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# Di-$\mu$-chloro-bis[bis(cumylcyclopentadienyl)-yttrium(III)]

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The title yttrocene, [$Y_2(C_{14}H_{15})_4Cl_2$] or [$Y_2(cCp)_4Cl_2$] (cCp = cumylcyclopentadienyl), belongs to a class of complexes bearing pendant phenyl substituents which are potentially active as catalytic precursors in the stereospecific polymerization of olefins. In the crystal structure, the molecules possess a crystallographically imposed inversion centre and may be described as centrosymmetric $\mu$-Cl-bridged dimers. No $\pi$–aryl coordination to the metal is observed. A distorted tetrahedral coordination geometry is found around the two metal atoms.

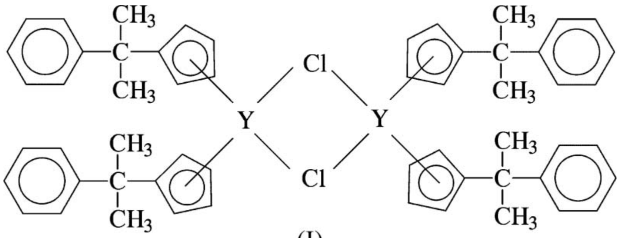
**Key indicators**

Single-crystal X-ray study
$T$ = 298 K
Mean $\sigma$(C–C) = 0.007 Å
$R$ factor = 0.051
$wR$ factor = 0.091
Data-to-parameter ratio = 17.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

Group 3 and 4 $d^0$ metallocenes are often efficient catalytic precursors in Ziegler–Natta polymerization (Kaminsky *et al.*, 1985; Ewen *et al.*, 1988; Brintzinger *et al.*, 1995; Resconi *et al.*, 2000). The proposed key intermediate has the metal atom bonded in a pseudo-tetrahedral fashion to a pair of cyclopentadienyl (or substituted cyclopentadienyl) rings, one alkyl (polymer chain) and one alkene (monomer). Recently, interest has grown in complexes with pendant phenyl substituents attached to the cyclopentadienyl ring, because these ligands may give rise to additional $\pi$–aryl coordination to the metal, producing *ansa*-arene complexes that are active as catalytic precursors in olefin polymerization (Sassmannshausen, 2000). A monomeric complex of $Ti^{IV}$ with cumylcyclopentadienyl ligand as the pendant phenyl group has already been studied (Centore *et al.*, 2004). Recently, a study of pendant phenyl cyclopentadienyl lanthanide chlorides as catalyst precursors for olefin polymerization has been conducted (Xie & Huang, 2004). On the basis of the results of mass spectroscopy and IR measurements, the formation of monomeric complexes with the general formula [$PhC(Me)_2C_2H_5]_2LnCl$ (*Ln* is Er, Sm, Gd, Y or Nd) was suggested. The metallocene chlorides of group III metals [lanthanide(III) and yttrium(III)] are normally dimeric and symmetric (Lappert & Singh, 1982). Only one case of a non-symmetric dimer is known (Evans *et al.*, 1985), and so the result reported by Xie & Huang (2004) is surprising and could be due to additional $\pi$-coordination of the pendant phenyl group.



(I)

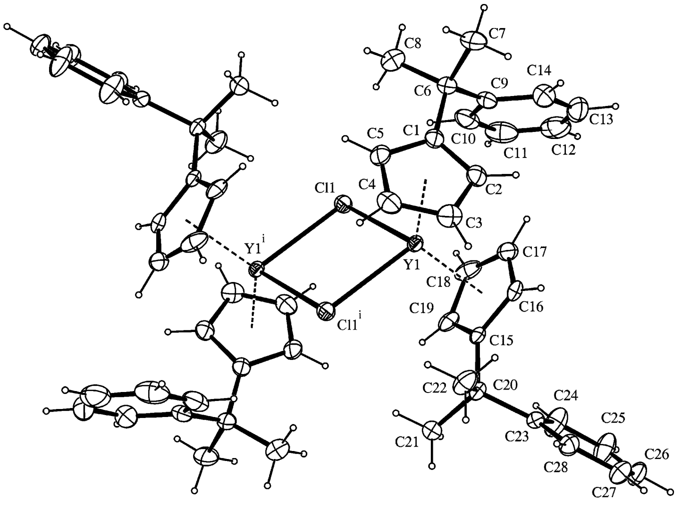


**Figure 1**

A view of (I), with the atom-numbering scheme and 30% probability displacement ellipsoids [symmetry code: (i) $-x$, $-y$, $-z$].

In this paper, we report the synthesis, $^1$H NMR analysis and X-ray crystal structure analysis of the title compound, (I), obtained from the salt methathesis reaction between yttrium trichloride and the lithium salt of the isopropylidene-bridged ligand [$PhC(Me_2)C_5H_4$]Li, in order to establish definitively the nature, monomeric or dimeric, of the complex.

The present structural analysis shows that complex (I) actually has a dimeric nature. As can be seen in Fig. 1, dimers are formed through the $\mu$-Cl bridge atoms, in a way similar to other bis($\eta^5$-cyclopentadienyl)lanthanoid(III) and yttrium (III) chloride compounds (Lappert & Singh, 1982; Lobkovskii *et al.*, 1984; Evans *et al.*, 1992). The geometry at the metal centres may be described as distorted tetrahedral. The distortion from ideal tethrahedral geometry involves both the $Cg$1—Y1—$Cg$2 angle [129.0 (1)°; $Cg$1 and $Cg$2 are the centroids of Cp rings C1–C5 and C15–C19, respectively] and the Cl1—Y1—Cl1$^i$ angle [80.28 (4)°]. In particular, the higher value of the former angle is probably due to repulsion between the Cp rings, while the smaller value of the latter is probably due to the $\mu$-Cl bridge. The distances from the metal to the Cp rings [$Cg$1—Y1 2.351 (4) Å and $Cg$2—Y1 2.352 (4) Å] and other geometric parameters within the coordination sphere of the metal are in a good agreement with those in other yttrium bis(cyclopentadienyl) complexes (Evans *et al.*, 1992; Broussier *et al.*, 1996; Evans & Foster, 1992).

The cyclopentadienyl ligands bonded to each metal atom are disposed in a staggered way with respect to each other, with a pseudo-*trans* configuration of the cumyl substituents. Different orientations of the two pendant phenyl rings are observed. One phenyl ring (C23–C28) is oriented toward the outer part of the dimeric complex (*i.e.* away from the metal), while the second (C9–C14) is oriented toward the inner part of the complex, with a T (face-to-edge) intramolecular contact with the C15–C19 cyclopentadienyl ring [the minimum distance is $Cg$3···C17 3.476 (7) Å, where $Cg$3 is the centroid of the C9–C14 phenyl ring]. There are no interactions between the phenyl ring and the metal, in view of the long $Cg$3···Y1 distance of 4.573 (5) Å.

The monomeric nature of the analogous Ti$^{IV}$ complex, recently reported by us (Centore *et al.*, 2004), is probably a consequence of the different oxidation state of the metal.

## Experimental

$[C_5H_4C(Me_2)Ph]^-Li^+$ was prepared as reported in the literature (Longo *et al.*, 2001). A solution of $[C_5H_4C(Me_2)Ph]^-Li^+$ (6.9 mmol) in hexane (10 ml) was slowly added to a suspension of $YCl_3$ in hexane (50 ml) at 195 K. The reaction mixture was allowed to warm to room temperature and was stirred for 72 h. The resulting yellow suspension was filtered and the filtrate was dried *in vacuo*, then extracted with $CH_2Cl_2$ and filtered to remove residual LiCl. The title complex was crystallized from solution in a 1:1 mixture of $CH_2Cl_2$–hexane at room temperature, yielding single crystals (yield 300 mg). The single crystal used for the present X-ray analysis was sealed in a Lindemann capillary under an inert ($N_2$) atmosphere. Spectroscopic analysis: $^1$H NMR (400 MHz, $CD_2Cl_2$, $\delta$, p.p.m.): 1.6 [*s*, 6H, $-C(CH_3)_2$], 5.96 (*t*, 2H, –Cp), 6.34 (*t*, 2H, –Cp), 7.14–7.26 (*m*, 5H, $C_6H_5$). The spectrum remains unchanged between 298 and 193 K. $^{13}$C NMR (400 MHz, $CD_2Cl_2$, $\delta$, p.p.m.): 30.3 [$-C(CH_3)_2$], 40.0 [$-C(CH_3)_2$], 111.9, 113.3 (–Cp), 126.2 (Cm Ph), 126.4 (Cp Ph), 128.6 (Co Ph), 140.0 (Cq, Cp), 151.5 (Cq Ph). The $^1$H and $^{13}$C NMR spectra are compatible with either a $[C_5H_4C(Me_2)Ph]YCl_2$ or a $[C_5H_4C(Me_2)Ph]_2YCl$ structure. Moreover, neither the $^1$H nor the $^{13}$C NMR analysis allows the distinction between a monomeric or a dimeric form of the yttrium compound.

*Crystal data*

$[Y_2(C_{14}H_{15})_4Cl_2]$
$M_r = 981.76$
Monoclinic, $P2_1/c$
$a = 11.777$ (1) Å
$b = 13.507$ (3) Å
$c = 15.141$ (5) Å
$\beta = 95.81$ (2)°
$V = 2396.1$ (10) Å$^3$
$Z = 2$
$D_x = 1.361$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 82 reflections
$\theta = 4.8$–20.1°
$\mu = 2.56$ mm$^{-1}$
$T = 298$ (2) K
Prism, pale yellow
0.48 × 0.24 × 0.18 mm

*Data collection*

Bruker Nonius KappaCCD area-detector diffractometer
Thick-slice $\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker Nonius, 2002)
$T_{min} = 0.351$, $T_{max} = 0.631$
14926 measured reflections
4906 independent reflections
2975 reflections with $I > 2\sigma(I)$
$R_{int} = 0.087$
$\theta_{max} = 26.5°$
$h = -12 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -19 \rightarrow 19$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.091$
$S = 1.02$
4906 reflections
275 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 1.2677P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å$^{-3}$
$\Delta\rho_{min} = -0.51$ e Å$^{-3}$

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**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Y1—Cl1 | 2.6941 (12) | Y1—C19 | 2.658 (4) |
| Y1—Cl1$^{i}$ | 2.7024 (12) | C1—C2 | 1.415 (6) |
| Y1—C1 | 2.692 (4) | C1—C5 | 1.420 (5) |
| Y1—C2 | 2.613 (4) | C2—C3 | 1.410 (6) |
| Y1—C3 | 2.589 (4) | C3—C4 | 1.399 (6) |
| Y1—C4 | 2.619 (4) | C4—C5 | 1.398 (6) |
| Y1—C5 | 2.680 (4) | C15—C16 | 1.411 (5) |
| Y1—C15 | 2.705 (4) | C15—C19 | 1.412 (6) |
| Y1—C16 | 2.644 (4) | C16—C17 | 1.401 (6) |
| Y1—C17 | 2.588 (4) | C17—C18 | 1.375 (7) |
| Y1—C18 | 2.593 (4) | C18—C19 | 1.418 (6) |
| Cl1—Y1—Cl1$^{i}$ | 80.28 (4) | Y1—Cl1—Y1$^{i}$ | 99.72 (4) |
| C2—C1—C6—C9 | 52.3 (6) | C16—C15—C20—C23 | −60.7 (5) |
| C1—C6—C9—C10 | 87.5 (5) | | |

Symmetry code: (i) $-x, -y, -z$.

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with $C_{ar}-H = 0.93$ Å and C-Me—H = 0.96 Å, and with $U_{iso}(H)$ set at $U_{eq}$ of the carrier atom.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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