

Synthesis and X-ray structural investigation of triindenyl tetrahydrofuranato praseodymium

Shaowu Wang^a, Deyuan Kong^a, Zhongwen Ye^{a,*}, Xiaoying Huang^b

^a Institute of Organic Chemistry, Anhui Normal University, Wuhu, Anhui 241000, People's Republic of China

^b Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China

Received 22 November 1994; in revised form 25 January 1995

Abstract

Reaction of PrCl_3 and $\text{C}_9\text{H}_7\text{Na}$ in 1:2 molar ratio affords the disproportionation product of $[(\text{C}_9\text{H}_7)_3\text{PrOC}_4\text{H}_8]$. It crystallizes into $[(\text{C}_9\text{H}_7)_3\text{Pr}(1)\text{OC}_4\text{H}_8][(\text{C}_9\text{H}_7)_3\text{Pr}(2)\text{OC}_4\text{H}_8]$, which is composed by pairs of disconnected molecules with slight differences in structure. The crystal is in monoclinic system, space group $P2_1/a$, with unit cell constants $a = 21.809(9)$, $b = 10.512(4)$ and $c = 23.586(9)$ Å, $\beta = 114.71(4)^\circ$, $V = 4912(4)$ Å³, $Z = 4$, $D_c = 1.51$ g cm⁻³, $F(000) = 2256$, and full-matrix least-squares refinement to final $R = 0.038$ and $R_w = 0.047$. The complex has also been characterized by IR and elemental analyses.

Keywords: Praseodymium; Crystal structure; Indenyl

1. Introduction

Although a series of triindenyl tetrahydrofuranato lanthanide complexes $(\text{C}_9\text{H}_7)_3\text{LnTHF}$ have been synthesized and studied by Tsutsui and Gysling [1] (where Ln = La, Sm, Gd, Tb, Dy, or Yb) and Huang et al. [2] (where Ln = Ce, Nd or Y), the related crystal structural studies have been limited [3,4]. In addition, X-ray studies have demonstrated that $(\text{C}_9\text{H}_7)_3\text{Ln}$ (Ln = Pr or Nd) can crystallize in two types in tetrahydrofuran (THF) solution, namely $[\text{Na}(\text{THF})_6][(\eta^5\text{-C}_9\text{H}_7)_3\text{Ln}(\mu\text{-Cl})\text{Ln}(\eta^5\text{-C}_9\text{H}_7)_3]$ (Ln = Sm [5b], Nd [5a] or Pr [6]) and $[(\eta^5\text{-C}_9\text{H}_7)_3\text{LnTHF}]$ (Ln = Nd [7] or Gd [7]); the synthesis and structural study of triindenyl tetrahydrofuranato praseodymium have not been reported in the literature. Finally, until now, only a few reports have focused on the study of the thermal stability of lanthanide–indenyl complexes [6,7]. For the above reasons, we decided to synthesize triindenyl tetrahydrofuranato praseodymium by disproportionation reaction and to carry out X-ray structural investigation of the complex.

2. Results and discussion

The crystal data are given in Table 1, and the final positional and thermal parameters are listed in Table 2. Selected bond lengths and bond angles are given in Table 3 and Table 4 respectively. Fig. 1 and Fig. 2 give the perspective view of the complex structure and the package of the molecules in the unit cell respectively.

2.1. Formation of $[(\text{C}_9\text{H}_7)_3\text{Pr}(1)\text{OC}_4\text{H}_8][(\text{C}_9\text{H}_7)_3\text{Pr}(2)\text{OC}_4\text{H}_8]$

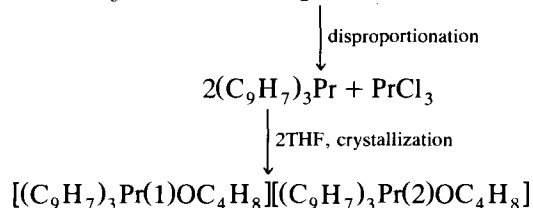
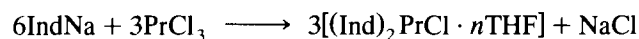
Several studies [8–15] have demonstrated that organolanthanide complexes with both Cp and other ligands are comparatively unstable upon heating. A disproportionation reaction would take place, owing to the rearrangement of ligands, at moderately high temperatures. They have also found that complexes of the type CpLnL_2 (L = ligand) are less thermally stable than those of Cp_2LnL , and the final disproportionation products of both types of complex are Cp_3Ln and LnL_3 . With respect to lanthanide–indenyl complexes, Chen and coworkers [7] have pointed out that the formation of $(\text{C}_9\text{H}_7)_3\text{LnTHF}$ (Ln = Nd, Gd or Er) is the result of the disproportionation reaction of $(\text{C}_8\text{H}_{11})\text{Ln}(\text{C}_9\text{H}_7)_2 \cdot n\text{THF}$ in THF solution. Recently, we reported [6] that

* Corresponding author.

Table 1
Crystallographic data of the complex

Empirical formula	C ₆₂ H ₅₈ O ₂ Pr ₂
Formula weight	1116.95
Crystal system	Monoclinic
Cell constants	
<i>a</i> (Å)	21.809(9)
<i>b</i> (Å)	10.512(4)
<i>c</i> (Å)	23.586(9)
β (°)	114.71(4)
<i>V</i> (Å ³)	4912(4)
Space group	<i>P</i> 2 ₁ / <i>a</i>
<i>Z</i>	4
<i>D</i> _c (g cm ⁻³)	1.51
<i>F</i> (000)	2256
Diffractometer	Enraf–Nonius CAD4
μ (cm ⁻¹)	19.97
Radiation	Mo Kα (λ = 0.71069 Å), graphite-monochromated
Temperature (°C)	23
2θ (maximum) (°)	49.9
Number of reflections collected	9422
Number of independent reflections	9298
Number of observations (<i>I</i> > 3σ(<i>I</i>))	6930
<i>R</i> ; <i>R</i> _w	0.038; 0.047
Largest peak in final difference map (electrons Å ⁻³)	0.95

reaction of 1:0.8 mole ratio of PrCl₃ with C₉H₇Na results in the formation of the disproportionation product [Na(THF)₆][(η⁵-C₉H₇)₃Pr(μ-Cl)Pr(η⁵-C₉H₇)₃]. A similar phenomenon has been encountered in the reaction of 1:2 mole ratio of anhydrous PrCl₃ and sodium indenyl in THF with the formation of [(C₉H₇)₃Pr(1)OC₄H₈][(C₉H₇)₃Pr(2)OC₄H₈] as the only pure product. So, we can conclude that the formation of the title complex is the result of the disproportionation reaction and the formation procedure is suggested below:



where Ind = C₉H₇ = Indenyl.

An important difference between (C₉H₇)₃Ln and Cp₃Ln is that (C₉H₇)₃Ln can crystallize in two types in THF solution: one is a chloride-bridged linear-type complex; the other is a tetrahydrofuranato-coordinated complex. In contrast, Cp₃Ln can crystallize in only one type in THF solution, Cp₃LnTHF [16]. Moreover, (C₉H₇)₃LnTHF can exist in a new form of structural

isomer, which is for the first time found with the structural series of (C₉H₇)₃LnTHF.

2.2. Property of [(C₉H₇)₃Pr(1)OC₄H₈][(C₉H₇)₃Pr(2)OC₄H₈]

The complex [(C₉H₇)₃Pr(1)THF][(C₉H₇)₃Pr(2)THF] is unstable to moisture and air both in solution and as a solid; it is soluble in THF and insoluble in toluene or *n*-hexane. An IR spectrum study shows characteristic absorptions of the indenyl group at 3060, 1615, 1472, 1020 and 770 cm⁻¹ and those of THF at 1063 and 910 cm⁻¹.

2.3. Structure of [(C₉H₇)₃Pr(1)OC₄H₈][(C₉H₇)₃Pr(2)OC₄H₈]

From Fig. 1 we can see that each praseodymium atom is surrounded by three indenyl ligands and one THF molecule; the Pr atom is coordinated in η⁵ fashion with five-membered rings of indenyl ligands, and in η¹ fashion with the oxygen atom of the THF molecule. So a distorted tetrahedron is formed around each praseodymium atom by setting the three centroids of five-membered rings of indenyl ligands and oxygen atom of THF molecule as the apices of the tetrahedron.

All carbon atoms in each indenyl group are coplanar with least-squares deviations of 0.0541, 0.0335, 0.0452, 0.0527, 0.0354 and 0.0307 Å respectively. The dihedral angles between the indenyl planes are listed in Table 5; from the table we can see that the dihedral angles of indenyl planes in one molecule of (C₉H₇)₃Pr(1)THF are different from those in the other. From Fig. 1, we can see that the orientations of six-membered rings of indenyl groups of the two molecules are different. These results suggest that the configurations of these two molecules are different. This structural character of the praseodymium complex is different from those of the reported neodymium and gadolinium complexes, which have crystallographic C₃ symmetry [7].

From Fig. 1 and Fig. 2, we can see that there are two disconnected structural isomers crystallizing in one asymmetrical unit, and there are eight (four pairs) of these isomers in the unit cell. This indicates that these two isomers have the same crystallization energy.

From Table 3 and Table 4, we can see that the bond lengths of the Pr(1)–C(average) (2.836 Å) are equal to that of Pr(2)–C(average) (2.836 Å), and the bond length of Pr(1)–O(1) (2.553(4) Å) is longer than that of Pr(2)–O(2) (2.542(4) Å) (an average of 2.548 Å) (the corresponding bond lengths of Nd–O and Gd–O in (C₉H₇)₃LnTHF (Ln = Nd or Gd) [3] are 2.557 Å and 2.459 Å respectively).

The triindenyl chloride-bridged praseodymium complex of [Na(THF)₆][(η⁵-C₉H₇)₃Pr(μ-Cl)Pr(η⁵-C₉H₇)₃] crystallizes in the triclinic system, of space group *P*1

Table 2
Positional and thermal parameters

Atom	x	y	z	B_{eq} (\AA^2)
Pr(1)	0.38109(1)	0.19909(3)	0.14132(1)	2.39(1)
Pr(2)	0.25278(2)	0.16475(3)	0.64839(1)	2.77(1)
O(1)	0.3795(2)	-0.0438(4)	0.1391(2)	4.1(2)
O(2)	0.2414(3)	-0.0744(4)	-0.6311(2)	4.7(2)
C(1)	0.3623(5)	-0.1202(8)	0.0850(4)	8.5(5)
C(2)	0.0390(1)	-0.2440(1)	0.1111(7)	20(1)
C(3)	0.4236(7)	-0.2440(1)	0.1705(6)	11.5(7)
C(4)	0.4310(5)	-0.1251(8)	0.1937(4)	7.4(4)
C(5)	0.1959(9)	-0.1320(1)	0.5794(6)	13.6(8)
C(6)	0.1784(9)	-0.2570(1)	0.6029(7)	12.2(9)
C(7)	0.2399(9)	-0.2950(1)	0.6449(7)	12.3(7)
C(8)	0.2718(7)	-0.1780(1)	0.6749(8)	12.6(8)
C(11)	0.2518(3)	0.3359(5)	0.0669(3)	3.1(2)
C(12)	0.3050(3)	0.3654(5)	0.0485(3)	3.1(2)
C(13)	0.3151(2)	0.2574(6)	0.0192(2)	3.0(2)
C(14)	0.2766(3)	0.1581(6)	0.0243(3)	3.2(2)
C(15)	0.2346(3)	0.2056(5)	0.0522(3)	2.8(2)
C(16)	0.1806(3)	0.1523(7)	0.0620(3)	4.2(3)
C(17)	0.1439(3)	0.2280(1)	0.0827(4)	6.0(4)
C(18)	0.1594(4)	0.3550(1)	0.0961(4)	5.4(4)
C(19)	0.2131(3)	0.4101(7)	0.0895(3)	4.5(3)
C(21)	0.4200(3)	0.3050(6)	0.2674(3)	4.1(3)
C(22)	0.3539(4)	0.3448(6)	0.2256(3)	4.3(3)
C(23)	0.3116(3)	0.2402(8)	0.2121(3)	4.6(3)
C(24)	0.3485(4)	0.1323(7)	0.2404(3)	4.6(3)
C(25)	0.4158(4)	0.1708(8)	0.2760(3)	4.2(3)
C(26)	0.4744(4)	0.1063(7)	0.3178(3)	5.2(3)
C(27)	0.5323(4)	0.1730(9)	0.3502(3)	6.3(4)
C(28)	0.5342(4)	0.3044(9)	0.3415(4)	6.4(4)
C(29)	0.4807(4)	0.3688(7)	0.3012(3)	5.3(3)
C(31)	0.4821(3)	0.1806(6)	0.0893(3)	3.8(3)
C(32)	0.5063(3)	0.1252(7)	0.1494(3)	4.7(3)
C(33)	0.5169(3)	0.2198(8)	0.1932(3)	4.8(3)
C(34)	0.4959(3)	0.3362(7)	0.1621(4)	4.6(3)
C(35)	0.4767(3)	0.3146(6)	0.0966(3)	3.8(3)
C(36)	0.4600(3)	0.3949(7)	0.0446(4)	4.6(3)
C(37)	0.4489(3)	0.3434(9)	-0.0119(4)	5.5(4)
C(38)	0.4522(4)	0.2115(9)	-0.0193(3)	5.3(4)
C(39)	0.4673(3)	0.1308(7)	0.0292(4)	4.7(3)
C(41)	0.3109(3)	0.1788(6)	0.5545(3)	3.6(2)
C(42)	0.2434(3)	0.1341(6)	0.5270(3)	4.0(3)
C(43)	0.2010(3)	0.2341(7)	0.5256(3)	3.9(3)
C(44)	0.2393(3)	0.3388(6)	0.5558(3)	3.9(3)
C(45)	0.3083(3)	0.3078(6)	0.5720(3)	3.7(3)
C(46)	0.3664(4)	0.3823(7)	0.5944(4)	5.5(3)
C(47)	0.4256(4)	0.3300(1)	0.6000(5)	7.8(5)
C(48)	0.4295(4)	0.2020(1)	0.5843(5)	7.2(5)
C(49)	0.3724(4)	0.1245(7)	0.5626(3)	5.1(3)
C(51)	0.1033(3)	0.1647(6)	0.6050(3)	3.7(3)
C(52)	0.1340(3)	0.0983(7)	0.6618(3)	4.7(3)
C(53)	0.1702(4)	0.1794(8)	0.7089(3)	5.4(4)
C(54)	0.1669(4)	0.3004(7)	0.6838(4)	5.0(3)
C(55)	0.1226(3)	0.2957(6)	0.6190(3)	3.9(3)
C(56)	0.0943(4)	0.3887(7)	0.5709(4)	5.3(3)
C(57)	0.0497(4)	0.3500(1)	0.5138(4)	6.0(4)
C(58)	0.0311(4)	0.2210(1)	0.5000(4)	5.7(4)
C(59)	0.0576(3)	0.1319(7)	0.5452(4)	4.9(3)
C(61)	0.3340(4)	0.2085(8)	0.7814(3)	5.3(3)
C(62)	0.3391(5)	0.0770(9)	0.7695(4)	6.8(4)
C(63)	0.3746(4)	0.0710(1)	0.7332(4)	7.1(4)

Table 2 (continued)

Atom	x	y	z	B_{eq} (\AA^2)
C(64)	0.3879(4)	0.1880(1)	0.7164(4)	6.1(4)
C(65)	0.3631(3)	0.2786(8)	0.7467(3)	5.3(3)
C(66)	0.3644(4)	0.4130(1)	0.7501(4)	7.5(5)
C(67)	0.3400(6)	0.4740(1)	0.7860(6)	9.0(5)
C(68)	0.3130(5)	0.4040(1)	0.8218(5)	8.6(5)
C(69)	0.3094(5)	0.2760(1)	0.8198(4)	7.3(5)

with an ionic pair in the unit cell; in contrast, the triindenyl tetrahydrofuranato praseodymium of the title complex crystallizes in the monoclinic system, of space group $P2_1/a$ with four pairs of structural isomers in the unit cell; these results may be due to different reactant ratios and crystallizing conditions.

3. Experimental details

All manipulations were carried out in an atmosphere of purified argon using Schlenk techniques; all solvents were refluxed and distilled over the sodium ketyl benzophenone under argon immediately before use. Elemental analysis data were obtained on a Yanaco MT-2 analyser. The analysis for Pr was obtained by the published method [17]. IR spectra were recorded on a Perkin-Elmer 983(G) spectrometer (CsI crystal plate; Nujol and Fluoroluble mulls). The melting point was determined in sealed argon-filled capillaries without correction. Sodium indenyl was prepared by the reaction of sodium hydride and freshly distilled indene.

Table 3
Selected bond lengths (\AA)

Pr(1)–O(1)	2.553(4)	Pr(2)–O(2)	2.542(4)
Pr(1)–C(11)	2.994(6)	Pr(1)–C(12)	2.750(6)
Pr(1)–C(13)	2.697(5)	Pr(1)–C(14)	2.783(6)
Pr(1)–C(15)	3.003(6)	Pr(1)–C(21)	2.949(6)
Pr(1)–C(22)	2.765(6)	Pr(1)–C(23)	2.719(6)
Pr(1)–C(24)	2.802(6)	Pr(1)–C(25)	2.957(6)
Pr(1)–C(31)	2.943(7)	Pr(1)–C(32)	2.768(6)
Pr(1)–C(33)	2.700(6)	Pr(1)–C(34)	2.748(7)
Pr(1)–C(35)	2.960(7)	Pr(2)–C(41)	2.979(8)
Pr(2)–C(42)	2.802(6)	Pr(2)–C(43)	2.731(6)
Pr(2)–C(44)	2.767(6)	Pr(2)–C(45)	2.964(4)
Pr(2)–C(51)	2.982(9)	Pr(2)–C(52)	2.825(6)
Pr(2)–C(53)	2.730(7)	Pr(2)–C(54)	2.750(7)
Pr(2)–C(55)	2.966(6)	Pr(2)–C(61)	2.923(9)
Pr(2)–C(62)	2.839(8)	Pr(2)–C(63)	2.755(8)
Pr(2)–C(64)	2.714(8)	Pr(2)–C(65)	2.817(7)
O(1)–C(1)	1.42(1)	O(1)–C(4)	1.462(9)
O(2)–C(5)	1.45(1)	O(2)–C(8)	1.460(1)
C(1)–C(2)	1.48(1)	C(2)–C(3)	1.53(2)
C(3)–C(4)	1.42(1)	C(5)–C(6)	1.54(2)
C(6)–C(7)	1.45(1)	C(7)–C(8)	1.44(2)
Pr(1)–C(average)	2.836	Pr(2)–C(average)	2.836

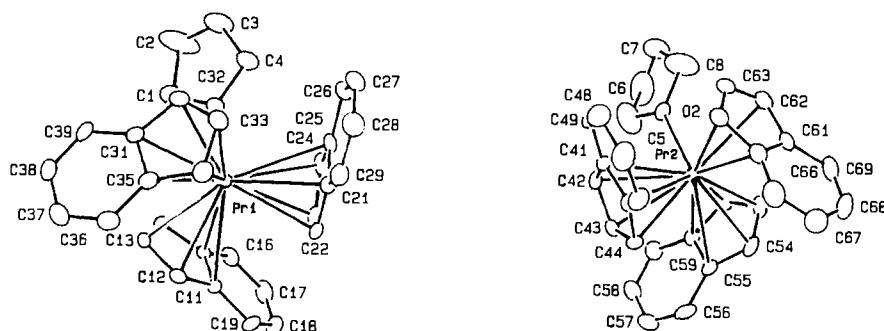


Fig. 1. The structure of $[(\eta^5\text{-C}_9\text{H}_7)_3\text{Pr}(1)\text{OC}_4\text{H}_8][(\eta^5\text{-C}_9\text{H}_7)_3\text{Pr}(2)\text{OC}_4\text{H}_8]$.

Table 4
Selected bond angles (°)

O(1)–Pr(1)–C(12)	128.3(2)	O(1)–Pr(1)–C(13)	102.0(2)
O(1)–Pr(1)–C(14)	80.0(2)	O(1)–Pr(1)–C(22)	124.4(2)
O(1)–Pr(1)–C(23)	99.6(2)	O(1)–Pr(1)–C(24)	76.2(2)
O(1)–Pr(1)–C(32)	74.0(2)	O(1)–Pr(1)–C(33)	95.3(2)
O(1)–Pr(1)–C(34)	122.0(2)	O(2)–Pr(2)–C(52)	75.1(2)
O(2)–Pr(2)–C(53)	95.7(2)	O(2)–Pr(2)–C(54)	122.0(2)
O(2)–Pr(2)–C(62)	79.6(2)	O(2)–Pr(2)–C(63)	76.3(3)
O(2)–Pr(2)–C(64)	101.2(3)	O(2)–Pr(2)–C(65)	123.7(2)
C(12)–Pr(1)–C(13)	29.6(2)	C(13)–Pr(1)–C(14)	29.0(2)
C(22)–Pr(1)–C(23)	29.2(2)	C(23)–Pr(1)–C(24)	29.1(2)
C(32)–Pr(1)–C(33)	29.2(2)	C(33)–Pr(1)–C(34)	29.8(2)
C(42)–Pr(2)–C(43)	29.1(2)	C(43)–Pr(2)–C(44)	29.2(2)
C(52)–Pr(2)–C(53)	28.3(2)	C(53)–Pr(2)–C(54)	29.4(2)
C(62)–Pr(2)–C(63)	28.4(2)	C(63)–Pr(2)–C(64)	28.8(2)
C(64)–Pr(2)–C(65)	29.8(2)	C(1)–O(1)–C(2)	107.9(6)
C(5)–O(2)–C(8)	104.5(8)	O(1)–C(1)–C(2)	102.9(8)
C(1)–C(2)–C(3)	113.0(1)	C(2)–C(3)–C(4)	109.0(1)
C(3)–C(4)–O(1)	106.0(8)	O(2)–C(5)–C(6)	105.0(1)
C(5)–C(6)–C(7)	102.0(1)	C(6)–C(7)–C(8)	103.0(1)
C(7)–C(8)–O(2)	108.0(1)	C(15)–C(11)–C(12)	107.2(5)
C(11)–C(12)–C(13)	106.9(5)	C(12)–C(13)–C(14)	110.3(5)
C(13)–C(14)–C(15)	107.9(5)	C(15)–C(16)–C(17)	119.1(7)
C(16)–C(17)–C(18)	121.8(6)	C(17)–C(18)–C(19)	121.2(6)
C(42)–C(41)–C(45)	106.7(5)	C(41)–C(42)–C(43)	108.3(6)
C(42)–C(43)–C(44)	109.6(5)	C(43)–C(44)–C(45)	107.3(5)
C(44)–C(45)–C(46)	131.6(6)	C(45)–C(46)–C(47)	119.0(7)
C(46)–C(47)–C(48)	121.5(8)	C(47)–C(48)–C(49)	120.9(7)

Table 5
The dihedral angles between the indenyl planes

Plane	Plane	Angle (°)	Plane	Plane	Angle (°)
Ind(2)	Ind(1)	117.6	Ind(5)	Ind(4)	116.1
Ind(3)	Ind(2)	61.5	Ind(6)	Ind(4)	56.6
Ind(3)	Ind(1)	65.7	Ind(6)	Ind(5)	65.3

Ind(1) represents the plane formed by C(11)–C(19), Ind(2) the plane formed by C(21)–C(29), Ind(3) the plane formed by C(31)–C(39), Ind(4) the plane formed by C(41)–C(49), Ind(5) the plane formed by C(51)–C(59), Ind(6) the plane formed by C(61)–C(69).

Anhydrous PrCl_3 was prepared according to the published procedure [18].

3.1. Preparation of $[(\text{C}_9\text{H}_7)_3\text{Pr}(1)\text{OC}_4\text{H}_8][(\text{C}_9\text{H}_7)_3\text{Pr}(2)\text{OC}_4\text{H}_8]$

To the suspension of anhydrous PrCl_3 (1.8635 g, 7.5 mmol) in 20 ml of THF was added dropwise 11.7 ml (15.0 mmol) sodium indenyl–THF solution: the resulting mixture was kept stirring overnight at room temperature. After usual centrifugation, a clear green–yellow solution was separated and concentrated to about one third of its original volume. The yellow crystals were obtained upon cooling the solution at -20°C for several days (yield, 30.1% (0.845 g, based on PrCl_3); melting point (decomposition), 102°C). Anal. Found: Pr, 24.89; C, 65.89; H, 5.14, Calc.: Pr, 25.23; C, 66.61; H, 5.19%.

3.2. Crystallography of $[(\text{C}_9\text{H}_7)_3\text{Pr}(1)\text{OC}_4\text{H}_8][(\text{C}_9\text{H}_7)_3\text{Pr}(2)\text{OC}_4\text{H}_8]$

A single crystal of the complex with dimensions $1.00 \times 0.50 \times 0.45$ mm was selected and sealed in a thin-walled glass capillary under argon and used in the data collection. The intensity data and unit cell parameters were collected on an Enraf–Nonius CAD4 diffractometer with Mo $\text{K}\alpha$ (graphite monochromator; $\lambda = 0.71069$ Å) radiation in the range $3^\circ < 2\theta < 50^\circ$ by 2θ – ω scanning. Lorentz, polarization and absorptions corrections with an empirical scanning technique were applied; 9422 reflections were measured; 6930 reflec-

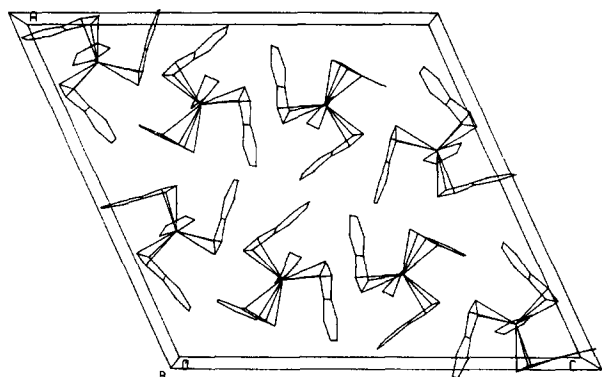


Fig. 2. The unit-cell package of $[(\eta^5\text{-C}_9\text{H}_7)_3\text{Pr}(1)\text{OC}_4\text{H}_8][(\eta^5\text{-C}_9\text{H}_7)_3\text{Pr}(2)\text{OC}_4\text{H}_8]$.

tions with $I > 3\sigma(I)$ among 9298 independent reflections were considered to be observed and used in the structure determination.

The structure was solved by the heavy-atom method; after the positional parameters of the Pr atom had been located, the coordinates of other non-hydrogen atoms were obtained by successive Fourier syntheses. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined by the full-matrix least-squares method. The coordinates of hydrogen atoms were added according to theoretical models. The final R , R_w and S were 0.038, 0.047 and 1.34 respectively ($W = 1/\sigma^2(F_0)$), and $(\Delta/\sigma)_{\max} = 0.26$. The final difference Fourier map of the complex showed no peaks higher than 0.95 electrons \AA^{-3} or lower than -0.75 electrons \AA^{-3} . All calculations were performed on a Micro VAX II computer with the TEXSAN v2.1 package.

Acknowledgments

We are grateful to Mrs. Jiping Hu and Mr. Baohui Du for their helpful assistance.

References

- [1] M. Tsutsui and H.J. Gysling, *J. Am. Chem. Soc.*, 91 (1969) 3175.
- [2] Z. Huang, R. Cai, W. Wu and W. Qiu, *J. Fudan Univ. Nat. Sci. Edn.*, 24 (1985) 476.
- [3] H. Schumann and W. Genthe, in K.A. Gschneider, Jr., and L. Eyring (eds.), *Handbook on the Physics and Chemistry of the Rare Earths*, Elsevier, Amsterdam, 1984, p. 445.
- [4] (a) A. Zazzetta and A. Greco, *Acta Crystallogr., Sect. B*, 35 (1979) 457; (b) J.L. Atwood, J.H. Burns and P.G. Laubereau, *J. Am. Chem. Soc.*, 95 (1973) 1830.
- [5] (a) M. Chen, G. Wu, W. Wu, S. Zhuang and Z. Huang, *Organometallics*, 7 (1988) 802; (b) Y. Su, Z. Jin and W. Chen, *J. Chin. Rare Earth Soc.*, 2 (1990) 106.
- [6] Z. Ye, S. Wang, D. Kong and X. Huang, *J. Organomet. Chem.*, 491 (1995) 57.
- [7] J. Xia, Z. Jin, G. Lin and W. Chen, *J. Organomet. Chem.*, 408 (1991) 173.
- [8] Z. Ye, Z. Zhou, Z. Luo, X. Wang and F. Shen, *Acta Chim. Sin.*, 44 (1986) 707.
- [9] Z. Ye, H. Ma and Y. Yu, *J. Less-Common Met.*, 126 (1986) 405.
- [10] H. Ma and Z. Ye, *J. Organomet. Chem.*, 326 (1987) 369.
- [11] Z. Ye, Y. Yu and H. Ma, *Polyhedron*, 7 (1988) 1095.
- [12] Z. Ye and Z. Wu, *Synth. React. Inorg. Met.-Org. Chem.*, 19 (1989) 157.
- [13] Z. Wu, Z. Ye and Z. Zhou, *Polyhedron*, 8 (1989) 2109.
- [14] Y. Yu, S. Wang, H. Ma and Z. Ye, *Polyhedron*, 11 (1992) 265.
- [15] R.D. Rogers, R.V. Bynum and J.L. Atwood, *J. Organomet. Chem.*, 192 (1980) 65.
- [16] S. Wang, Y. Yu, Z. Ye, C. Qian and X. Huang, *J. Organomet. Chem.*, 464 (1994) 55.
- [17] C. Qian, C. Ye, H. Lu, Y. Li, J. Zhou, Y. Ge and M. Tsutsui, *J. Organomet. Chem.*, 247 (1983) 161.
- [18] M.D. Taylor and C.P. Carter, *J. Inorg. Nucl. Chem.*, 24 (1962) 387.