Synthesis and characterization of Ti$(C_5H_5)(2,4$-$C_7H_{11})$ [POCH$_2$CH(O)C$_2$H$_4$O] and Ti$(2,4$-$C_7H_{11})_2$[POCH$_2$CH(O)C$_2$H$_4$O], chiral phosphite adducts of an open and a half open titanocene

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Abstract

The chiral phosphite derived from *S*-1,2,4-butanetriol has been found to bind both half-open and open titanocene moieties (Ti$(C_5H_5)(2,4$-$C_7H_{11})$ and Ti$(2,4$-$C_7H_{11})_2$, C_7H_{11} = dimethylpentadienyl) strongly. The expected reduction in symmetry upon coordination was evidenced through ^{1}H and ^{13}C NMR spectroscopies. Although the compounds were found to be thermally unstable, presumably as a result of the presence of a strained five-membered ring, an X-ray diffraction study of the latter complex could be achieved at low temperatures. Two nonequivalent conformations were observed in the solid state. © 1998 Elsevier Science S.A.

Keywords: Chiral phosphite; Titanocene; NMR spectroscopy

1. Introduction

The field of chiral organometallic chemistry has grown impressively since its inception, and a number of important applications have been developed [1]. As with classic organic compounds, chirality in organometallic complexes may arise by virtue of an asymmetric metal center, or additionally, through the presence of either axial or planar chirality [2,3]. In general, the presence of an asymmetrically substituted ligand, especially a delocalized π system, will give rise to planar chirality. This form of chirality has been established for some time, especially for cyclopentadienyl metal complexes, which generally have quite large barriers to racemization (as in Eq. (1)) [4].
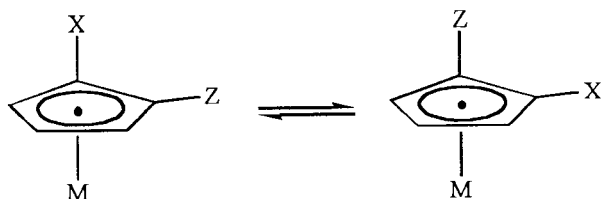

(1)

There would also seem to be a number of advantages that could be taken of planar chirality in metal pentadienyl chemistry; in fact, such has already proven to be the case for related cyclized pentadienyl ligands (cyclohexadienyl, etc.) [5–7], whose edge-bridges greatly impede the racemization process (vide infra). However, the greater flexibility for the non-bridged pentadienyl ligands should be expected to greatly facilitate racemization processes. While it might appear at first glance that the obvious method by which this could occur would involve the intermediacy of an η^1-bound ligand (e.g., 1), a much more subtle path could be available in which unusual η^3-bound pentadienyl ligands [8–10] could be involved (Eq. (2)). As Eq. (2) shows, it is possible to sequentially reverse the face of the nonbonded interior carbon atoms directed toward the metal, thereby bringing about racemization with a great deal less bond breakage than would take place through a η^1 intermediate. [1] Some early puzzling observations have suggested that this in fact could be occur-

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[1] During this process, the endo and exo substituents on the terminal carbon atoms change places; hence, this process would be greatly retarded if not prevented entirely by placement of bulky substituents or edge-bridges on the terminal carbon atoms.

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ring, [2] and a quite analogous process has actually already been established for η^4-diene species [12]. In any event, as possible applications for chiral metal pentadienyl complexes are now suggesting themselves [13], it appears important to attempt to establish the relative susceptibilities of representative classes of chiral metal pentadienyl compounds to racemization. For the purposes of their initial enantiomeric resolutions, a few approaches seem particularly viable, such as use of a chiral counterion with a charged metal complex, or via coordination of chiral donor ligands to electron deficient pentadienyl complexes. Herein we take a first step toward this latter approach through the preparation of a 16-electron complex formed from an open titanocene, $Ti(2,4-C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl), and a sterically nondemanding chiral phosphite derived from *S*-1,2,4-butanetriol [14–16]. It will be seen that the chiral phosphite not only brings about some of the effects that would be expected, but it provides for some surprises as well.

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(2)
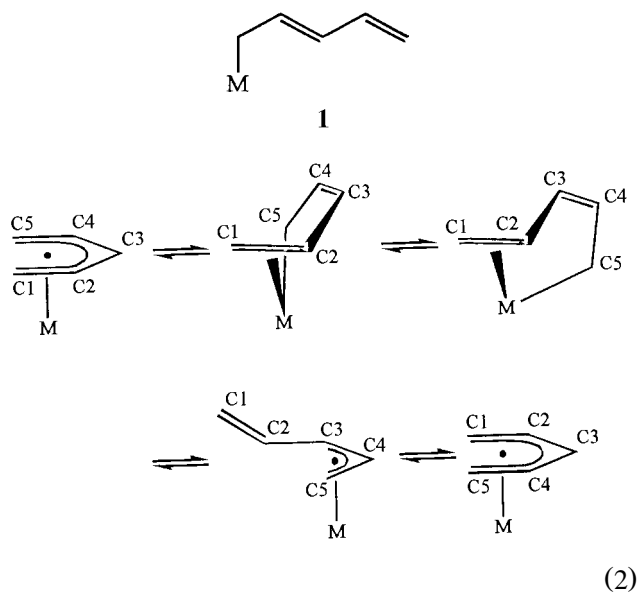
2. Experimental

All operations were conducted under a nitrogen atmosphere, either in Schlenk apparatus or in a glovebox. Hydrocarbon, ethereal, and aromatic solvents were dried and deoxygenated by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. Spectroscopic data were obtained as previously described [17]. The ^{13}C NMR spectra were not integrated, but numbers

of carbon atoms present are provided in accord with the assignments. $Ti(2,4-C_7H_{11})_2(PMe_2Ph)$ [18], $Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)$ [19] (C_7H_{11} = dimethylpentadienyl), and S-$PO_3C_4H_7$ [14–16] were prepared as previously described. For the chiral phosphite, proton decoupled ^{13}C NMR data in C_6D_6 (δ 71.8, d, CH, J = 4 Hz; 68.3, d, J = 6 Hz; 59.1, s; 32.4, d, J = 5 Hz) were found to be similar to those previously reported [14–16].

2.1. Preparation of Ti(C₅H₅)(2,4-C₇H₁₁)[S-PO₃C₄H₇]

A 250 ml three-neck flask, equipped with magnetic stirring bar and nitrogen inlet, was charged with 0.18 g (0.55 mmol) of $Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)$ and 20 ml ether. To this was added slowly 0.11 ml (0.82 mmol) of 2,7,8-trioxa-1-phospha-[3.2.1]octane at room temperature. The reaction mixture immediately turned green. Stirring was continued for 1 h, after which time the solvent was removed in vacuo. The green residue was extracted with pentane and filtered through a pad of Celite on a frit. The resulting green solution was concentrated in vacuo. The green polycrystalline product was obtained in 45% yield (87 mg) upon cooling the solution to $-90°C$ for several days.

^{1}H NMR (toluene-d_8, ambient): δ 6.18 (s, 1H, H3), 5.30 (d, J = 3 Hz, 5H, Cp), 3.98 (d of m, J = 13 Hz, 1H, phos), 3.89 (t of m, J = 12 Hz, 1H, phos), 3.43–3.67 (multiplets, 3H, phos), 2.17 (m, 1H, H1, 5_{exo}), 2.11 (m, 1H, H1, $5'_{exo}$), 2.06 (m, 1H, phos), 1.64 (d, J = 3 Hz, 6H, 2,4-CH$_3$), 0.59 (d of m, J = 14 Hz, 1H, phos), -0.14 (t of m, J = 8 Hz, 1H, H1, 5_{endo}), -0.22 (t of m, J = 8 Hz, 1H, H1, $5'_{endo}$).

^{13}C {^{1}H} NMR (toluene-d_8, ambient): δ 111.7 (s, C-3), 102.8 and 102.7 (2C, 2s, C-2,4), 100.9 (5C, s), 73.3 (1C, d, J = 6 Hz, phos), 69.2 (1C, d, J = 9 Hz, phos), 61.1 (1C, d, J = 6 Hz, phos), 53.9 (1C, app. d, J = 13 Hz, C-1 or C-5), 53.5 (1C, app. d, J = 12 Hz, C-5 or C-1), 31.4 (1C, s, phos), 30.4 (2C, s, CH$_3$).

^{31}P NMR (toluene-d_8, ambient): δ 96.6.

2.2. Preparation of Ti(2,4-C₇H₁₁)₂[S-PO₃C₄H₇]

A 250 ml three-neck flask, equipped with magnetic stirring bar and nitrogen inlet, was charged with 0.080 g (0.28 mmol) $Ti(2,4-C_7H_{11})_2(PMe_2Ph)$ and 20 ml Et_2O. To this was added 0.060 ml (0.44 mmol) of the chiral phosphite at room temperature. The solution turned yellow immediately. The mixture was stirred for 30 min after which time the solvent was removed in vacuo. The residue was extracted with several portions of Et_2O and filtered through a pad of Celite on a coarse frit. Orange crystals (*m.p.* 77°, dec) were obtained upon cooling the solution to $-30°C$.

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[2] This involved the slow apparent conversion of one open fulvalene complex of cobalt to another [11].

^{1}H NMR (C$_6$D$_6$, ambient): δ 4.70 (s, 1H, H-3), 3.67–3.85 (2 m, 2H, phos), 3.50 (dd, 1H, phos, $J = 4$, 9 Hz), 3.24–3.34 (2 m, 2H, phos), 2.87 (br, 1H, H-2), 2.84 (br, 1H, H-4), 1.98 (t of m, 1H, phos), 1.66 (coinc. s, 6H), 1.20 (d of d, 1H, H-1 or H-5, $J = 5$, 12 Hz), 1.14 (d of d, 1H, H-5 or H-1, $J = 5$, 12 Hz), 0.40 (d of m, 1H, phos, $J = 14$ Hz).

^{31}P NMR (toluene-d$_8$, ambient): δ 122.5.

2.3. X-ray diffraction study

Single crystals of Ti(2,4-C$_7$H$_{11}$)$_2$(S-PO$_3$C$_4$H$_7$) were obtained as described above. One well formed crystal was placed on a glass fiber with oil, and immediately placed in a cold nitrogen stream on a diffractometer, causing it to be held fixed. The molecule was found to adopt the polar space group $P2_1$, and the structure was solved by direct methods, which revealed two independent molecules in the unit cell. Tests for the enan-

Table 1
Crystallographic data

(a) Crystal parameters

Formula	C$_{18}$H$_{29}$O$_3$PTi
Formula weight	372.30
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	10.476(4)
b (Å)	11.396(5)
c (Å)	15.556(5)
β	98.78(3)
V (Å^3)	1835.3
Z	4
Crystal dimensions (mm^3)	$0.31 \times 0.28 \times 0.07$
D (calc) (g cm^{-3})	1.347
μ (MoK$_\alpha$) (cm^{-1})	5.57
Temperature (K)	173
T(max)$/T$(min)	1.093

(b) Data collection

Diffractometer	Enraf-Nonius CAD-4
Monochromator	Graphite
Radiation	MoK$_\alpha$($\lambda = 0.71073$ Å)
2θ scan range (deg)	2.0–50.0
Data collected (h, k, ℓ)	$(0, 0, -18)$–$(12, 13, 18)$
Independent reflections	3408
Independent observed reflections	2524 ($n = 3$)
$F_o \geq n\sigma(F_o)$	

(c) Refinement

$R(F)$ (%)	3.87
$R(wF)$ (%)	4.45
Δ/σ (max)	0.004
Max. diff. Fourier peak (e Å^{-3})	0.364
N_o / N_v	6.1
GOF	1.31

Table 2
Positional parameters for Ti(2,4-C$_7$H$_{11}$)$_2$[POCH$_2$CH(O)C$_2$H$_4$O]

	x	y	z	B (Å^2)
Ti	0.54306(8)	0.471	1.26651(6)	1.33(2)
P	0.4748(1)	0.4712(2)	1.11112(8)	1.58(3)
O(1)	0.3454(4)	0.5438(4)	1.0687(2)	2.14(9)
O(2)	0.5659(4)	0.5341(4)	1.0482(2)	2.11(9)
O(3)	0.4486(4)	0.3457(4)	1.0623(3)	2.07(9)
C(1)	0.3172(5)	0.4868(7)	1.2581(4)	2.2(1)
C(2)	0.3759(5)	0.5041(6)	1.3461(4)	2.0(1)
C(3)	0.4776(6)	0.5822(6)	1.3747(4)	1.8(1)
C(4)	0.5479(6)	0.6568(5)	1.3257(4)	1.6(1)
C(5)	0.5212(6)	0.6671(6)	1.2338(4)	2.1(1)
C(6)	0.3253(6)	0.4277(7)	1.4126(4)	2.6(1)
C(7)	0.6585(7)	0.7224(6)	1.3759(5)	3.0(2)
C(8)	0.5387(6)	0.2644(6)	1.2476(4)	2.4(1)
C(9)	0.5997(6)	0.2890(6)	1.3338(4)	2.0(1)
C(10)	0.7034(6)	0.3690(6)	1.3566(4)	1.8(1)
C(11)	0.7671(5)	0.4407(6)	1.3026(4)	1.9(1)
C(12)	0.7358(5)	0.4450(6)	1.2108(4)	2.5(1)
C(13)	0.5457(7)	0.2313(6)	1.4081(4)	2.7(1)
C(14)	0.8707(6)	0.5226(6)	1.3454(5)	3.0(2)
C(15)	0.3612(6)	0.5998(7)	0.9870(4)	2.8(1)
C(16)	0.4847(6)	0.5492(7)	0.9627(4)	2.6(1)
C(17)	0.4726(6)	0.4314(6)	0.9197(4)	2.7(1)
C(18)	0.3980(6)	0.3458(7)	0.9709(4)	2.5(1)
Ti′	0.07454(8)	−0.0144(1)	1.26444(6)	1.36(2)
P′	0.0645(1)	−0.0206(2)	1.10923(8)	1.65(3)
O(1)′	0.1636(4)	−0.1074(4)	1.0680(3)	2.18(9)
O(2)′	−0.0642(4)	−0.0695(4)	1.0457(3)	2.21(9)
O(3)′	0.0877(4)	0.1016(4)	1.0596(3)	2.00(9)
C(1)′	0.0689(6)	0.1901(6)	1.2449(4)	2.3(1)
C(2)′	0.1061(6)	0.1657(6)	1.3339(4)	1.8(1)
C(3)′	0.2075(6)	0.0887(6)	1.3690(4)	1.9(1)
C(4)′	0.2875(5)	0.0181(5)	1.3250(5)	1.9(1)
C(5)′	0.2860(5)	0.0146(6)	1.2351(4)	2.2(1)
C(6)′	0.0332(6)	0.2246(6)	1.4010(5)	2.8(1)
C(7)′	0.3779(6)	−0.0642(6)	1.3811(5)	2.9(2)
C(8)′	−0.1493(5)	−0.0315(7)	1.2262(4)	2.3(1)
C(9)′	−0.1215(5)	−0.0454(6)	1.3178(4)	2.0(1)
C(10)′	−0.0264(6)	−0.1263(6)	1.3593(4)	1.9(1)
C(11)′	0.0565(6)	−0.1999(6)	1.3227(4)	2.1(1)
C(12)′	0.0605(7)	−0.2142(6)	1.2313(4)	2.5(1)
C(13)′	−0.1899(6)	0.0300(7)	1.3758(4)	2.7(1)
C(14)′	0.1567(7)	−0.2677(6)	1.3861(4)	2.8(2)
C(15)′	0.1013(6)	−0.1578(7)	0.9869(4)	2.8(2)
C(16)′	−0.0261(7)	−0.0931(7)	0.9604(4)	2.9(2)
C(17)′	−0.0106(6)	0.0252(7)	0.9181(4)	2.9(2)
C(18)′	0.0999(6)	0.0955(7)	0.9677(4)	2.6(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)^*[a2^*B(1,1) + b2^*B(2,2) + c2^*B(3,3) + ab(\cos \ \ gamma)^*B(1,2) + ac(\cos \ beta)^*B(1,3) + bc(\cos \ alpha)^*B(2,3)]$.

tiomorph confirmed the presence of the expected S form of the chiral phosphite. Nonhydrogen atoms were refined anisotropically, while hydrogen atoms were placed in fixed locations revealed from difference Fourier maps. Pertinent data collection and refinement parameters are given in Table 1, while positional and bonding parameters are contained in Tables 2 and 3, respectively.

Table 3
Bond distances and bond angles for Ti(2,4-C$_7$H$_{11}$)$_2$ [POCH$_2$CH(O)C$_2$H$_4$O]

Bond distances (Å)

Ti–P	2.414(2)
Ti–C(1)	2.357(6)
Ti–C(2)	2.326(6)
Ti–C(3)	2.296(7)
Ti–C(4)	2.310(8)
Ti–C(5)	2.299(8)
Ti–C(8)	2.368(9)
Ti–C(9)	2.355(8)
Ti–C(10)	2.326(7)
Ti–C(11)	2.354(6)
Ti–C(12)	2.334(6)
P–O(1)	1.638(5)
P–O(2)	1.633(5)
P–O(3)	1.623(5)
O(1)–C(15)	1.454(9)
O(2)–C(16)	1.475(7)
O(3)–C(18)	1.439(8)
C(1)–C(2)	1.427(9)
C(2)–C(3)	1.408(10)
C(2)–C(6)	1.509(10)
C(3)–C(4)	1.420(10)
C(4)–C(5)	1.420(11)
C(4)–C(7)	1.494(10)
C(8)–C(9)	1.422(12)
C(9)–C(10)	1.421(10)
C(9)–C(13)	1.511(11)
Ti′ –P′	2.402(2)
Ti′ –C(1)′	2.350(9)
Ti′ –C(2)′	2.319(8)
Ti′ –C(3)′	2.298(7)
Ti′ –C(4)′	2.315(6)
Ti′ –C(5)′	2.353(6)
Ti′ –C(8)′	2.337(6)
Ti′ –C(9)′	2.356(6)
Ti′ –C(10)′	2.323(7)
Ti′ –C(11)′	2.318(8)
Ti′ –C(12)′	2.334(9)
P′ –O(1)′	1.635(5)
P′ –O(2)′	1.642(4)
P′ –O(3)′	1.628(5)
O(1)′ –C(15)′	1.447(9)
O(2)′ –C(16)′	1.468(8)
O(3)′ –C(18)′	1.457(8)
C(1)′ –C(2)′	1.407(11)
C(2)′ –C(3)′	1.421(10)
C(2)′ –C(6)′	1.539(10)
C(3)′ –C(4)′	1.412(9)
C(4)′ –C(5)′	1.396(9)
C(4)′ –C(7)′	1.512(10)
C(8)′ –C(9)′	1.418(9)
C(9)′ –C(10)′	1.436(10)
C(9)′ –C(13)′	1.504(10)
C(10)–C(11)	1.410(9)
C(11)–C(12)	1.418(9)
C(11)–C(14)	1.506(10)
C(15)–C(16)	1.516(11)
C(16)–C(17)	1.497(11)
C(17)–C(18)	1.545(11)
C(10)′ –C(11)′	1.390(11)
C(11)′ –C(12)′	1.439(12)
C(11)′ –C(14)′	1.534(10)
C(15)′ –C(16)′	1.526(11)

Table 3 (continued)

Bond distances (Å)

C(16)′ –C(17)′	1.520(11)
C(17)′ –C(18)′	1.518(11)

Bond angles (deg)

Ti–P–O(1)	120.3(2)
Ti–P–O(2)	119.4(2)
Ti–P–O(3)	118.0(2)
O(1)–P–O(2)	93.5(3)
O(1)–P–O(3)	100.7(2)
O(2)–P–O(3)	100.3(2)
P–O(1)–C(15)	112.1(4)
P–O(2)–C(16)	106.4(4)
P–O(3)–C(18)	118.2(5)
C(1)–C(2)–C(3)	125.8(7)
C(1)–C(2)–C(6)	115.7(6)
C(3)–C(2)–C(6)	118.5(6)
C(2)–C(3)–C(4)	129.7(6)
C(3)–C(4)–C(5)	123.4(7)
C(3)–C(4)–C(7)	116.3(7)
C(5)–C(4)–C(7)	120.2(7)
C(8)–C(9)–C(10)	125.3(7)
C(8)–C(9)–C(13)	117.9(7)
Ti′ –P′ –O(1)′	118.7(2)
Ti′ –P′ –O(2)′	121.4(2)
Ti′ –P′ –O(3)′	117.7(2)
O(1)′ –P′ –O(2)′	94.1(3)
O(1)′ –P′ –O(3)′	100.4(3)
O(2)′ –P′ –O(3)′	100.0(2)
P′ –O(1)′ –C(15)′	110.7(4)
P′ –O(2)′ –C(16)′	107.1(4)
P′ –O(3)′ –C(18)′	117.8(5)
C(1)′ –C(2)′ –C(3)′	125.4(7)
C(1)′ –C(2)′ –C(6)′	119.3(7)
C(3)′ –C(2)′ –C(6)′	115.3(6)
C(2)′ –C(3)′ –C(4)′	129.0(6)
C(3)′ –C(4)′ –C(5)′	125.8(6)
C(3)′ –C(4)′ –C(7)′	116.1(6)
C(5)′ –C(4)′ –C(7)′	118.0(6)
C(8)′ –C(9)′ –C(10)′	123.0(6)
C(8)′ –C(9)′ –C(13)′	119.7(7)
C(10)–C(9)–C(13)	116.7(6)
C(9)–C(10)–C(11)	129.6(7)
C(10)–C(11)–C(12)	124.2(6)
C(10)–C(11)–C(14)	118.1(6)
C(12)–C(11)–C(14)	117.6(6)
O(1)–C(15)–C(16)	105.5(6)
O(2)–C(16)–C(15)	102.5(6)
O(2)–C(16)–C(17)	107.2(6)
C(15)–C(16)–C(17)	115.8(7)
C(16)–C(17)–C(18)	110.6(6)
O(3)–C(18)–C(17)	111.7(6)
C(10)′ –C(9)′ –C(13)′	117.2(6)
C(9)′ –C(10)′ –C(11)′	129.6(7)
C(10)′ –C(11)′ –C(12)′	126.0(7)
C(10)′ –C(11)′ –C(14)′	116.7(7)
C(12)′ –C(11)′ –C(14)′	117.2(7)
O(1)′ –C(15)′ –C(16)′	107.6(6)
O(2)′ –C(16)′ –C(15)′	101.1(6)
O(2)′ –C(16)′ –C(17)′	106.9(7)
C(15)′ –C(16)′ –C(17)′	113.5(7)
C(16)′ –C(17)′ –C(18)′	111.8(6)
O(3)′ –C(18)′ –C(17)′	110.5(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

3. Results and discussion

The chiral phosphite S-$PO_3C_4H_7$ (2) derived from S-1,2,4-butanetriol reacts readily with phosphine adducts of open and half-open titanocenes to yield the corresponding diamagnetic 16 electron monophosphite complexes (Eqs. (3) and (4)). As would be expected based upon the small cone angles of such

$$Ti(2,4-C_7H_{11})_2(PMe_2Ph) + PO_3C_4H_7$$

$$\rightarrow Ti(2,4-C_7H_{11})_2(PO_3C_4H_7) \qquad (3)$$

$$Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3) + PO_3C_4H_7$$

$$\rightarrow Ti(C_5H_5)(2,4-C_7H_{11})(PO_3C_4H_7) \qquad (4)$$
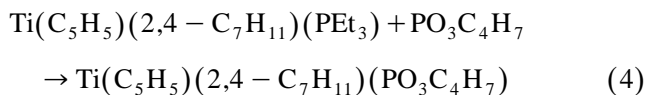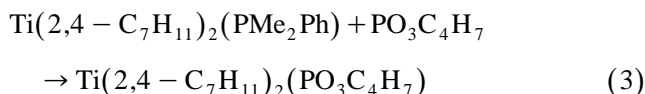
ligands [18,20], the chiral cage phosphites appear to be strongly bound, and the adducts are most likely formed in essentially quantitative yields, although isolated yields (not optimized) tended to be closer to 50%. Unfortunately, however, complexes 3 and 4 ($L = S$-$PO_3C_4H_7$) are not thermally stable, and undergo decomposition at room temperature, presumably via a metal-initiated opening of the ligand's five-membered ring. As a result, characterization of these species has relied heavily on spectroscopic methods.

2

3   **4**
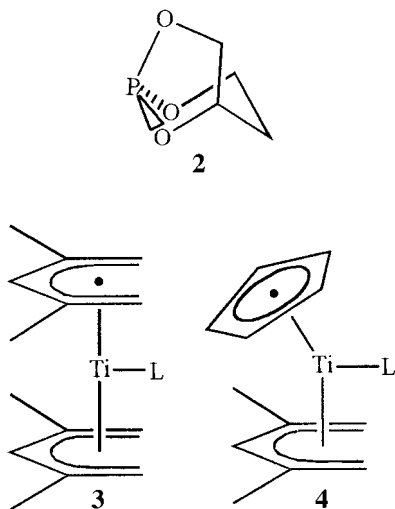
The NMR spectroscopic data for 3 and 4 are consistent with their expected structures, and with data for related achiral phosphite adducts [18,20]. The presence of the chiral phosphite brings about the expected reduction in effective symmetry of their attached $Ti(2,4$-$C_7H_{11})_2$ and $Ti(C_5H_5)(2,4$-$C_7H_{11})$ fragments from C_{2v} and C_s to C_2 and C_1, respectively, the retention of the C_2 axis in 3 being due to facile Ti–P bond rotation. As a result, the two C_7H_{11} ligands in 3 remain equivalent, although the ends of a given ligand are no longer

equivalent, as is also true for 4. Hence, seven line patterns are exhibited by the 2,4-C_7H_{11} ligands (5) in both the ^{1}H and ^{13}C NMR spectra. In this regard the spectra of these adducts differ from those of achiral phosphite ligands, although chemical shift and coupling constant parameters for the C_7H_{11} ligands are quite similar. The observed NMR shifts for the bound chiral phosphite ligands are reasonably similar to those of the free ligand; however, some variation in coupling constants is observed, which may be attributed to a conformational change upon coordination.

5
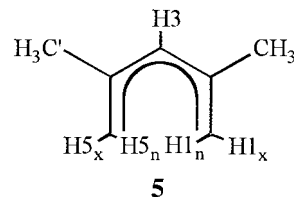
Structural confirmation of the above formulation could be obtained for 3, which was found to yield well formed single crystals fairly readily. As expected, a polar space group ($P2_1$) was adopted, and standard methods confirmed the presence of the appropriate phosphite enantiomer. However, the asymmetric unit was comprised of two independent molecules, which unexpectedly differed in the relative orientations of their phosphite ligands. As can be seen, the structures correspond to forms 6 (Fig. 1) and 7 (Fig. 2). Notably, both forms have been observed in $M(2,4$-$C_7H_{11})_2(L)$ complexes, that of 6 being observed for complexes of PX_3 ligands with substituent chains, such as $X = Et$, OMe, or OEt, while that of 7 is adopted by adducts of PF_3 or PMe_3 [20,21]. Interestingly, $Ti(2,4$-$C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$ has been found to adopt a form twisted ca. 7° from the extreme of 7 toward that of 6, a 30° twist being required for the change between 6 and 7 [20]. It seems that the tied back nature of that cage phosphite led to steric characteristics more in line with those of $X = Me$ or F rather than OMe, Et, or OEt, consistent with recent cone angle considerations [20]. However, for the adduct of 2, there appears to be an increased steric component, presumably as a result of the sideways bend of the P–O1–C15 chains. In fact, it is this chain that occupies the unique, sterically more open position in the idealized forms 6 (top) or 7 (side). As an apparent result of the intermediate steric requirements of 2, its adduct forms 6 and 7 seem to become energetically comparable. In any case, from the appropriate C(3,10)–Ti–P–O(1) and C(3′,10′)–Ti′–P′–O(1)′ torsion angles, the respective structures of 6 and 7 in Figs. 1 and 2 may be described as having P–O rotations from their idealized conformations such that O1 becomes twisted 9.4° from C5 toward C1, while O1′
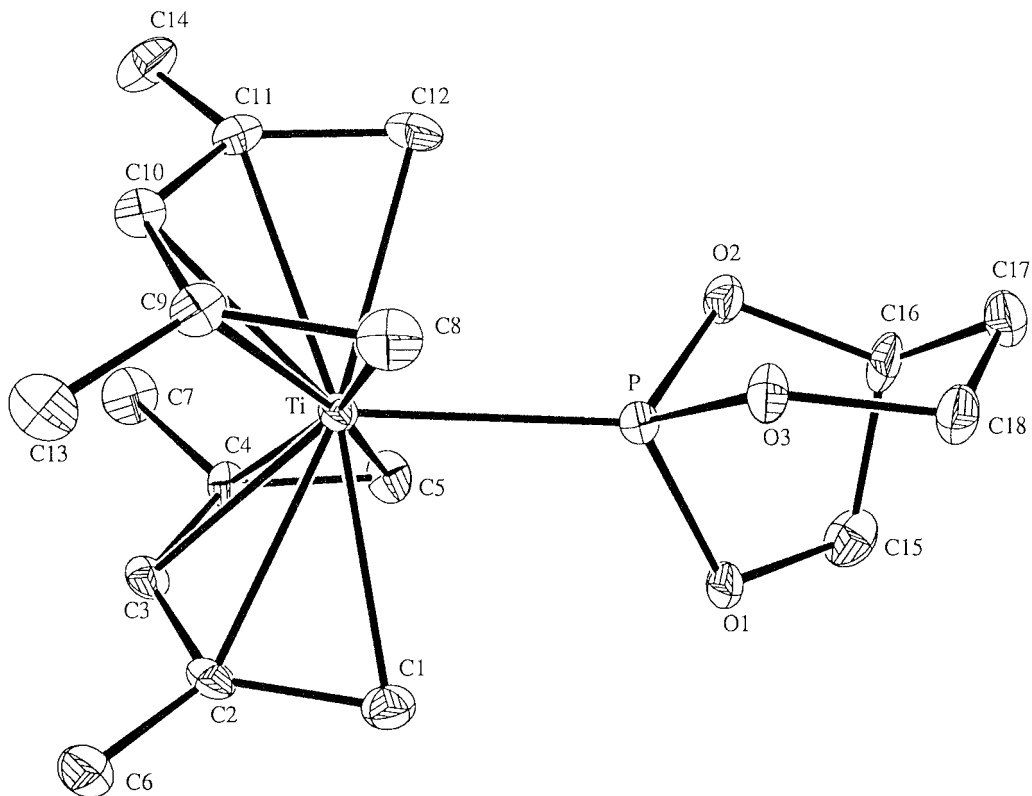
Fig. 1. Perspective view of one form of the chiral phosphite adduct of $Ti(2,4-C_7H_{11})_2$.

becomes twisted 2.4° from C12′ toward C5′. However, those values are highly idealized due to other distortions within the molecule. Thus, both conformers would be affected by the small O1–P–O2 (vs. O1–P–O3) angles.

However, even more important for the second conformation is a twist of the Ti–P vector relative to the open pentadienyl edges. Thus, the P′–Ti′–(C2′,C9′) angles of 118.4(2)° and 116.3(2)° are significantly greater than the
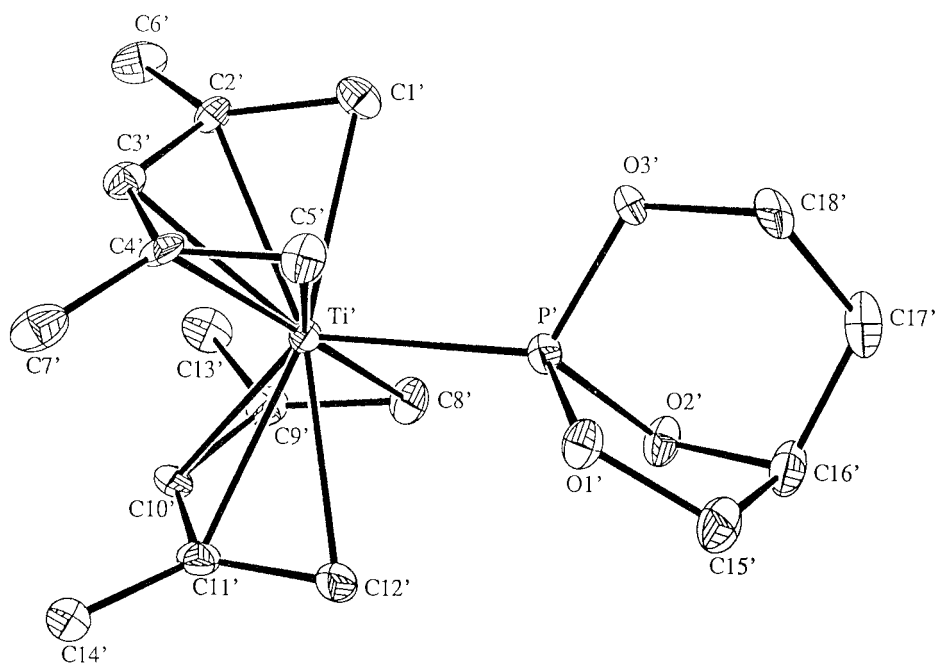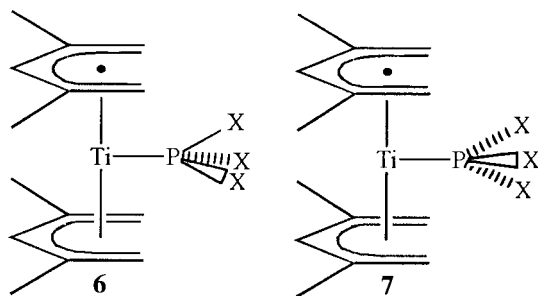

Fig. 2. Perspective view of the second independent molecule.

P'–Ti'–(C4',C11') angles of 107.8(2)° and 111.9(2)°, respectively, reflecting a twist of P' away from the C(1',8') side, toward the C(5',12') side.

6   **7**

The average Ti–C bond distances for the two conformations of 3 are similar, at 2.332(8) and 2.330(6) Å, respectively. However, as in other complexes of type 6, for which two ligand arms are oriented toward the ends of a single dienyl ligand, one ligand seems situated further from the metal in the first isomer, the average Ti–C distances being 2.318(3) and 2.347(3) Å for the C(1–5) and C(8–12) ligands, respectively. Similar to other Ti(2,4-C$_7$H$_{11}$)$_2$(PX$_3$) complexes [21], the Ti–C[3] bonds appear shorter than the Ti–C[1,5] or Ti–C[2,4] bonds.

Although it is possible that the Ti'–P' bond could be shorter than the Ti–P bond, the difference is probably of little significance. These values do appear significantly shorter than those of the P(OCH$_3$)$_3$CC$_2$H$_5$ and P(OC$_2$H$_5$)$_3$ adducts, 2.437(2) and 2.472(4) Å, respectively [21]. The difference between these achiral ligand values could be ascribed to differences in bond energies, cone angles, and/or their relative donor/acceptor properties. However, the shortening in 2 and 3 relative to the P(OCH$_2$)$_3$CC$_2$H$_5$ adduct is harder to explain, given their similar steric and electronic properties [22–26]. Furthermore, the isolation of the symmetric phosphite complex is much easier, as crystallization occurs readily at higher temperatures, which might suggest more effective binding. However, it seems more likely that the achiral, more symmetric nature of the P(OCH$_2$)$_3$CC$_2$H$_5$ ligand simply leads to more effective solid state packing, and hence much lower solubility for both it (*m.p.* 54–56°) and its complexes. An interesting property displayed by many of the phosphite adducts of the open titanocenes is their thermochromicity, which may be the result of the thermal population of excited vibrational states within the electronic ground state [27]. Notably, the structure of the chiral phosphite adduct had to be determined from low temperature data, which would be less influenced by vibrational effects. It seems unlikely, however, that this could be responsible for the differences observed in Ti–P bond lengths.

The parameters involving the 2,4-C$_7$H$_{11}$ ligands are

similar to those of other Ti(2,4-C$_7$H$_{11}$)$_2$(PX$_3$) complexes [21]. The two dienyl planes are nearly parallel, with an average angle of 1.5° between them. As a result of the methyl substituents on the C[2 or 4] positions, the C[2]–C[3]–C[4] angles are larger than those around C[2,4], 129.4(4) vs. 125.1(3)°. The methyl groups tilt by 1.8–4.8° (average, 3.5°) out of their dienyl planes, toward the metal center. This tilt can be attributed to an attempt to improve metal–ligand overlap, and generally appears greater for the better accepting PX$_3$ ligands.

Some relevant observations can be made for the phosphite ligands. The P–O bond distances are all similar, averaging 1.633(3) Å, although the ones not involved in the five-membered rings are slightly shorter. However, the P–O distances in the Ti(2,4-C$_7$H$_{11}$)$_2$[P(OCH$_2$)$_3$CC$_2$H$_5$] compound appear to be shorter, at 1.614(5) Å. While this could impact on the discussion concerning the relative bindings of these cage phosphites (vide supra), it can be argued that their coordination could lead either to P–O bond lengthening or shortening [28,29]. Finally, while the O(1,2)–P–O(3) angles are similar to those in the P(OCH$_2$)$_3$CC$_2$H$_5$ adduct (99.5(3)°) [20], the O1–P–O2 angles are much smaller, averaging 93.8(2)°, which is the apparent cause for the low thermal stabilities of the chiral ligand adducts. Other parameters for the chiral phosphite ligand are reasonably similar to those observed in some related complexes [30–32].

Although the low thermal stability of the adducts of the chiral phosphite reported herein seems to preclude its convenient use in resolving unsymmetric (and enantiomeric) half-open titanocenes, it seems possible that related vanadium and chromium complexes [33,34] (or even complexes of late transition metals) will be more robust. Further studies of such chiral species are continuing.

4. Supplementary materials available

Anisotropic thermal parameters and structure factor tables may be obtained from the authors.

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