ELSEVIER

Journal of Organometallic Chemistry 495 (1995) 203–208

Journal of Organometallic Chemistry

Synthesis and crystal structure of $[(\eta^5:\eta^5\text{-}C_5H_4PPh_2)Tl]_\infty$ and the divalent ytterbium derivative $[(\eta^5\text{-}C_5H_4PPh_2)_2Yb(DME)]$

Guanyang Lin, Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong

Received 5 January 1995

Abstract

The complex [(diphenylphosphino)cyclopentadienyl]thallium $[(\eta^5:\eta^5\text{-}C_5H_4PPh_2)Tl]_\infty$ (**1**) and the divalent ytterbium compound $[(\eta^5\text{-}C_5H_4PPh_2)_2Yb(DME)]$ (**2**) (DME = dimethoxyethane) made from it have been synthesized and characterized by IR, ^1H NMR and ^{31}P NMR spectroscopy and X-ray diffraction studies. In the crystal **1**, polymeric zigzag chains of alternating thallium ions and cyclopentadienyl rings form, with the neighboring chains were connected by the weak interactions between phosphorus and thallium atoms. In contrast, **2** is a neutral monomer with two dangling phosphorus atoms.

Keywords: Thallium; Ytterbium; Cyclopentadienyl; Crystal structure

1. Introduction

In recent years, organometallic complexes containing elements of Group 13 have attracted a great deal of interest because of their important role in semiconductor technology and optoelectronics. Several types of complex have been prepared and structurally characterized [1–4]. Among these, cyclopentadienylthallium and its ring-substituted analogues are much valued as mild reagents for the synthesis of cyclopentadienyl derivatives of main group elements and transition metals [5–10]. The cyclopentadienyl thallium complexes which have so far been characterized by single-crystal X-ray crystallographic studies are $[TlC_5H_5]_\infty$ [11], $[TlC_5H_4C(CN)C(CN)_2]_\infty$ [12], $[TlC_5Me_5]_\infty$ [13], $[TlC_5H_4SiMe_3]_\infty$ [14], $[TlC_5H_3(SiMe_3)_2]_6$ [14], $[TlC_5(CH_2Ph)_5]$ [15], $[TlC_5Me_4(SiMe_2Ph)]_\infty$ [16], $[TlC_5Me_4(SiMe_2CH_2Ph)]_\infty$ [16], $[Tl(^tBu_2C_5H_2\text{–}C_5H_2{}^tBu_2)Tl]_\infty$ [17], $[TlAu(C_5H_4PPh_2)_2]_2$ [18], $[TlC_5HMe_4]_\infty$ [19], $[TlC_5Me_4PPh_2]$ [20], $[TlC_5H_4CMe_2C_{13}H_9]$ (isomers **a** and **b**) [21], $[\{Tl(C_5H_5)_2\}^-\{C_5H_5Mg(Me_2NCH_2CH_2)_2NMe\}^+]$ [22] and $[(C_5H_5)Tl(C_5H_5)Li(Me_2NCH_2CH_2)_2NMe]$ [22]. These studies revealed that most complexes containing cyclopentadienyl–thallium linkages have polymeric structures in the solid state. Some exceptions are $[TlC_5H_3(SiMe_3)_2]_6$ [14] which forms a hexagonal doughnut compound, $[TlAu(C_5H_4PPh_2)_2]_2$ [18] which is dimeric, $[TlC_5(CH_2Ph)_5]$ [15] and $[TlC_5Me_4PPh_2]$ [20] which are monomeric, and $[\{Tl(C_5H_5)_2\}^-\{C_5H_5Mg(Me_2NCH_2CH_2)_2NMe\}^+]$ [22] and $[(C_5H_5)Tl(C_5H_5)Li(Me_2NCH_2CH_2)_2NMe]$ [22] which form ion pairs. We describe here $[(\eta^5:\eta^5\text{-}C_5H_4PPh_2)Tl]_\infty$ which forms a two-dimensional network and report its use in the preparation of the organolanthanide complex $[(\eta^5\text{-}C_5H_4PPh_2)_2Yb(DME)]$ whose structure is also reported.

2. Experimental details

The complexes are air and moisture sensitive and so the syntheses and subsequent manipulations were conducted under dinitrogen with strict exclusion of air and moisture by the use of vacuum line techniques. Solvents were thoroughly dried by refluxing over sodium benzophenone ketyl and distilled under nitrogen immediately prior to use. The reagents Ph_2PCl (Aldrich), TlOEt (Strem) and metallic ytterbium (Strem) were used as recieved. IR spectra were recorded on a BIO-RAD FTS-7 IR spectrophotomer and ^1H and ^{31}P NMR spectra on a JEOL GSX 270 FT spectrometer. The residual proton resonance of the solvent was used as the reference for the ^1H spectra and a glass capillary filled with

---

* Corresponding author.

Elsevier Science S.A.
SSDI 0022-328X(95)05463-4

phosphoric acid (85%) was used as external reference for ^{31}P spectra, which were proton decoupled.

2.1. Preparation of $[(\eta^5:\eta^5\text{-}C_5H_4PPh_2)Tl]_\infty$

Chlorodiphenylphosphine (50 mmol) was added by syringe to a solution of C_5H_4Na (50 mmol) in tetrahydrofuran (THF) at −78 °C. The mixture was stirred for 1 h at room temperature and the solvent then removed under vacuum to leave a yellow oily residue. Extraction of this residue with diethyl ether gave a yellow solution of $Ph_2PC_5H_5$ to which was added TlOEt (40 mmol). The mixture was stirred at room temperature for 2 h; the yellowish powder formed was then isolated by centrifugation, washed twice with hexane and dried under vacuum for 1 h (97.6% yield based on the amount of TlOEt taken). IR (KBr): ν 3066w, 3044w, 1470vs, 1421vs, 1189s, 1168s, 1083s, 1055m, 1020vs, 822s, 724vs, 689vs, 618s, 505vs, 456s and 421s cm^{-1}, ^1H NMR (THF-d_8): δ 7.37m, 7.21m, 6.18m and 6.66d ppm. ^{31}P NMR (THF, 85%H_3PO_4, ext.): δ 24.89 and −21.06 ppm.

2.2. Preparation of $[(\eta^5\text{-}C_5H_4PPh_2)_2Yb(DME)]$

Complex **1** (1 mmol) was mixed with an excess of ytterbium powder (about 0.4 g) and a small amount of metallic mercury (about 0.1 g) in a Schlenk flask and THF (30 ml) was added from a syringe. The suspension was stirred at 60 °C for 20 h. The mixture was then centrifuged to give a purple solution and dark thallium metal. Removal of the THF in vacuo left a purple residue, which was extracted with dimethylether (DME) (15 ml). Centrifugation of the extract gave a green solution, and removal of the solvent gave 67% yield of **2** (based on the amount of **1** taken). IR (KBr): ν 3067w, 3051w, 1473s, 1432vs, 1350w, 1337m, 1210w, 1117s, 1086m, 1062m, 1020w, 990m, 893m, 736s, 715m,

Table 1
Crystallographic data for **1** and **2**

	1	**2**
Empirical formula	$C_{17}H_{14}PTl$	$C_{38}H_{38}O_2P_2Yb$
Color; habit	Off-white, block	Dark green, plate
Crystal size (mm)	0.20 × 0.22 × 0.44	0.20 × 0.40 × 0.42
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/a$ (No. 14, non-standard)	*Pbcn* (No. 60)
Unit cell dimensions		
a (Å)	12.200(7)	8.506(2)
b (Å)	9.951(3)	15.344(2)
c (Å)	12.373(4)	26.966(4)
β (°)	92.85(4)	
Volume (Å³)	1500.3(9)	3519(2)
Z	4	4
Formula weight	453.64	761.70
Density (calculated) (g cm^{-1})	2.008	1.437
Absorption coefficient (cm^{-1})	108.39	27.78
F(000)	848	1528
Radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
Temperature (K)	293	293
2θ range (°)	4–50	4–50
Scan type	ω–2θ	ω–2θ
Scan speed (° min^{-1})	16.0 (in ω)(up to 4 scans)	16.0 (in ω)(up tp 4 scans)
Scan range ω	1.47 + 0.35 tan θ	0.79 + 0.35 tan θ
Background measurement	25% at both ends	25% at both ends
Number of reflections collected	2893	3535
Number of independent reflections	2762 (R_{int} = 0.031)	3535
Number of observed reflections	1495 ($I > 3\sigma(I)$)	1558 ($I > 3\sigma(I)$)
Absorption correction	ψ scan method	ψ scan method
Refinement method	Full-matrix least-squares	Full-matrix least-squares
Weighting scheme	$\omega = 1/\sigma^2(F_0)$	$\omega = 1/\sigma^2(F_o)$
R; R_w (observed data)	0.044; 0.040	0.039; 0.041
Goodness of fit	2.700	2.091
Largest Δ/σ	0.05	0.05
Number of parameters	87	95
Residual extrema in the final difference map (electrons Å^{-3})	1.28 to −1.25 close to Tl	0.65 to −0.38

690vs, 568s, 532s and 497m cm^{-1}, ^{1}H NMR (THF-d_8): δ 7.26br, 6.60br and 3.24m ppm. ^{31}P NMR (THF, 85% H_3PO_4, ext.): δ −20.12 ppm.

2.3. Determination of the crystal structures of 1 and 2

Off-white crystals of **1** suitable for the X-ray study were obtained by slow cooling of a hot solution of **1** in THF and green crystals of **2** by keeping a saturated solution of **2** in DME at −20 °C overnight. Single crystals of **1** and **2** were selected under a dinitrogen stream and sealed in glass Lindemann capillaries. Crystal intensity data were collected at room temperature on a Rigaku AFC7R diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The data were corrected for Lorentz and polarization effects and absorption by the ψ scan method [23]. The structures were solved by the Patterson method and refined by full-matrix least-squares analysis. Hydrogen atoms were were placed at calculated positions and not refined. The crystallographic data for both **1** and **2** are listed in Table 1. All calculations were performed on a Silicon-Graphics computer using the package TeXsan from MSC [24].

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

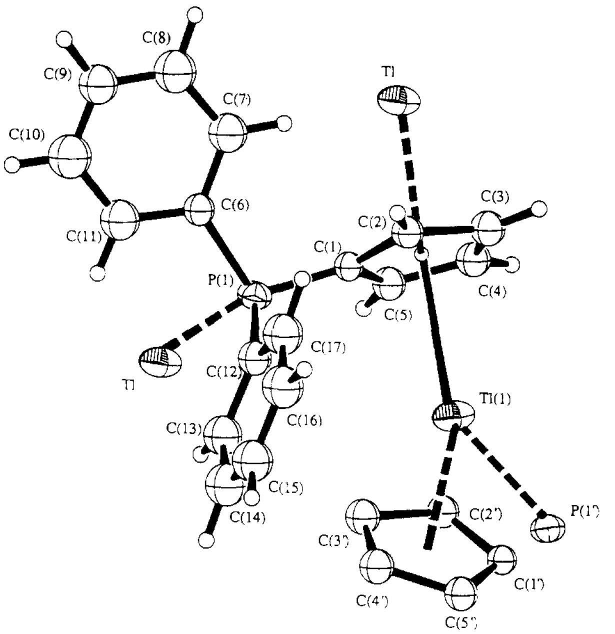

Fig. 1. Quasi-molecular unit of $[TlC_5H_4PPh_2]_\infty$ (**1**).

3. Results and discussion

(Diphenylphosphino)cyclopentadienide is a useful ligand for the synthesis of homobimetallic and heterobimetallic complexes [9]. The compound $Ph_2PC_5H_5$ was first obtained with quantitative yield, by Mathey and Lampin [25] by treating CpTl with Ph_2PCl. In 1982, Casey et al. [26] produced it with an 81% yield from reaction CpNa · DME with Ph_2PCl and we recently prepared it with an 80% yield from CpNa · THF and Ph_2PCl [27]. However, since $Ph_2PC_5H_5$ undergoes decomposition at room temperature, it is usually converted into lithium [26], sodium [27] or thallium salts for storage [8,9]; all these are convenient reagents for the introduction of a $Ph_2PC_5H_4$ group into a transition metal complex. The thallium compound $TlC_5H_4PPh_2$ was first reported in 1983 by Rausch et al. [8], but we used a different procedure to make it.

The X-ray study showed **1** to form a infinite zigzag chain polymer with neighboring chains connected by interactions between phosphorus and thallium atoms to form of a two-dimensional network. Fig. 1 shows a perspective view of the basic unit of the polymer. The distance P · · · Tl (3.580 Å) is significantly longer than the sum (2.65 Å) of the covalent radii of phosphorus atoms (1.10 Å) and the thallium atoms (1.55 Å) [28] which indicates that the P · · · Tl interaction is weak. In the ^{31}P NMR spectrum of **1** in THF at room temperature there are two singlets, at 24.89 and −21.06 ppm respectively. The former signal can be assigned to the phosphorus atoms coordinated to thallium, indicating

Table 2
Selected bond lengths (Å) and bond angles (°) for $[TlC_5H_4PPh_2]_\infty$(**1**) [a]

Bond lengths					
C(1)–Tl(1)	3.10(1)	C(2)–Tl(1)	3.16(1)	C(3)–Tl(1)	3.22(2)
C(4)–Tl(1)	3.15(2)	C(5)–Tl(1)	3.03(1)	C(1')–Tl(1)	3.20(1)
C(2')–Tl(1)	3.10(1)	C(3')–Tl(1)	2.97(1)	C(4')–Tl(1)	2.95(1)
C(5')–Tl(1)	3.08(1)	P(1')–Tl(1)	3.58(1)	P(1)–C(1)	1.70(1)
P(1)–C(6)	1.83(1)	P(1)–C(12)	1.83(2)	C_{cent}–Tl(1)	2.88(1)
C'_{cent}–Tl(1)	2.80(1)				
Bond angles					
C_{cent}–Tl(1)–C'_{cent}	122(1)	C_{cent}–Tl(1)–P(1')	142(1)		
C'_{cent}–Tl(1)–P(1')	94(1)	C(1)–P(1)–C(6)	107.2(7)		
C(6)–P(1)–C(12)	99.4(7)	C(1)–P(1)–C(12)	104.4(7)		

[a] C_{cent} and C'_{cent} denote the centroids of the cyclopentadienyl rings C(1)–C(5) and C(1')–C(5') respectively.

Table 3
Atomic coordinates and isotropic displacement coefficients B_{eq} for $[TlC_5H_4PPh_2]_\infty$ (**1**)

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Tl(1)	0.15467(5)	0.23129(6)	0.43773(7)	5.44(2)
P(1)	0.4087(3)	0.4198(4)	0.3237(4)	4.2(1)
C(1)	0.316(1)	0.469(1)	0.414(1)	3.4(3)
C(2)	0.213(1)	0.539(1)	0.409(1)	4.0(3)
C(3)	0.162(1)	0.538(2)	0.522(1)	4.7(4)
C(4)	0.236(1)	0.469(2)	0.588(1)	4.7(4)
C(5)	0.329(1)	0.426(1)	0.522(1)	4.3(3)
C(6)	0.448(1)	0.570(1)	0.249(1)	3.9(3)
C(7)	0.416(1)	0.701(2)	0.271(2)	6.0(4)
C(8)	0.465(1)	0.807(2)	0.215(2)	7.1(5)
C(9)	0.538(1)	0.787(2)	0.140(2)	6.1(4)
C(10)	0.571(1)	0.662(2)	0.119(2)	7.5(5)
C(11)	0.524(1)	0.554(2)	0.171(2)	6.2(4)
C(12)	0.326(1)	0.335(2)	0.217(1)	4.4(3)
C(13)	0.358(1)	0.205(2)	0.187(2)	6.0(4)
C(14)	0.292(1)	0.137(2)	0.108(2)	6.9(5)
C(15)	0.208(1)	0.192(2)	0.056(2)	6.6(5)
C(16)	0.175(1)	0.318(2)	0.080(2)	6.9(5)
C(17)	0.236(1)	0.391(2)	0.161(2)	6.4(4)

$B_{eq} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table 4
Structural data for crystalline TlCp′ species and their derivatives (Cp′ = cyclopentadienyl or substituted cyclopentadienyl)

Complex	C_{cent}–Tl –C'_{cent} [a] (°)	Tl–C_{cent} (Å)	Reference
$[TlC_5H_4]_\infty$	137	3.19	[11]
$[TlC_5H_4C(CN)C(CN)_2]_\infty$	113.6	3.01, 3.06	[12]
$[TlC_5Me_5]_\infty$	[b]	2.91, 2.99	[13]
$[TlC_5H_4SiMe_3]_\infty$	149	2.71, 2.84	[14]
$[TlC_5H_3(SiMe_3)_2]_6$	127, 133	2.74, 2.78	[14]
$[TlC_5(CH_2Ph)_5]$	[c]	2.49	[15]
$[TlC_5Me_4(SiMe_2Ph)]_\infty$	142	2.62, 2.86	[16]
$[TlC_5Me_4(SiMe_2Ph)]_\infty$	147	2.74	[16]
$[TlAu(C_5H_4PPh_2)_2]_2$	135	2.71, 2.74	[18]
$[TlC_5Me_4PPh_2]$	[c]	2.50	[20]
$[TlC_5H_4CMe_2C_{13}H_9]$ (isomer a)	[b]	2.56, 3.06	[21]
$[TlC_5H_4CMe_2C_{13}H_9]$ (isomer b)	[c]	2.50	[21]
$[TlC_5H_4PPh_2]_\infty$	122.6	2.80, 2.88	This work

[a] C_{cent} and C'_{cent} denote the centroids of cyclopentadienyl rings.
[b] The data are not available.
[c] No angle in the molecule.

that the P · · · Tl interaction is retained in solution, and the latter signal to the phosphorus atoms is not coordinated to thallium. The selected bond lengths and angles are listed in Table 2, and atomic coordinates and thermal parameters are shown in Table 3. Fig. 2 shows the packing diagram for **1**.

Some important bond angles and lengths reported for crystalline TlCp′ complexes are listed in Table 4. From the column for C_{cent}–Tl(1)-C'_{cent}, it can be seen that in **1** this angle, of 122.6° is markedly smaller than those in the other complexes except for $[TlC_5H_4C(CN)C(CN)_2]_\infty$ (113.6°). This seems to be the result of the P · · · Tl interaction in **1** and a relatively short Tl · · · Tl interaction (4.60 Å) in $[TlC_5H_4C(CN)C(CN)_2]_\infty$. The Tl–$C_{cent}$ distances in **1** (2.88 and 2.80 Å) are within the range observed for other substituted cyclopentadieyl-containing Tl reagents. The compound TlCp has found extensive use as a mild reagent for the synthesis of metallocenes [5,6]. In 1983, Rausch et al. [8] explored the possibility of using **1** as a similar reagent, and some results of its use have been reported [9,10,18]. However, use of **1** in the synthesis of organolanthanide complexes is relatively rare [10].

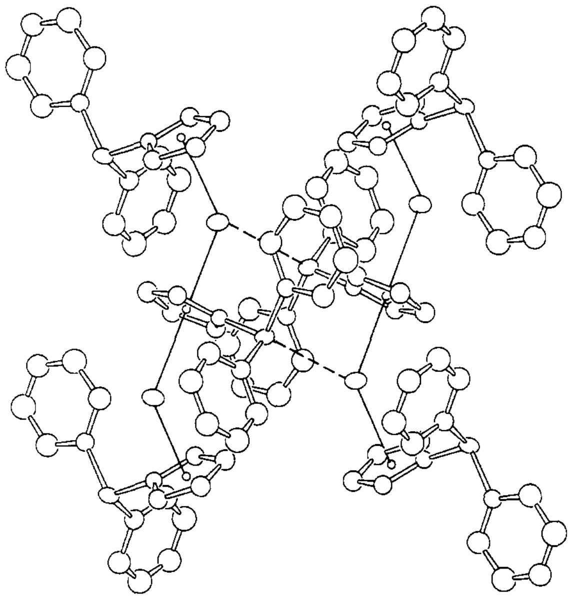
Fig. 2. Packing diagram for $[TlC_5H_4PPh_2]_\infty$ (**1**).

Fig. 3 is a perspective drawing of the molecular structure of **2**. Crystals of **2** consist of discrete neutral monomeric molecules, in which the phosphorus atoms

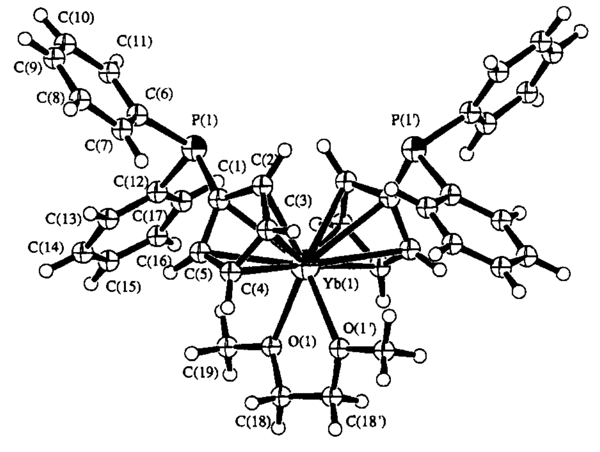

Fig. 3. A perspective view of the structure of $[(\eta^5\text{-}(C_6H_5)_2PC_5H_4)_2Yb(DME)]$ (**2**).

Table 5
Selected bond lengths (Å) and bond angles (°) for $[(\eta^5\text{-}(C_6H_5)_2PC_5H_4)_2Yb(DME)]$ (**2**)

Bond lengths					
Yb(1)–O(1)	2.404(7)	Yb(1)–C(1)	2.694(9)	Yb(1)–C(2)	2.666(10)
Yb(1)–C(3)	2.70(1)	Yb(1)–C(4)	2.74(1)	Yb(1)–C(5)	2.747(10)
P(1)–C(1)	1.800(9)	P(1)–C(12)	1.82(1)	P(1)–C(6)	1.86(1)
O(1)–C(19)	1.37(1)	O(1)–C(18)	1.39(1)	C(1)–C(2)	1.43(1)
C(2)–C(3)	1.36(1)	C(3)–C(4)	1.41(1)	C(4)–C(5)	1.38(1)
C(1)–C(5)	1.41(1)				
Bond angles					
O(1)–Yb(1)–O(1′)	67.7(4)	P(1)–C(1)–C(2)	121.2(7)		
P(1)–C(1)–C(5)	131.6(8)	C(2)–C(1)–C(5)	106.9(9)		
C(6)–P(1)–C(1)	101.6(5)	C(6)–P(1)–C(12)	102.3(5)		
C(10)–P(1)–C(12)	103.0(4)	Yb(1)–O(1)–C(19)	124.1(8)		
Yb(1)–O(1)–C(18)	116.0(7)	C(18)–O(1)–C(19)	114.3(10)		

are not coordinated to the ytterbium ion. The singlet appearing at −20.12 ppm in the ^{31}P NMR spectrum of **2** also indicates that the phosphorus atoms are dangling. Selected bond lengths and angles are summarized in Table 5, and atomic coordinates and thermal parameters in Table 6. From the charge balance and in the absence of any paramagnetic effect on the ^1H NMR spectrum of **2**, the central ion of ytterbium is divalent. The Yb–C distance, ranging from 2.666 to 2.747 Å with a mean value of 2.710 Å, is significantly longer than that in $[(\eta^5\text{-}(C_6H_5)_2PC_5H_4)_2Yb(\mu\text{-}Cl)_2Na(DME)_2]$ (mean Yb–C distance, 2.620 Å) [27], but almost the same as that in $[Yb(THF)_2C_5H_4P(C_6H_5)_2PtMe_2]$ (mean Yb–C distance, 2.71 Å) [10]. The coordination geometry around Yb^{2+} is that of a distorted tetrahedron if the cyclopentadienyl rings are regarded as points.

Table 6
Atomic coordinates and isotropic displacement coefficients B_{eq} for $[(\eta^5\text{-}(C_6H_5)_2PC_5H_4)_2Yb(DME)]$ (**2**)

Atom	x	y	z	B_{eq} (Å^2)
Yb(1)	0.0000	0.19967(4)	0.2500	4.59(1)
P(1)	0.0084(4)	0.3817(2)	0.14804(10)	5.77(6)
O(1)	0.0993(9)	0.0695(5)	0.2115(3)	7.1(2)
C(1)	−0.118(1)	0.3052(6)	0.1794(3)	4.8(2)
C(2)	−0.196(1)	0.3279(6)	0.2245(4)	5.7(2)
C(3)	−0.294(1)	0.2606(7)	0.2354(4)	6.5(3)
C(4)	−0.280(1)	0.1931(7)	0.2002(4)	6.5(3)
C(5)	−0.174(1)	0.2223(7)	0.1652(4)	5.8(2)
C(6)	−0.131(1)	0.4355(7)	0.1053(4)	5.9(3)
C(7)	−0.285(2)	0.4163(8)	0.1016(4)	7.4(3)
C(8)	−0.387(2)	0.4627(9)	0.0703(5)	9.2(4)
C(9)	−0.326(2)	0.5264(10)	0.0431(6)	10.1(4)
C(10)	−0.173(2)	0.546(1)	0.0426(6)	12.7(5)
C(11)	−0.072(2)	0.500(1)	0.0753(6)	11.2(5)
C(12)	0.121(1)	0.3124(7)	0.1062(4)	5.6(2)
C(13)	0.060(1)	0.2717(7)	0.0642(4)	6.6(3)
C(14)	0.152(2)	0.2166(8)	0.0345(5)	8.2(3)
C(15)	0.303(2)	0.2015(8)	0.0478(5)	8.0(3)
C(16)	0.366(2)	0.2390(8)	0.0888(5)	8.6(4)
C(17)	0.280(2)	0.2957(8)	0.1179(4)	7.5(3)
C(18)	0.024(2)	−0.0077(7)	0.2245(4)	8.5(3)
C(19)	0.171(2)	0.0676(9)	0.1658(5)	11.4(4)

$B_{eq} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Acknowledgments

We thank the Hong Kong Research Grants Council and the University of Hong Kong for financial support.

References

[1] O.T. Beachley, Jr., M.R. Churchill, J.C. Fettinger, J.C. Pazik and L. Victoriano, *J. Am. Chem. Soc., 108* (1986) 4666.

[2] C. Dohmeier, C. Robl, M. Tacke and H. Schnockel, *Angew. Chem., Int. Edn. Engl., 30* (1991) 564.

[3] S. Schulz, H.W. Roesky, H.J. Koch, G.M. Sheldrick, D. Stalke and A. Kuhn, *Angew. Chem., Int. Edn. Engl., 32* (1993) 1729.

[4] S.D. Waezsadu, T. Belgardt, M. Noltemeyer and H.W. Roesky, *Angew. Chem., Int. Edn. Engl., 33* (1994) 1351.

[5] G.B. Deacon, A.J. Koplik and T.D. Tuong, *Polyhedron, 1* (1982) 423.

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

[7] G.B. Deacon, A.J. Koplick and T.D. Tuong, *Aust. J. Chem., 37* (1984) 517.

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

[9] D.L. DuBois, C.W. Eigenbrot, Jr., A. Miedaner, J.C. Smart and R.C. Haltiwanger, *Organometallics, 5* (1986) 1405.

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

[11] E. Frasson, F. Mengus and C. Panattoni, *Nature, 199* (1963) 1087.

[12] G. Zweifel, S.J. Backlund and T. Leung, *J. Am. Chem. Soc.,* (1977) 5194.

[13] H. Werner, H. Otto and H.J. Kraus, *J. Organomet. Chem., 315* (1986) C57.

[14] S. Harvey, C.L. Raston, B.W. Skelton, A.H. White, M.F. Lappert and G. Srivastava, *J. Organomet. Chem., 328* (1987) C1.

[15] H. Schumann, C. Janiak, M.A. Khan and J.J. Zuckerman, *J. Organomet. Chem., 354* (1988) 7.

[16] H. Schumann, H. Kucht, A. Dietrich and L. Esser, *Chem. Ber., 123* (1990) 1811.

[17] P. Jutzi, J. Schnittger and M.B. Hursthouse, *Chem. Ber., 124* (1991) 1693.

[18] G.K. Anderson and N.P. Rath, *J. Organomet. Chem., 414* (1991) 129.

[19] H. Schumann, H. Kucht, A. Kucht, H.F. Goerlitz and A. Dietrich, *Z. Naturforsch.* Teil B: *478* (1992) 1241.

[20] H. Schumann, T. Ghodsi, L. Esser and E. Hahn, *Chem. Ber., 126* (1993) 591.

[21] W. Frank, D. Kuhn, S. Muller-Becker and A. Razavi, *Angew. Chem., Int. Edn. Engl., 32* (1993) 90.

[22] D.R. Armstrong, R. Herbst-Irmer, A. Kuhn, D. Moncrieff, M.A. Paver, C.A. Russel, D. Stalke, A. Steiner and D.S. Wright, *Angew. Chem., 105* (1993) 1807.

[23] A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.

[24] *TeXsan, Crystal Structure Analysis Package*, Molecular Structure Corporation, 1985, 1992.

[25] F. Mathey and J.P. Lampin, *Tetrahedron, 31* (1975) 2685.

[26] L.P. Casey, R.M. Bullock, W.C. Fultz and A.L. Rheingold, *Organometallics, 1* (1982) 1591.

[27] G.Y. Lin and W.T. Wong, *Polyhedron, 13* (1994) 3027.

[28] J. Emsley, *The Elements*, Clarendon, Oxford, 1989.