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Synthesis of bis(diphenylphosphinocyclopentadienyl) yttrium chloride complexes and heterodimetallic derivatives. X-ray structure of bis[(μ -chloro) bis(diphenylphosphinocyclopentadienyl) yttrium(III)]

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Abstract

Reaction of lithium diphenylphosphinocyclopentadienide with YCl_3 or $YCl_3(THF)_3$ and working lead to the formation of three ytrocene phosphines: the lithium metal adduct isolated as $(Ph_2PC_5H_4)_2Y(\mu-Cl)_2Li(THF)_2 \cdot 0.5 LiCl$ (1), the chloride-bridged dimeric species $\{(Ph_2PC_5H_4)_2Y(\mu-Cl)_2\}_2$ (2), and the coordinated monometal species $[(Ph_2PC_5H_4)_2YCl(THF)]$ (3). The X-ray structure of 2 is remarkable in that the crystal exhibits two independent chloride-bridged dimers that differ in the arrangement (*syn*, *anti*) of the diphenylphosphino groups.

Chelation of phosphorus atoms to a molybdenum carbonyl moiety is also reported.

Keywords: Yttrium; Dinuclear; X-ray structure; Phosphinocyclopentadienyl complexes

1. Introduction

Diphenylphosphinocyclopentadienide $(Ph_2PC_5H_4)^-$ has been used to link early and late transition metals [1–5] (for example, $[CpMn(CO)_2(Ph_2PC_5H_4)CpTiCl_2]$ [1] and $[(CO)_4Mo(Ph_2PC_5H_4)_2ZrCl_2]$ [3]). Recently, lanthanoid and actinoid complexes of this heterodifunctional ligand have been employed as precursors for the synthesis of novel f block/d block heterodimetallics [6–11]. Key examples are $[Me_2Pt(Ph_2PC_5H_4)_2Yb(THF)_2]$ [6] and $[(CO)_2Ni(Ph_2PC_5H_4)_2Yb(THF)_2]$ [8] whose molecular structures have been determined.

In this paper the synthesis of the dimeric, monomeric and heterodimetallic derivatives of the parent yttrium chlorobis(diphenylphosphinocyclopentadienyl)yttrium is reported. The molecular structure of $\{(Ph_2PC_5H_4)_2Y(\mu-Cl)_2\}_2$ was determined and the reaction of this dimer with $[Mo(CO)_6]$ is described.

2. Experimental section

All the organoyttrium complexes reported in this paper decompose rapidly in air. Consequently, all manipulations were carried out under argon. Solvents were dried over sodium benzophenone ketyl. The 1H , ^{13}C and ^{31}P NMR spectra were registered on a BRUKER AC-200 instrument in C_6D_6 or $CDCl_3$ at room temperature. The IR spectra were recorded on a BRUKER IFS66V instrument. Elemental analyses were performed by the Service de Microanalyses ICSN-CNRS, Gif sur Yvette. $Ph_2PC_5H_4Li$ was prepared by the literature method [12]. $[YCl_3(THF)_3]$ was prepared from the commercial YCl_3 by extraction with THF by the Soxhlet method.

2.1. Bis(tetrahydrofuran)lithium dichlorobis(diphenylphosphinocyclopentadienyl)yttrate(III) (1)

A solution of 1.1 g (4.3 mmol) of $Ph_2PC_5H_4Li$ in 30 ml of THF was added dropwise at $0^\circ C$ to a suspension of 0.88 g (2.15 mmol) of $[YCl_3(THF)_3]$ in 10 ml of THF. The yellow solution was then stirred for 2 h under ambient conditions. A colourless solid ($LiCl$) precipi-

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tated upon addition of 20 ml of hexane and the suspension was filtered. The volatiles were evaporated and the residue was washed with 10 ml of THF/hexane (1/4). Small pale yellow crystals were obtained by recrystallization from THF/hexane (yield 2.57 g, 74%).

Anal. Found: C, 60.72; H, 5.27. $C_{42}H_{44}Cl_2LiO_2P_2Y \cdot 0.5LiCl$. Calc.: C, 60.80; H, 5.22%.

1H NMR, C_6D_6 , δ ppm: phenyl, 7.50 (m, 8H); 7.05 (m, 12H); Cp, 6.39 (m, 4H); 6.25 (m, 4H); THF, 3.57 (m, 8H); 1.37 (m, 8H).

^{31}P NMR, C_6D_6 , δ ppm: -19.9.

2.2. Bis[(μ -chloro)bis(diphenylphosphinocyclopentadienyl)yttrium(III)] (2)

A suspension of 0.88 g (4.51 mmol) of YCl_3 and 2.31 g (9.02 mmol) of $Ph_2PC_5H_4Li$ in 80 ml of toluene was heated under reflux for 24 h. The suspension was then filtered. The filtrate was concentrated to 40 ml and 25 ml of hexane was added. After the solution was left at room temperature for 1 day, pale yellow crystals were obtained (yield 1.89 g, 67%).

Anal. Found: C, 65.58; H, 4.49. $C_{68}H_{56}Cl_2P_4Y_2$. Calc.: C, 65.56; H, 4.53.

IR(Nujol): 3375(br), 2479(m), 1621(br), 1260(m), 1151(s), 1119(s), 1028(s), 997(m), 864(w), 795(s), 741(s).

1H NMR, C_6D_6 , δ ppm: phenyl, 7.46 (m, 16H); 7.05 (m, 24H); Cp, 6.39 (m, 8H); 6.11 (m, 8H).

^{13}C NMR, $CDCl_3$, δ ppm: phenyl rings, *ipso*, 138.8 (d, $J(P-C) = 11$ Hz); *ortho*, 133.6 (d, $J(P-C) = 20.2$ Hz); *meta*, 128.5 (d, $J(P-C) = 7.8$ Hz); *para*, 128.8; Cp rings, *ipso*, 119.9 (d, $J(P-C) = 8$ Hz); α , 119.15 (d, $J(P-C) = 14$ Hz); β , 116.5 (d, $J(P-C) = 4$ Hz).

^{31}P NMR, C_6D_6 , δ ppm: -20.3.

2.3. X-ray structure determination of $\{[(Ph_2PC_5H_4)_2Y(\mu-Cl)]_2\}$

A single crystal suitable for X-ray structure analysis of approximate dimensions $0.16 \times 0.30 \times 0.44$ mm³ was mounted under dinitrogen in a Lindemann glass capillary and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The refined lattice parameters and other pertinent crystallographic information are provided in Table 1.

Intensity data were measured with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and ω scans with variable scan rates of 3–10° min⁻¹. The intensities of three standard reflections were measured periodically during data collection and they decreased monotonically by ca. 30% over the data collection period of 9 days. Sample decomposition was accompanied by the crystal becoming noticeably more yellow. The data were corrected for Lorentz-polarization effects and crystal decomposition. An empirical absorption cor-

Table 1

Crystal data and structure refinement of $\{[(Ph_2PC_5H_4)_2Y(\mu-Cl)]_2\}$

Empirical formula	$C_{34}H_{28}ClP_2Y$
Formula weight	934.30
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	13.825(1)
<i>b</i> (Å)	15.866(1)
<i>c</i> (Å)	22.755(2)
α (°)	93.19(1)
β (°)	106.61(1)
γ (°)	108.90(1)
Volume (Å ³)	4464.2(6)
Z	3
Density (g cm ⁻³)	1.390
Absorption coefficient (cm ⁻¹)	21.78
<i>F</i> (000)	1908
Crystal size (mm ³)	0.16 × 0.30 × 0.44
θ range for data collection	1.54 to 24.83°
Index range	0 ≤ <i>h</i> ≤ 14, -17 ≤ <i>k</i> ≤ 17, -24 ≤ <i>l</i> ≤ 23
Reflections collected	11946
Independent reflections	11375
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9520/0/1027
Goodness-of-fit on F^2	0.988
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0597$, $wR_2 = 0.0850$
<i>R</i> indices (all data)	$R_1 = 0.1650$, $wR_2 = 0.1278$
Largest difference peak and hole	0.644 and -0.336 e Å ⁻³

rection based upon the angular variation in the measured PSI scan intensities of 10 reflections ($6^\circ < 2\theta < 35^\circ$, $\chi \sim 90^\circ$) was applied. The transmission coefficients ranged from 0.632 to 0.991. The symmetry equivalent reflections were averaged.

Approximate positions for all but two of the non-hydrogen atoms were located by a combination of Patterson and direct methods (SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo computer). The remaining non-hydrogen atoms were revealed on the subsequent difference Fourier synthesis. Following anisotropic refinement of the non-hydrogen atoms, the hydrogen atoms were included as fixed contributions using a riding model with their isotropic temperature factor set at 1.2 times that of the adjacent carbon. Full-matrix least-squares refinement [13] based upon the minimization of $\sum w_i(F_o^2 - F_c^2)^2$, with $w_i^{-1} = \sigma^2(F_o^2) + 0.0309 P$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$, converged to give final discrepancy indices of $R_1 = 0.0597$, $wR_2 = 0.0850$ and GOF 0.99 for 5652 reflections with $I > 2\sigma(I)$ where $R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$ and $wR_2 = [\sum(w_i(F_o^2 - F_c^2)^2) / \sum(w_i(F_o^2))]^{1/2}$ and the standard deviation of an observation of unit weight (GOF) is equal to $[\sum(w_i(F_o^2 - F_c^2)^2) / \sum(n - p)]^{1/2}$ where *n* is the number of reflections and *p* is the number of parameters varied during the last refinement cycle.

2.4. Chlorobis(diphenylphosphinocyclopentadienyl)(tetrahydrofuran)yttrium (3)

A 0.2 g sample of the dimer **2** was dissolved in 5 ml of THF. The mixture was stirred for 10 min at room temperature. Then, the solvent was removed, leaving a yellow powder of **3** in a quantitative yield. Several attempts at recrystallizing **3** by cooling solution or by vapour diffusion have been unsuccessful so far.

Anal. Found: C, 65.01, H, 5.28. $C_{38}H_{36}ClO_2Y$. Calc.: C, 65.67, H, 5.22%.

1H NMR, C_6D_6 , δ ppm: phenyl, 7.50 (m, 8H); 7.05 (m, 12H); Cp, 6.34 (m, 4H); 6.18 (m, 4H); THF, 3.57 (m, 4H); 1.37 (m, 4H).

^{13}C NMR, $CDCl_3$, δ ppm: phenyl rings, *ipso*, 139.05 (d, $J(P-C) = 11$ Hz); *ortho*, 133.5 (d, $J(P-C) = 20$ Hz); *meta*, 128.4 (d, $J(P-C) = 8$ Hz); *para*, 128.15; Cp rings, *ipso*, 118.47 (d, $J(P-C) = 13$ Hz); α , 118.75 (d, $J(P-C) = 10$ Hz); β , 116.5 (d, $J(P-C) = 4$ Hz); THF, $O-CH_2$, 70.0 (s); $O-C-CH_2$, 25.46 (s).

^{31}P NMR, C_6D_6 , δ ppm: -20.0 .

2.5. Bis[tetracarbonylmolybdenum(chlorobis(diphenylphosphinocyclopentadienyl))yttrium(III)]

A 0.93 g sample (3.53 mmol) of solid $[Mo(CO)_6]$ was added to a solution of 2.2 g (1.76 mmol) of **2** in 30 ml of toluene and heated under reflux for 7 h. A brown precipitate was formed and was isolated by filtration. The solid was washed twice with 10 ml of toluene and dried under vacuum. The product was recrystallized in CH_2Cl_2 /hexane. 2.05 g of brown powder was obtained (yield 70%).

Anal. Found: C, 54.23, H, 3.29. $C_{76}H_{56}Cl_2O_8Mo_2P_4Y_2$. Calc.: C, 54.93, H, 3.40%.

^{31}P NMR, $CDCl_3$, δ ppm: $+38.5$ (d, $^2J(P-P) = 28$ Hz); 24.6 (d, $^2J(P-P) = 28$ Hz).

IR (CH_2Cl_2 or THF), $\nu(CO)$: 2017(s), 1946(m), 1922(s), 1896(vs).

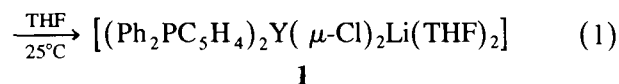
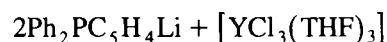
3. Results and discussion

3.1. Synthesis

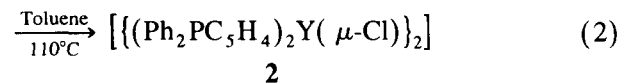
The chlorobis(cyclopentadienyl)lanthanoids are usually prepared by the metathesis of $LnCl_3$ and an alkali metal cyclopentadienide [14] or by the cleavage of the tris(cyclopentadienyl) derivatives. The thallium(I) cyclopentadienide was generally used in the preparation of the dimeric dichlorotetra(cyclopentadienyl)bislanthanoid form.

We used lithium diphenylphosphinocyclopentadienide to prepare both the dimeric species, $[(Ph_2PC_5H_4)_2Y(\mu-Cl)]_2$ (**2**), and the heterodimetallic species, $[(Ph_2PC_5H_4)_2Y(\mu-Cl)_2Li(THF)_2]$ (**1**). Complex **1** was

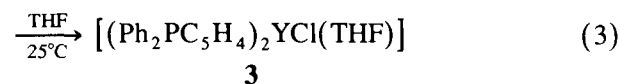
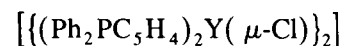
obtained by reaction of the lithium salt with $[YCl_3(THF)_3]$ in tetrahydrofuran (Eq. (1)). It was identified by 1H and ^{31}P NMR spectroscopy. Some pale yellow crystals, which were not suitable for an X-ray analysis, were grown from the crude material (in the presence of lithium chloride) by recrystallization from THF/hexane. Analytical data of the crystals were consistent with the composition $[(Ph_2PC_5H_4)_2Y(\mu-Cl)_2Li(THF)_2] \cdot 0.5 LiCl$. However, this stoichiometry could not be confirmed by the mass spectrum due to the thermal instability of **1**.



The dimeric species **2** was prepared by reaction of the lithium salt with YCl_3 in refluxing toluene (Eq. (2)). **2** was identified by 1H , ^{13}C , ^{31}P NMR spectroscopic studies and further characterized by IR, microanalysis and X-ray crystallography. The presence in the ^{31}P NMR spectrum of a single signal at $\delta -20.3$ ppm without coupling to the yttrium atom indicates that the phosphorus atoms of **2** are not coordinated and that they do not take part in the $Y-Cl-Y$ bridge cleavage.



Finally, the monomeric derivative **3** was obtained by dissolution of **2** in neat THF (Eq. (3)). Microanalysis is consistent with the formulation shown in Eq. (3). The single ^{31}P resonance at $\delta -20, 0$ ppm is only slightly shifted from that observed for **2**. These results and the observed 1H NMR spectrum seem to show the coordination of one molecule of THF.



The ability of the phosphorus donor sites to coordinate an Mo carbonyl fragment was examined by the reaction of **2** with $[Mo(CO)_6]$ in refluxing toluene (Eq. (4)).

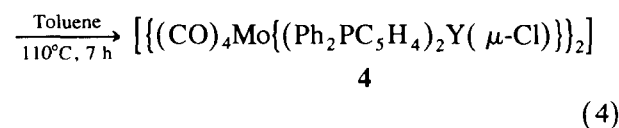
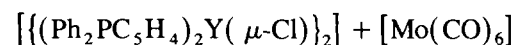


Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})_2]$.

	x	y	z	U_{eq}
Y(1)	608(1)	3586(1)	1448(1)	47(1)
Y(2)	-1414(1)	4383(1)	2096(1)	43(1)
Y(3)	4635(1)	8859(1)	4394(1)	40(1)
Cl(1)	-1205(2)	2852(1)	1724(1)	54(1)
Cl(2)	423(2)	5125(1)	1857(1)	57(1)
Cl(3)	3668(2)	9687(1)	4985(1)	46(1)
P(1)	-144(2)	1457(2)	223(1)	56(1)
P(2)	3337(2)	5263(2)	2640(1)	71(1)
P(3)	-4139(2)	2629(2)	983(1)	53(1)
P(4)	591(2)	6421(2)	3386(1)	52(1)
P(5)	5718(2)	8455(2)	2985(1)	59(1)
P(6)	7055(2)	8032(2)	5097(1)	49(1)
C(1)	-1(8)	2643(5)	336(3)	42(2)
C(2)	-756(7)	3065(6)	309(3)	52(3)
C(3)	-260(9)	3996(6)	364(4)	65(3)
C(4)	824(9)	4153(6)	422(4)	64(3)
C(5)	985(7)	3338(7)	398(3)	54(3)
C(6)	-1044(7)	1067(6)	-584(4)	53(3)
C(7)	-1186(8)	1646(6)	-1005(4)	76(3)
C(8)	-1859(9)	1294(8)	-1614(5)	81(3)
C(9)	-2366(9)	392(9)	-1803(5)	96(4)
C(10)	-2211(8)	-182(7)	-1392(5)	91(4)
C(11)	-1560(8)	149(7)	-790(4)	74(3)
C(12)	-1082(8)	945(5)	644(4)	52(3)
C(13)	-2149(9)	875(6)	463(4)	65(3)
C(14)	-2814(9)	519(6)	808(5)	89(4)
C(15)	-2390(12)	218(8)	1336(5)	110(5)
C(16)	-1334(12)	273(8)	1542(5)	111(5)
C(17)	-686(8)	628(5)	1182(4)	74(3)
C(18)	2503(8)	4057(6)	2329(5)	61(3)
C(19)	1742(9)	3532(9)	2595(4)	72(3)
C(20)	1326(8)	2649(8)	2259(5)	72(3)
C(21)	1821(9)	2643(7)	1815(5)	72(3)
C(22)	2549(8)	3528(8)	1860(4)	62(3)
C(23)	3601(10)	5646(7)	1916(5)	78(4)
C(24)	4293(10)	5416(7)	1681(6)	105(4)
C(25)	4348(11)	5679(8)	1104(6)	121(5)
C(26)	3724(14)	6169(11)	825(7)	140(9)
C(27)	3089(12)	6419(12)	1086(8)	136(8)
C(28)	3023(8)	6160(7)	1651(5)	85(4)
C(29)	4637(8)	5149(8)	3081(4)	61(3)
C(30)	4717(8)	4384(7)	3295(4)	79(3)
C(31)	5648(11)	4374(8)	3699(4)	87(4)
C(32)	6509(10)	5127(11)	3869(5)	98(4)
C(33)	6494(10)	5897(9)	3653(6)	91(4)
C(34)	5562(10)	5922(7)	3251(5)	81(3)
C(35)	-3344(7)	3817(5)	1226(4)	50(2)
C(36)	-2580(7)	4281(7)	936(3)	56(3)
C(37)	-2151(8)	5201(7)	1192(5)	74(3)
C(38)	-2628(8)	5305(7)	1634(5)	68(3)
C(39)	-3348(7)	4470(7)	1667(4)	56(3)
C(40)	-5413(7)	2669(7)	491(3)	49(2)
C(41)	-6288(9)	1888(6)	246(4)	66(3)
C(42)	-7250(8)	1860(8)	-166(4)	79(4)
C(43)	-7320(9)	2640(9)	-361(4)	86(4)
C(44)	-6482(9)	3424(7)	-131(4)	82(3)
C(45)	-5532(7)	3438(7)	290(4)	69(3)
C(46)	-4471(7)	2336(5)	1688(4)	49(2)
C(47)	-5262(7)	2546(5)	1861(4)	61(3)
C(48)	-5470(8)	2325(6)	2403(4)	70(3)
C(49)	-4866(9)	1923(7)	2788(5)	81(3)
C(50)	-4076(9)	1732(6)	2626(5)	84(4)
C(51)	-3886(8)	1921(6)	2079(5)	74(3)

Table 2 (continued)

	x	y	z	U_{eq}
C(52)	-403(8)	5300(6)	3232(3)	49(2)
C(53)	-1521(8)	5008(6)	3152(3)	55(3)
C(54)	-1939(8)	4073(7)	3097(4)	66(3)
C(55)	-1079(11)	3764(7)	3148(4)	69(3)
C(56)	-161(8)	4496(7)	3225(3)	60(3)
C(57)	778(6)	6749(6)	4210(3)	44(2)
C(58)	1123(7)	7655(6)	4463(4)	61(3)
C(59)	1382(7)	7913(6)	5093(4)	73(3)
C(60)	1358(8)	7297(7)	5478(4)	79(3)
C(61)	1049(7)	6405(6)	5238(4)	73(3)
C(62)	752(7)	6130(6)	4607(4)	56(3)
C(63)	-218(7)	7065(5)	2993(4)	50(2)
C(64)	-977(8)	7271(6)	3193(4)	68(3)
C(65)	-1574(8)	7728(6)	2849(5)	77(3)
C(66)	-1418(10)	7990(7)	2314(6)	93(4)
C(67)	-660(9)	7798(7)	2106(5)	81(4)
C(68)	-63(7)	7334(6)	2452(4)	66(3)
C(69)	4784(7)	8835(6)	3260(3)	42(2)
C(70)	4807(7)	9707(5)	3439(3)	44(2)
C(71)	3824(8)	9646(7)	3496(3)	53(4)
C(72)	3149(8)	8743(7)	3340(3)	58(3)
C(73)	3738(8)	8237(5)	3200(3)	46(2)
C(74)	5318(7)	8563(6)	2158(4)	50(2)
C(75)	4687(8)	9035(7)	1897(4)	77(3)
C(76)	4419(9)	9108(8)	1271(5)	99(4)
C(77)	4796(9)	8669(8)	911(5)	90(4)
C(78)	5426(9)	8191(7)	1145(5)	90(4)
C(79)	5669(7)	8118(6)	1776(5)	68(3)
C(80)	6998(7)	9420(6)	3268(4)	57(3)
C(81)	7327(9)	10096(7)	2944(4)	77(3)
C(82)	8357(10)	10768(7)	3162(5)	85(3)
C(83)	9047(10)	10717(8)	3701(6)	98(4)
C(84)	8771(11)	10073(10)	4049(5)	108(5)
C(85)	7744(10)	9415(7)	3815(5)	83(3)
C(86)	5617(7)	7782(5)	4947(4)	39(2)
C(87)	5053(8)	7967(5)	5323(4)	48(2)
C(88)	3944(8)	7574(6)	5017(5)	64(3)
C(89)	3819(7)	7145(5)	4431(5)	55(3)
C(90)	4840(8)	7284(5)	4382(4)	48(2)
C(91)	7189(7)	6960(5)	5299(3)	43(2)
C(92)	6376(7)	6257(6)	5393(3)	53(3)
C(93)	6542(8)	5470(6)	5535(4)	70(3)
C(94)	7525(9)	5388(6)	5598(4)	68(3)
C(95)	8320(8)	6077(7)	5498(4)	74(3)
C(96)	8171(7)	6860(6)	5354(4)	56(3)
C(97)	7670(6)	8738(6)	5865(4)	47(2)
C(98)	7534(7)	8445(5)	6408(4)	59(3)
C(99)	8058(8)	9025(7)	6970(4)	73(3)
C(100)	8712(8)	9881(7)	7003(5)	76(3)
C(101)	8869(8)	10176(6)	6482(6)	78(3)
C(102)	8353(7)	9622(6)	5914(4)	60(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The IR spectrum of **4** displays four bands at 2017, 1946, 1922 and 1896 cm^{-1} , both in dichloromethane and in THF, assigned to the *cis*- $\text{Mo}(\text{CO})_4$ moiety. These frequencies are similar to those reported for tetracarbonylmolybdenum complexes of organometallic bis(phosphinocyclopentadienyls) [3,15]. Microanalysis is in accordance with the formulation shown in Eq. (4) (1:1 for the ratio Mo:Y). We have not observed any

changes in THF solution and the ^1H NMR spectroscopy of the product from the hydrolysis of **4** established the absence of any additional ligands. This suggests that complex **4** is a stable dimeric species in THF solution, in contrast to **2**.

Surprisingly, the ^{31}P NMR spectrum of **4** in solution at ambient temperature displayed two doublets, at 24.7 and 38.5 ppm with $^2J(\text{P}-\text{P}) = 28$ Hz. Variable-tempera-

ture NMR measurements, within the range -20 to 80°C , show no discernible change in the spectrum. Thus, the two phosphorus atoms linked to the same molybdenum atom are inequivalent. This non-equivalence is probably due to a non-fluxional conformation of the P–Mo–P bridges, and accounts for the existence of only one static non-centrosymmetric isomer. The low solubility of this derivative precluded ^1H and ^{13}C NMR analyses with the available NMR instrumentation.

3.2. X-ray structure of $[\{(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})\}_2]$

The atomic coordinates for $[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})_2]$ are given in Table 2; the two structures characterized are shown in Fig. 1 and selected interatomic distances and angles are listed in Tables 3 and 4 respectively.

This compound crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with three molecules per unit cell. The geometry of one dinuclear unit is constrained by a crystallographic centre of inversion at the middle point of the $\text{Y}\cdots\text{Y}$ line. The other independent molecule of **2** lacks any crystallographically-imposed symmetry.

In the non-centrosymmetric molecule (A) the P–C(Cp) bonds adopt an *anti* orientation, whereas in the centrosymmetric molecule (B) these bonds are *syn*. The corresponding dihedral $\text{P}(1)\cdots\text{Cp}(1)\cdots\text{Cp}(2)\cdots\text{P}(2)$ and $\text{P}(3)\cdots\text{Cp}(3)\cdots\text{Cp}(4)\cdots\text{P}(4)$ in the *anti* structure are 162.2 and 168.5° respectively, whereas the $\text{P}(5)\cdots\text{Cp}(5)\cdots\text{Cp}(6)\cdots\text{P}(6)$ dihedral angle in the *syn* structure is 37.6° . The central four-membered $\text{Y}_2(\mu\text{-Cl})_2$ ring in the *anti* structure is folded by 2.2° along the $\text{Cl}\cdots\text{Cl}$ line, whereas the corresponding ring in the *syn* structure is rigorously planar (Fig. 1).

Except for the noticeable differences in the orienta-

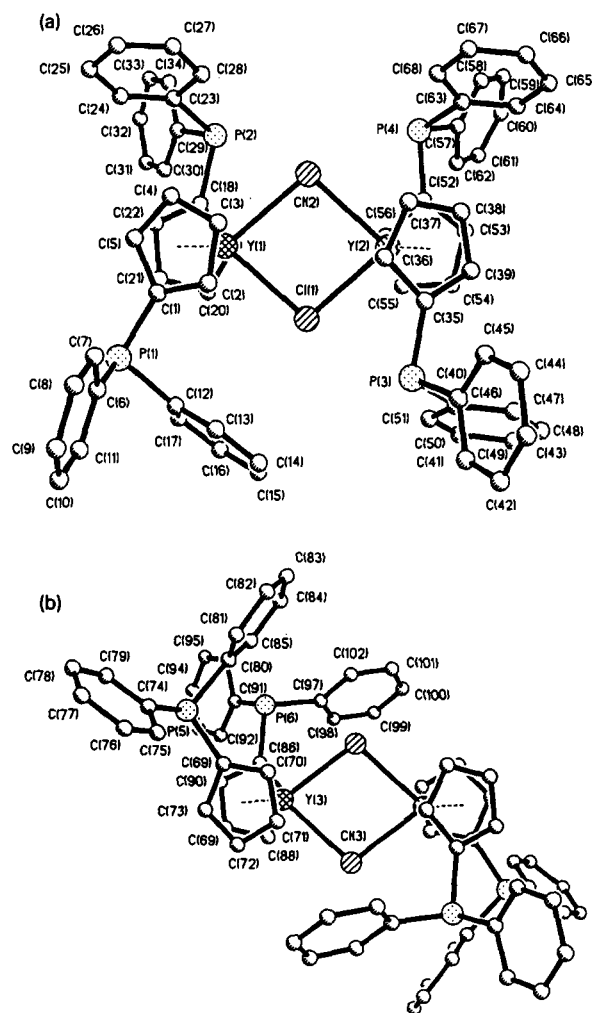


Fig. 1. Perpendicular view to the central four-membered $\text{Y}_2(\mu\text{-Cl})_2$ ring of $[\{(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})\}_2]$ showing the configuration of Ph_2P groups in (a) dimer A (*anti* Ph_2P groups) and (b) dimer B (*syn* Ph_2P groups).

Table 3
Selected interatomic distances (Å) for $[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})_2]$

<i>Dimer A</i>			
Y(1)–Cl(1)	2.668(2)	Y(2)–Cl(1)	2.658(2)
Y(1)–Cl(2)	2.680(2)	Y(2)–Cl(2)	2.655(2)
Y(1)–C(Cp ¹)	2.610(8)–2.635(8)	Y(1)–Cp ¹ (c) ^a	2.340
Y(1)–C(Cp ²)	2.591(9)–2.655(8)	Y(1)–Cp ² (c) ^a	2.340
Y(2)–C(Cp ³)	2.611(8)–2.659(8)	Y(2)–Cp ³ (c) ^a	2.345
Y(2)–C(Cp ⁴)	2.609(8)–2.637(8)	Y(2)–Cp ⁴ (c) ^a	2.331
<i>Dimer B</i>			
Y(3)–Cl(3)	2.699(2)	Y(3)–Cl(3')	2.657(2)
Y(3)–C(Cp ⁵)	2.621(7)–2.645(7)	Y(3)–Cp ⁵ (c) ^a	2.348
Y(3)–C(Cp ⁶)	2.607(7)–2.667(7)	Y(3)–Cp ⁶ (c) ^a	2.345
$\langle\text{P}-\text{C}(\text{C}_5\text{H}_4)\rangle$	1.823	$\langle\text{P}-\text{C}(\text{Ph})\rangle$	1.840
Y(1) \cdots Y(2)	4.002	Y(3) \cdots Y(3')	4.082

^a Cpⁿ(c) is the centroid of the cyclopentadienyl ring defined by the five carbon atoms C(17n – 16) to C(17n – 12).

Table 4
Selected bond angles (°) for $[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})_2]$

Dimer A			
$\text{Cp}^1(\text{c})\text{-Y}(1)\text{-Cp}^2(\text{c})^a$	129.6	$\text{Cl}(1)\text{-Y}(1)\text{-Cl}(2)$	82.34(7)
$\text{Cp}^3(\text{c})\text{-Y}(2)\text{-Cp}^4(\text{c})^a$	130.5	$\text{Cl}(2)\text{-Y}(2)\text{-Cl}(1)$	82.99(7)
$\text{Y}(2)\text{-Cl}(1)\text{-Y}(1)$	97.43(7)	$\text{Y}(2)\text{-Cl}(2)\text{-Y}(1)$	97.19(7)
$\text{Cp}^1(\text{c})\text{-Y}(1)\text{-Cl}(2)^a$	107.6	$\text{Cp}^1(\text{c})\text{-Y}(1)\text{-Cl}(1)^a$	108.1
$\text{Cp}^2(\text{c})\text{-Y}(1)\text{-Cl}(2)^a$	111.2	$\text{Cp}^2(\text{c})\text{-Y}(1)\text{-Cl}(1)^a$	107.7
$\text{Cp}^3(\text{c})\text{-Y}(2)\text{-Cl}(2)^a$	108.8	$\text{Cp}^3(\text{c})\text{-Y}(2)\text{-Cl}(1)^a$	109.4
$\text{Cp}^4(\text{c})\text{-Y}(2)\text{-Cl}(2)^a$	106.9	$\text{Cp}^4(\text{c})\text{-Y}(2)\text{-Cl}(1)^a$	108.1
Dimer B			
$\text{Cp}^5(\text{c})\text{-Y}(3)\text{-Cp}^6(\text{c})^a$	129.4	$\text{Cl}(3)\text{-Y}(3)\text{-Cl}(3')^b$	80.69(7)
$\text{Y}(3)\text{-Cl}(3)\text{-Y}(3')^b$	99.30(7)		
$\text{Cp}^3(\text{c})\text{-Y}(3)\text{-Cl}(3')^a$	108.8	$\text{Cp}^5(\text{c})\text{-Y}(3)\text{-Cl}(3)^a$	106.2
$\text{Cp}^6(\text{c})\text{-Y}(3)\text{-Cl}(3')^a$	112.8	$\text{Cp}^6(\text{c})\text{-Y}(3)\text{-Cl}(3)^a$	107.7

^a $\text{Cp}^n(\text{c})$ is the centroid of the cyclopentadienyl ring defined by the five carbon atoms $\text{C}(17n-16)$ to $\text{C}(17n-12)$. ^b Symmetry transformations used to generate equivalent atoms: (') notation corresponds to $-x+1, -y+2, +z+1$.

tion of diphenylphosphino groups, the metal coordination environments in both dimers are similar. The yttrium atoms are in a distorted tetrahedral environment with two $\text{Ph}_2\text{PC}_5\text{H}_4$ groups and two $\mu\text{-Cl}$, giving formal eight-coordination.

A striking feature in the *anti* structure (A) is the noticeably different spatial orientation of one of the PPh_2 groups with respect to the other three.

In the *syn* structure, the major difference is in the position of the phosphorus atom P(5) which is displaced on the other side of the Cp ring away from the corresponding Y atom. The angle between the P(5)–C(ring) line and the Cp ring plane (8.8°) is twice as large as the other values ($3.2\text{--}4.6^\circ$). This arrangement indicates that bulky phosphino groups are more adaptable auxiliary ligands, whereas the conformations of cyclopentadienyl rings are similar in both *syn* and *anti* structures.

Only two structures of dimeric species with chlorides as bridging atoms have been described, $[(\text{Cp}_2\text{YCl})_2]$ [16] $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{YCl}]_2$ [17]. Both adopt centrosymmetric structures. A comparison of bonding parameters of **2** and of these closely related yttrium complexes shows no great differences. No example of a structure containing two different conformations for a dimeric structure analogous to **2** is known for bis(cyclopentadienyl)yttrium chloride. However, the molecular structure $[(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})\text{YCl}(\text{C}_5\text{Me}_5)_2]$ [18] is asymmetric with only one bridging Cl. Several examples of structures close to **2**,

i.e. containing both centrosymmetric and non-centrosymmetric dimers in a 1:2 ratio, are described, for example $[(\text{Cp}_2\text{YbBr})_2]$ [19]; one form of $[(\text{Cp}_2\text{YbCl})_2]$ [20], and $[(\text{Cp}_2\text{GdBr})_2]$ [21]. Our structures are very similar to the structures of $[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{YbCl}]_2$ which have recently been established by Deacon et al. [22] (Table 5). The close similarity in the geometry of the two $[\text{Cp}_2\text{MCl}_2\text{MCp}_2]$ compounds reflects the small difference in the metal radii of yttrium (0.88 Å) and ytterbium (0.858 Å) [18].

Complete lists of bond lengths and angles and tables of hydrogen atom coordinates and anisotropic displacements parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Table 5
Selected interatomic distances (Å) and angles (°) for $[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})_2]$ and $[(\text{Ph}_2\text{PC}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})_2]$.

	$[(\text{Ph}_2\text{PCp})_2\text{YCl}]_2$	$[(\text{Ph}_2\text{PCp})_2\text{YbCl}]_2$
$\text{M}\cdots\text{M}$	4.002–4.082	3.964–4.036
$\text{M}\text{-Cl}$	2.655(2)–2.699(2)	2.627(5)–2.676(5)
$\text{M}\text{-C}$	2.591(9)–2.659(8)	2.53(2)–2.63(2)
	av. 2.626	av. 2.59
$\text{Cl}\text{-M}\text{-Cl}$	80.69–82.99	80.9–82.7
$\text{Cp}(\text{c})\text{-M}\text{-Cp}(\text{c})$	129.3–130.6	129.4–130.5

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