands, giving formal eight coordination and a distorted tetrahedral arrangement of cyclopentadienyl centroids (Ct) and chlorides. Higher Ct–Yb–Ct than Cl–Yb–Cl angles (Table 2) reflect the relative steric demands of $C_5H_4PPh_2$ and Cl ligands. The diphenylphosphino groups are uncoordinated, and the dimers differ notably in the orientations of these groups (anti in Dimer A; syn in dimer B), as displayed in the simplified diagrams in Fig. 2. Of the Yb $\cdots$ P separations, the six closest (Table 2) may be considered to be intramolecular van der Waals contacts since they correspond closely to the sum (3.84 Å) of the van der Waals radius of phosphorus [12] and the metallic radius [13] (pseudo van der Waals radius) of ytterbium. By contrast, the closest intermolecular Yb $\cdots$ P approach is ca. 1.5 Å longer (Table 2). The Yb $\cdots$ Yb separations in the dimers just exceed the sum of two metallic radii and are non-bonding.

Except for the difference in the configuration of the Ph_2P groups, the geometries of dimers A and B are

(a)

(b)
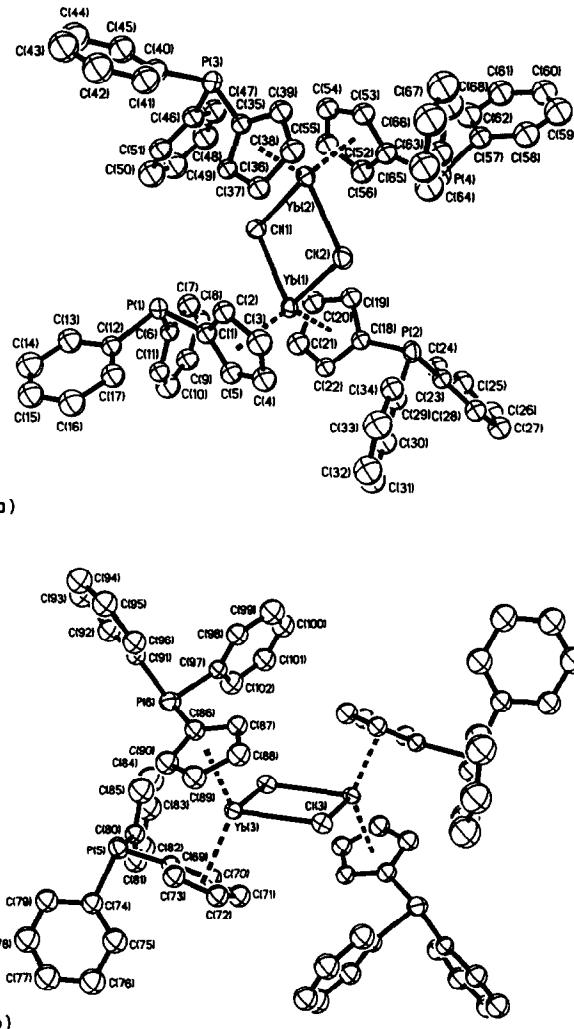
Fig. 1. The structure of $[Yb(\eta^5\text{-}C_5H_4PPh_2(\mu\text{-}Cl)]_2$, (a) dimer A (non-centrosymmetric) and (b) dimer B (centrosymmetric). Dimer A:dimer B = 2:1 in the unit cell. The thermal ellipsoids enclose 40% of the electron probability distribution.

similar. For example, there is little difference in $\langle$Yb–Cl$\rangle$ and $\langle$Yb–C$\rangle$ between the two dimers. Subtraction of an ionic radius for eight coordinate ytterbium (0.985 Å) [14] from $\langle$Yb–C$\rangle$ of A and B (Table 2) gives 1.61 Å, which is within the usual range 1.64 ± 0.04 Å [15] for the cyclopentadienyl ionic radius. The Yb_2Cl_2 unit is necessarily planar in B and is almost planar in A, where Yb(1), Yb(2), Cl(1) and Cl(2) are -0.0183, -0.0181, 0.0182 and 0.0182 Å, respectively, from the mean plane.

Established structures of unsubstituted bis(cyclopentadienyl)lanthanoid chlorides, $LnCp_2Cl$, belong to three classes: (i) the $(ScCp_2Cl)_2$ structure [16], (ii) the $ErCp_2Cl)_2$ structure [17], (iii) the $[(LnCp_2X)_2]_n$ (X = Cl or Br) type [18]. The first has geometrically similar centrosymmetric and non-centrosymmetric dimers in a

1:2 ratio, and has recently been established for (YbCp₂Br)₂ [19] and one form of (GdCp₂Br)₂ [18] and (YbCp₂Cl)₂ [20]. The second has one centrosymmetric dimer, and is also observed in sublimed (YbCp₂Cl)₂ [19], whilst in the third, dimers are linked into a polymeric chain by additional Ln–X bonding [18,21,22]. Structurally characterized analogues with non-coordinating substituents in the cyclopentadienyl ligands generally are centrosymmetric dimers, e.g. [Yb(C₅H₄-Me)₂Cl]₂ [23], [Ln(C₅H₃(SiMe₃)₂)₂Cl]₂ (Ln = Pr, Yb or

Sc) [24] and [Ln(C₅H₄ᵗBu)₂Cl]₂ (Ln = Sm or Lu) [25]. However, [Ce(C₅H₃ᵗBu₂)₂Cl]₂ is non-centrosymmetric but with a C₂ axis through the two Ce atoms [26], by contrast with non-centrosymmetric dimer A of [Yb(C₅H₄PPh₂)₂Cl]₂. The present structure is the first containing two different dimers for a substituted bis(cyclopentadienyl)lanthanoid chloride. It is also of interest that the orientation of the Ph₂P groups in the non-centrosymmetric dimer A is similar to that of the methyl groups in the symmetric dimer [Yb(C₅H₄

TABLE 2. Selected bond length (Å) and angles (°) for [Yb(C₅H₄PPh₂)₂Cl]₂

Dimer A			
Yb(1)–C(1)	2.63(2)	Yb(2)–C(37)	2.61(2)
Yb(1)–C(2)	2.61(2)	Yb(2)–C(38)	2.55(2)
Yb(1)–C(3)	2.61(2)	Yb(2)–C(39)	2.61(2)
Yb(1)–C(4)	2.58(2)	Yb(2)–Ct(3) ᵃ	2.30
Yb(1)–C(5)	2.60(2)	Yb(2)–C(52)	2.62(2)
Yb(1)–Ct(1) ᵃ	2.32	Yb(2)–C(53)	2.56(2)
Yb(1)–C(18)	2.62(2)	Yb(2)–C(54)	2.53(2)
Yb(1)–C(19)	2.61(2)	Yb(2)–C(55)	2.56(2)
Yb(1)–C(20)	2.59(2)	Yb(2)–C(56)	2.59(2)
Yb(1)–C(21)	2.53(2)	Yb(2)–Ct(4) ᵃ	2.28
Yb(1)–C(22)	2.59(2)	Yb(1)–Cl(1)	2.624(5)
Yb(1)–Ct(2) ᵃ	2.30	Yb(1)–Cl(2)	2.627(5)
Yb(2)–C(35)	2.57(2)	Yb(2)–Cl(1)	2.640(5)
Yb(2)–C(36)	2.61(1)	Yb(2)–Cl(2)	2.643(5)
Cl(1)–Yb(1)–Cl(2)	82.7(2)	Ct(2)–Yb(1)–Cl(2)	108.3
Cl(1)–Yb(2)–Cl(2)	82.1(2)	Ct(3)–Yb(2)–Cl(1)	107.8
Ct(1)–Yb(1)–Ct(2)	130.6	Ct(3)–Yb(2)–Cl(2)	107.9
Ct(3)–Yb(2)–Ct(4)	129.3	Ct(4)–Yb(2)–Cl(1)	108.7
Ct(1)–Yb(1)–Cl(1)	109.2	Ct(4)–Yb(2)–Cl(2)	110.9
Ct(1)–Yb(1)–Cl(2)	108.4	Yb(1)–Cl(1)–Yb(2)	97.7(1)
Ct(2)–Yb(1)–Cl(1)	107.3	Yb(1)–Cl(2)–Yb(2)	97.5(1)
Dimer B			
Yb(3)–C(69)	2.63(2)	Yb(3)–C(87)	2.61(2)
Yb(3)–C(70)	2.61(2)	Yb(3)–C(88)	2.57(2)
Yb(3)–C(71)	2.57(2)	Yb(3)–C(89)	2.57(2)
Yb(3)–C(72)	2.59(2)	Yb(3)–C(90)	2.56(2)
Yb(3)–C(73)	2.62(2)	Yb(3)–Ct(6) ᵃ	2.30
Yb(3)–Ct(5) ᵃ	2.31	Yb(3)–Cl(3)	2.676(5)
Yb(3)–C(86)	2.63(2)	Yb(3)–Cl(3A)	2.628(4)
Cl(3)–Yb(3)–Cl(3A)	80.9(2)	Ct(6)–Yb(3)–Cl(3)	107.9
Ct(5)–Yb(3)–Ct(6)	129.3	Ct(6)–Yb(3)–Cl(3A)	112.4
Ct(5)–Yb(3)–Cl(3)	106.4	Yb(3)–Cl(3)–Yb(3A)	99.1(2)
Ct(5)–Yb(3)–Cl(3A)	108.9		
Both dimers			
⟨P–C(Ph)⟩	1.84	⟨C$_i$–C$_{i+1}$⟩ ᵇ	1.40
⟨Yb–C⟩	2.59	⟨P–C(C₅H₄)⟩	1.82
Non-bonding contacts			
Yb(1) ··· Yb(2)	3.964(2)	Yb(2) ··· P(4)	3.933
Yb(3) ··· Yb(3A)	4.036(2)	Yb(3) ··· P(5)	3.933
Yb(1) ··· P(1)	3.908	Yb(3) ··· P(6)	3.928
Yb(1) ··· P(2)	3.885	Yb(3) ··· P(2)	5.425
Yb(2) ··· P(3)	3.892		

ᵃ Ct(n) is the centroid of the cyclopentadienyl ring defined by the preceding five carbon atoms. ᵇ C_i, C_{i+1} are adjacent carbon atoms of a cyclopentadienyl ring.
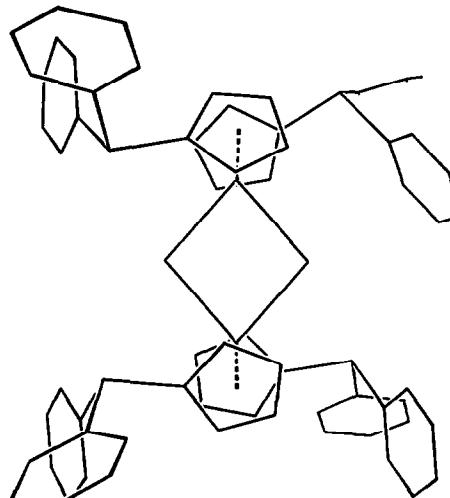
(a)
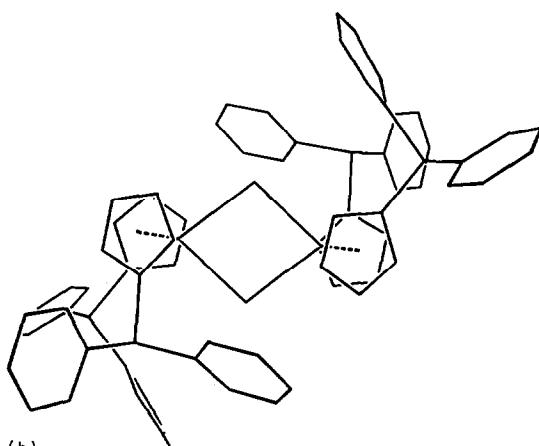
(b)

Fig. 2. Simplified diagram of the structure of [Yb(η⁵-C₅H₄PPh₂)₂(μ-Cl)]₂ showing the configuration of Ph₂P groups in (a) dimer A (*anti* Ph₂P groups) and (b) dimer B (*syn* Ph₂P groups).

Me)₂Cl]₂ [23] and of the t-butyl groups in the symmetric dimers [(Ln(C₅H₄ᵗBu)₂Cl]₂ [25]. The dimer geometry of [Yb(C₅H₄PPh₂)₂Cl]₂ is very similar to those of [Yb(C₅H₄Me)₂Cl]₂ [23] and the various (YbCp₂Cl)₂ structures (Table 3).

3.3. Behaviour in solution

The electronic spectra of Yb(C₅H₄PPh₂)₂Cl in THF and toluene (Experimental section), both in the visible (L → Yb charge transfer) and near infrared ($^2f_{7/2}$ → $^2f_{5/2}$ transitions [27]) regions, indicate some differences in the solution species. Further, a single broad $^{31}P\{^1H\}$ resonance (δ 9.3) for the compound in THF contrasts two resonances (δ 10.3 and 45.5) in toluene. These have pronounced paramagnetic shifts from the value (δ −20.5) for Yb(C₅H₄PPh₂)₂(THF) [3]. In THF, some splitting of the chloride bridges giving eight coordinate monomeric Yb(η⁵-C₅H₄PPh₂)₂Cl(THF) is likely (see e.g. [28]) [reaction (3), L = THF].

$$[Yb(C_5H_4PPh_2)_2Cl]_2 + 2L \rightleftharpoons$$
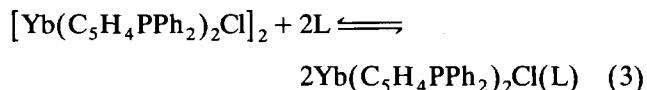
$$2Yb(C_5H_4PPh_2)_2Cl(L) \quad (3)$$

The single ^{31}P resonance can be explained by rapid ligand interchange. Persistence of some [Yb(C₅H₄PPh₂)₂Cl]₂ in THF is likely since the dimer rather than the expected Yb(C₅H₄PPh₂)₂Cl(THF) is isolated from THF/petrol, cf. crystallization of Yb(C₅H₄ᵗBu)₂Cl-(THF) from the same solvent mixture [28]. The upfield and downfield resonances of Yb(C₅H₄PPh₂)₂Cl in toluene are assigned to free and complexed Ph₂P groups respectively, since the former is close to the single resonance in THF, whilst the substantial downfield shift of the latter is characteristic of M(η⁵-C₅H₄-PPh₂) groups coordinated through phosphorus to another metal [3,29–33]. In the non-coordinating toluene, ligand exchange is evidently slow enough on the ^{31}P NMR timescale for observation of separate resonances for coordinated and free Ph₂P. As another example of slowed ligand exchange in lanthanoid chemistry, separate resonances are observed for terminal and bridging aryloxide ligands of [Ln(OAr)₂(μ-OAr)₂Na(THF)₂] and [Yb(OAr)(μ-OAr)Cl]₂ (OAr = OC₆H₂ᵗBu₂-2,6-Me-4) complexes [34]. Although the structures of the solution species are not known, it is likely that, in the absence of a donor solvent, pendant Ph₂P groups can take part in bridge cleavage, e.g. reaction (3), L = Ph₂PX, giving a product analogous to the crystallographically charac-

TABLE 3. Selected bond lengths (Å) and angles (°) for [Yb(C₅H₄PPh₂)₂(μ-Cl)]₂, [Yb(C₅H₄Me)₂Cl]₂ [23] and [YbCp₂Cl]₂ [19,20]

	[Yb(C₅H₄PPh₂)₂Cl]₂	[Yb(C₅H₄Me)₂Cl]₂	(Yb(C₅H₅)₂Cl)₂ [a]	[Yb(C₅H₅)₂Cl]₂ [b]
Yb ··· Yb	3.964(2) [c], 4.036(2) [d]	3.979(1)	3.9875(7)	3.996(1) [c], 4.019(2) [d]
Yb–Cl	2.627(5)–2.676(5)	2.628(2), 2.647(2)	2.639(3), 2.645(3)	2.633(5)–2.669(5)
Yb–C	2.53(2)–2.63(2)	2.563(6)–2.641(6)	2.56(2)–2.61(2)	2.51(3)–2.65(2)
	av. 2.59	av. 2.585	av. 2.58	av. 2.57
Cl–Yb–Cl	80.9(2)–82.7(2)	82.05(5)	82.0(1)	80.7(2)–82.8(2)
Ct–Yb–Ct [e]	129.3–130.6	126.7		128.4(15)–132.3(15)

[a] Sublimed - (ErCp₂Cl)₂ structure [19]. [b] Crystallized - (ScCp₂Cl)₂ structure [20]. [c] Non-centrosymmetric dimer. [d] Centrosymmetric dimer. [e] Ct refers to the centroid of the cyclopentadienyl ring.

terized eight coordinate $Yb(C_5Me_5)_2Cl(PMe_2CH_2P-Me_2)$ [35]. Even if separate dimers A and B were to persist in toluene (which is unlikely owing to ring rotation), they would not give the observed widely disparate ^{31}P resonances.

Evidence for coordination of the Ph_2P groups of $Yb(C_5H_4PPh_2)_2Cl$ in solution indicates that the compound should be a useful reagent in the preparation of Yb(III) heterobimetallics, and this is being explored.

Acknowledgments

References

1 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; J.H. Forsberg and T. Moeller, in T. Moeller, U. Kruerke and E. Schleitzer-Rust (eds.), *Gmelin Handbook of Inorganic Chemistry, 8th Ed., Sc, Y, La–Lu Part D6*, Springer-Verlag, Berlin 1983, p. 137; H. Schumann, *Angew. Chem., Int. Ed. Engl., 23* (1984) 474; H. Schumann and W. Genthe, Organometallic Compounds of the Rare Earths in K.A. Gscheidner and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths, Vol. 7*, Elsevier, Amsterdam, 1984, Ch. 53.

2 G.B. Deacon, A. Dietrich, C.M. Forsyth and H. Schumann, *Angew. Chem., Int. Ed. Engl., 28* (1989) 1370.

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

4 A. Dormond, P. Hepiègne, A. Hafid and C. Moïse, *J. Organomet. Chem., 398* (1990) C1.

5 H. Schumann, J.A. Meese-Marktscheffel, B. Gorella and F.H. Görlitz, *J. Organomet. Chem., 428* (1992) C27.

6 M. Visseaux, A. Dormond, M.M. Kubicki, C. Moïse, D. Baudry and M. Ephritikhine, *J. Organomet. Chem., 433* (1992) 95.

7 G.M. Sheldrick, SHELXTL PLUS Revision 3.4, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1988.

8 J.A. Ibers and W.C. Hamilton (eds.), *International Tables for X-ray Crystallography, Vol. IV*, Kynoch Press, Birmingham, 1974.

9 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.

10 M.F. Lappert and A. Singh, *J. Organomet. Chem., 239* (1982) 133.

11 W.J. Evans and M.A. Hozbor, *J. Organomet. Chem., 326* (1987) 299.

12 L. Pauling, *The Nature of the Chemical Bond, 3rd Ed.*, Ithaca, NY, 1960.

13 A.F. Wells, *Structural Inorganic Chemistry, 4th Ed.*, Clarendon, Oxford, 1975.

14 R.D. Shannon, *Acta Crystallogr., Sect. A, 32* (1976) 751.

15 K.N. Raymond and C.W. Eigenbrot, *Acc. Chem. Res., 13* (1980) 276.

16 J.L. Atwood and K.D. Smith, *J. Chem. Soc., Dalton Trans.*, (1973) 2487.

17 W. Lamberts, H. Leuken and B. Hessner, *Inorg. Chim. Acta, 134* (1987) 155.

18 W. Lamberts, H. Lueken and U. Eisenhans, *Inorg. Chim. Acta, 121* (1986) 81.

19 H. Lueken, J. Schmitz, W. Lamberts, P. Hannibal and K. Handrick, *Inorg. Chim. Acta, 156* (1989) 119.

20 T. Akhnoukh, J. Müller, K. Qiao, X.-F. Li and R.D. Fischer, *J. Organomet. Chem., 408* (1991) 47.

21 W. Lamberts and H. Lueken, *Inorg. Chim. Acta, 132* (1987) 119.

22 W. Lamberts, B. Hessner and H. Lueken, *Inorg. Chim. Acta, 139* (1987) 215.

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

24 M.F. Lappert, A. Singh, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Chem. Commun.*, (1981) 1190.

25 Y.K. Bel'skii, S.Ya. Knyazhanskii, Yu.K. Gunko, B.M. Bulychev and G.L. Soloveichik, *Organomet. Chem. USSR, 4* (1991) 560.

26 E.B. Lobkovsky, Yu.K. Gunko, B.M. Bulychev, V.K. Belsky, G.L. Soloveichik and M.Yu. Antipin, *J. Organomet. Chem., 406* (1991) 343.

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

28 Q. Shen, M. Qi, J. Guan and Y. Lin, *J. Organomet. Chem., 406* (1991) 353, see also J. Guan, Y. Lin and Q. Shen, *Youji Huazue, 11* (1991) 261 (*Chem. Abstr., 115* (1991) 114688d).

29 D.L. Dubois, C.W. Eigenbrot, A. Miedaner, J.C. Smart and R.C. Haltiwanger, *Organometallics, 5* (1986) 1405.

30 W. Tikkanen, Y. Fujita and J.L. Petersen, *Organometallics, 5* (1986) 888.

31 A.L. Bandini, G. Banditelli, M.A. Cinellu, G. Sanna, G. Minghetti, F. Demartin and M. Manassero, *Inorg. Chem., 28* (1989) 404.

32 G.K. Anderson and M. Lin, *Organometallics, 7* (1988) 2285.

33 X.D. He, A. Maisonnat, F. Dahan and R. Poilblanc, *Organometallics, 8* (1989) 2618.

34 P.B. Hitchcock, M.F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, (1983) 1499.

35 T.D. Tilley, R.A. Andersen and A. Zalkin, *Inorg. Chem., 22* (1983) 856.