

A sterically hindered bis- η -alkylcyclopentadienylzirconium compound as catalyst for the polymerisation of ethene and propene

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Abstract

The compound bis[η -(1,3,3,5,5-pentamethylcyclohexyl)-cyclopentadienyl] zirconium dichloride has been prepared and the crystal structure determined. The compound together with the cocatalyst methylaluminoxane will catalyse the polymerisation of ethene and propene.

Keywords: Zirconium; Metallocene; X-ray structure; Ziegler–Natta catalyst; Polymerisation

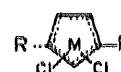
1. Introduction

Since the discovery in 1979 that Group 4 *ansa*-bridged metallocenes/alumoxane systems can be active catalysts in the stereospecific polymerisation of α -olefins [1], a great deal of attention has been focused on metallocene derivatives in order to find improved isospecific polymers [2–5]. The stereoselectivity of these catalysts is believed to arise mainly from steric interactions between the incoming olefin monomer and components of the cyclopentadienyl ligands [6].

The synthesis of many chiral metallocenes leads to mixtures of *meso* and *racemic* isomers. Only the isomers belonging to the *racemic* mixture give isospecific polymerisation of propene, while the *meso* stereoisomer produces only stereoirregular polypropylene [7]. The separation of the stereoisomers of metallocenes is normally difficult, and one approach to simplify the synthetic procedure may be to introduce very bulky, and possibly chirally differentiated, substituents on the cyclopentadienyls or indenyl groups [4,5]. Here we describe the synthesis of a zirconium metallocene with very bulky substituents on the η -cyclopentadienyl rings.

It was expected that the introduction of the bulky

substituents would lead to restricted rotation of the η -cyclopentadienyl rings and give rise to a staggered conformation [8], in which the substituents were *trans* to each other in the lateral sectors of the bent metallocene units.



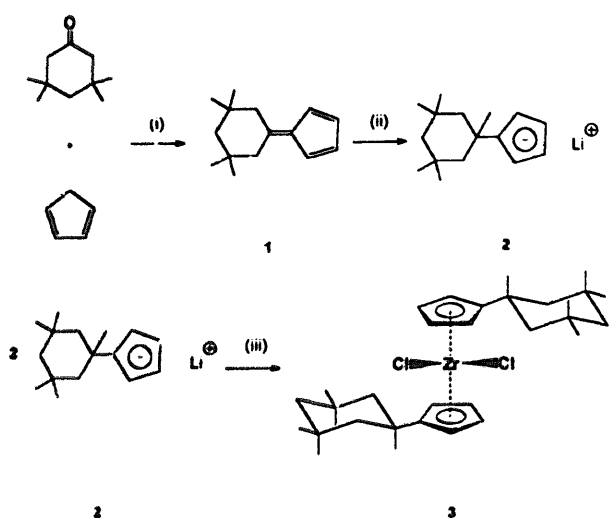
This spatial array allows the unilateral coverage of each coordination site (considered essential for the stereoselectivity) and the conformationally constrained cyclopentadienyl and indenyl ligands give these complexes chiral structures which could be expected to be retained even under catalysis conditions [9].

2. Results and discussion

2.1. Synthesis of the complex

The fulvene 6,6-(3,3,5,5-tetramethylpenta-methylene)fulvene (1) was synthesised in good yield

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Scheme 1. (i) Pyrrolidine in CH_3OH at 0°C for 18 h, then acetic acid, Et_2O and water; (ii) CH_3Li in Et_2O at 0°C ; (iii) ZrCl_4 in THF at -78°C .

from cyclopentadiene and commercially available 3,3,5,5-tetramethyl cyclohexanone under conditions similar to those employed by Stone and Little [10]. The compound lithium (1,3,3,5,5-pentamethylcyclohexyl)-cyclopentadienyliide (**2**) was prepared in near quantitative yield from the corresponding 6,6'-pentafulvene system **1** by treatment with methyl lithium at 0°C . Treatment of zirconium tetrachloride with the lithium salt **2** in 2:1 molar ratio in THF gave white crystals of the desired metallocene, bis[η -(1,3,3,5,5-pentamethylcyclohexyl)-cyclopentadienyl] zirconium dichloride (**3**), in 68% yield (Scheme 1).

2.2. Single crystal X-ray analyses

The crystal structure of **3** has been determined and an ORTEP view with atom-numbering scheme is shown in Fig. 1. The compound crystallises in the space group $C2/c$. The crystal structure is formed by well-separated molecules in which the coordination geometry around the zirconium is the usual distorted tetrahedron.

The bulky 1,3,3,5,5-pentamethyl(cyclohexyl) substituents adopt a *trans* arrangement in the lateral sectors of the bent metallocene units and the methyl group is practically coplanar with the cyclopentadienyl ring in the direction of the 'open' side of the metallocene, with a torsion angle $\text{C}(5)\text{--C}(1)\text{--}(6)\text{--C}(12)$ of $170.6(4)^\circ$. Of particular interest is the chiral geometry of the complex whereby the η -cyclopentadienyl substituted ligands assume a staggered conformation. The bite angle ($\text{Cp}\text{--Zr}\text{--Cp}$) of the bent metallocene is $129.9(1)^\circ$, which is typical of non-bridged Group 4 metallocenes, while the angle $\text{Cl}\text{--Zr}\text{--Cl}$ is $92.9(1)^\circ$. This is about 6° smaller than found in other $[\text{Zr}(\eta\text{-RCp})_2\text{Cl}_2]$ compounds bearing bulky *tert*-alkyl substituents R on the cyclopentadi-

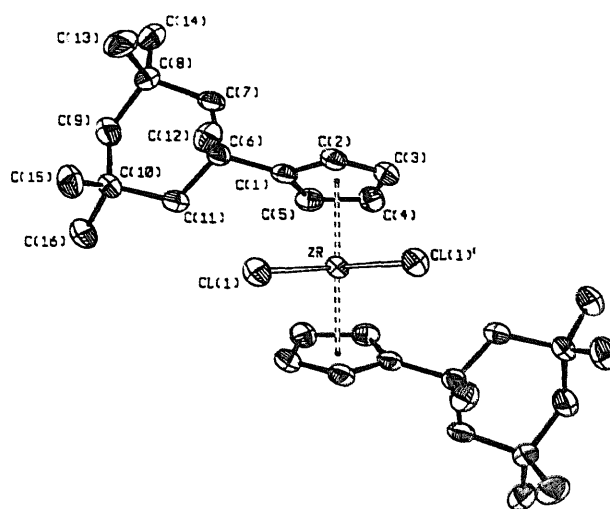


Fig. 1. ORTEP drawing of complex **3** with atom numbering scheme. Thermal ellipsoids are shown at the 40% probability level.

enyl rings [5]. The $\text{Zr}\text{--Cl}$ bond distance is $2.450(1)^\circ$ and the $\text{Zr}\text{--Cp}$ (gravity site) $2.227(4)^\circ$.

2.3. NMR spectra

In order to elucidate whether the structure in the solid state is representative of the conformational features of the complex in solution, we carried out a detailed NMR analysis. Complete spectral assignments were made through multi-dimensional NMR (in particular ^{13}C , ^1H -HMQC) techniques, and the data are summarised in Tables 1 and 2.

At room temperature the ^1H and ^{13}C NMR spectra exhibit only two sets of multiplets corresponding to an $\text{AA}'\text{BB}'$ system for the two pairs of hydrogens on each of the $\text{C}_5\text{H}_4\text{R}$ rings ($\text{R} = 1,3,3,5,5\text{-pentamethylcyclohexyl}$). Since a *meso* structure for compound **3** in which the cyclohexyl groups are eclipsed is very unlikely on steric grounds, the occurrence of an $\text{AA}'\text{BB}'$ system must arise from the interconversion of the R and

Table 1
 ^1H NMR data of complex **3** in CDCl_3 solution

^1H resonances (ppm)	Multiplicity (J, Hz)	Number of equivalent nuclei	Assignment
6.43	tt	4H	Cp (proximal)
6.30	m	4H	Cp (distal)
1.62	pseudo-q; AB system (13.94)	8H	CH_2 on C(7) and C(11)
1.50	s	6H	CH_3 on C(6)
1.30	pseudo-q; AB system (13.94)	4H	CH_2 on C(9)
1.11	s	12H	CH_3 equatorial
0.88	s	12H	CH_3 axial

Table 2
 ^{13}C NMR data of complex 3 in CD_2Cl_2 solution

^{13}C NMR resonance (ppm)	$J_{\text{C-H}}$ (Hz)	Assignment
148.41		C(1) <i>ipso</i>
115.97	171.74	C(2), C(5) <i>proximal</i>
113.44	173.20	C(3), C(4) <i>distal</i>
51.10	124.38 (equatorial protons) 126.68 (axial protons)	C(9)
50.54	124.81 (equatorial protons) 126.48 (axial protons)	C(7), C(11)
38.65		C(6)
36.32	126.00 (axial methyl)	C(13), C(15)
32.18		C(8), C(10)
31.47	126.00 (equatorial methyl)	C(14), C(16)
30.41	125.00	C(12)

S enantiomers of the molecule by a suitably rapid rotation of the cyclopentadienyl ligands about the zirconium– C_5 ring axis. On cooling solutions of 3 in CD_2Cl_2 from +20 to -80°C , the NMR spectra showed a broadening of the peaks, which is not surprising in view of the presence of the very bulky cyclopentadienyl substituents.

2.4. Polymerisation studies

We have examined the catalytic activity of the new metallocene 3, in the presence of methylalumoxane (MAO) as cocatalyst, for the polymerisation of ethene and propene. The catalyst mixture shows an appreciable activity (3.2×10^5 g of PE/M \times h) for the ethene polymerisation, giving a polymer of high molecular weight.

The polymerisation activity of the catalyst mixture towards propene is 2.3×10^3 g of PP/M \times h, and this is about two orders of magnitude lower than the corresponding activity towards ethylene. The lower activity for propene compared with ethene is normally observed and reflects the greater steric demand of propene.

The polypropylene was a mixture of low molecular weight oligomers and was found to be essentially atactic. We note that the recently reported [11] *tert*-alkyl-substituted *ansa*-zirconocenes of the type $[\text{ZrMe}_2\text{Si}(2\text{-Me-4-R-C}_5\text{H}_2)_2\text{Cl}_2]$, where R = *tert*-butyl or 1-methyl-cyclohexyl, are active catalysts for the polymerisation of ethene, but show low activities for propene polymerisation.

The ^{13}C NMR spectra of the low molecular weight polypropylene show the resonances assignable to chain-end structures at δ 40, 29.5 and 14.7, attributable to Pr^n groups, and at δ 144, 111.8 and 22.4, indicating vinylidene groups. These end-groups appear in almost equal amounts [12], and show that the insertion is primary and that chain termination proceeds by β -elimination. Also, the ^1H NMR spectrum showed there are only reso-

nances ($\delta = 4.6$ ppm) attributable to the presence of vinylidene groups and no traces of any vicinal group to the vinyl chain-ends. Finally, the methyl pentad region shows the presence of large numbers of *rr* and *mr* triads in the polymer chain, indicating that this polymer is an atactic polypropylene.

3. Experimental section

3.1. General procedures

All manipulations of air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques or in a dry-box under an atmosphere of nitrogen (less than 10 ppm oxygen, less than 20 ppm water). Nitrogen gas was purified by passage through a column containing BTS catalyst and 4 Å molecular sieves. Solvents and solutions were transferred, using a positive pressure of nitrogen, through stainless-steel cannulae (diameter 0.5–2.0 mm), and mixtures were filtered in a similar way using modified cannulae which could be fitted with glass-fibre filter disks (Whatman GFC). Unless otherwise specified, all reagents were purchased from commercial suppliers (Aldrich and Fluka) and used without further purification. All solvents were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under a nitrogen atmosphere. The following drying agents were used: molten sodium for toluene; molten potassium for tetrahydrofuran; potassium–sodium alloy (1:3 w/w) for diethylether, petroleum ether (b.p. $40\text{--}60^\circ\text{C}$) and pentane; phosphorus pentoxide for dichloromethane and 4 Å molecular sieves for methanol.

Deuterated solvents (CDCl_3 , CD_2Cl_2) for use in NMR experiments of air-sensitive compounds were distilled over CaH_2 and stored under nitrogen in Young's ampoules, while $\text{C}_2\text{D}_4\text{Cl}_4$, for polypropylene NMR, was used without further purification.

NMR spectra were recorded on the following instruments: ^1H , 200.13 MHz, Bruker AC-200 and 300 MHz, Bruker AM-300; ^{13}C , 50.32 MHz, Bruker AC-200. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane ($\delta = 0$). All chemical shifts are quoted in δ (ppm) and coupling constants are given in hertz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), quartet (q), triplet (t), multiplet (m). The two-dimensional correlation experiments, ^{13}C , ^1H -HMQC ($\Delta = 3.6$ ms) [13], were carried out using standard sequences. Elemental analyses were obtained by the Microanalytical Laboratory of the Inorganic Chemistry Laboratory, Oxford.

3.2. Synthesis of 6,6-(3,3,5,5-tetramethylpentamethylene)fulvene (1)

Pyrrolidine (4.18 g, 58.77 mmol, freshly distilled under nitrogen) was slowly added to a solution of 3,3,5,5-tetramethylcyclohexanone (6 g, 39 mmol) and cyclopentadiene (3.5 g, 97.2 mmol) in reagent grade degassed methanol (50 cm³) at 0°C. The mixture was stirred under nitrogen at room temperature until TLC analysis (Merck silica gel, diethylether/petroleum ether 1:2) showed no traces of the starting ketone (about 18 h). Acetic acid was added (2.35 cm³, 62.68 mmol) to the bright yellow solution, then the reaction mixture was diluted with diethyl ether and water (30 cm³ each). After separation of the organic phase, the aqueous portion was washed twice with ether and the combined organic extracts were washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash column chromatography over silica gel using petroleum ether (b.p. 40–60°C). Removal of the solvent gave a yellow viscous oil. Yield 5.38 g (68%). Anal. Found: C, 89.0; H, 11.0. C₁₅H₂₂ (202.33) Calc.: C, 89.0; H, 10.85%. ¹H NMR (CDCl₃): 0.99 (s, 12H), 1.43 (s, 2H), 2.41 (s, 4H), 6.54 (s, 4H) ppm.

3.3. Synthesis of lithium (1,3,3,5,5-pentamethylcyclohexyl)-cyclopentadienylide (2)

The compound 6,6-(3,3,5,5-tetramethylpentamethylene)fulvene (2 g, 9.88 mmol) in diethyl ether (20 cm³) was cooled to 0°C. Methyl lithium (7.08 cm³, 9.88 mmol, 1.4 M in ether) was added dropwise, causing the yellow solution to become colourless with concomitant precipitation of a white solid. The mixture was allowed to stir overnight at room temperature. The solid was then filtered via a cannula and washed twice with petroleum ether. The residual solvent was pumped off overnight. The lithium salt was isolated as a white pyrophoric powder. Yield 1.19 g (86.6%).

3.4. Synthesis of bis[η-(1,3,3,5,5-pentamethylcyclohexyl)-cyclopentadienyl] zirconium dichloride (3)

The lithium salt 2 (1 g, 4.452 mmol) dissolved in THF (100 cm³) at –78°C was slowly added to a stirred slurry of zirconium tetrachloride (0.35 g, 1.486 mmol) in THF (30 cm³) at –78°C. The cooling bath was removed and the suspension was allowed to stir at room temperature overnight. The solvent was removed under reduced pressure to give a white solid which was dissolved in toluene, leaving a precipitate of white LiCl. The extract was then filtered through a cannula and reduced in volume (about 80%). Cooling to –20°C overnight gave a white powder which was filtered and dried under vacuum. Crystallisation from dichlorometh-

ane gave white crystals of the zirconium complex. Yield 0.6 g (68%). Anal. Found: C, 64.4; H, 8.95; Cl, 11.9. C₃₂H₅₀Cl₂Zr (596.88) Calc.: C, 64.4; H, 8.4; Cl, 11.9%.

3.5. Polymerisation studies

Ethene and propene (pure grade) were purified by passage through 4 Å molecular sieves and then over finely divided potassium metal supported on glass wool. Polymerisations were performed in a 500 cm³ Fischer–Porter reactor equipped with a magnetic stirrer and placed in a thermostatically heated bath (30°C). The polymerisations were carried out under conditions similar to those employed by Kaminsky et al. [14].

3.5.1. Polymerisation of ethene

Methylaluminoxane (MAO) (250 mg) was weighed into a Fischer–Porter apparatus, which was evacuated and then filled with ethene. Toluene was then added (200 cm³), the ethene pressure increased to 2 bar and the mixture stirred at 30°C until saturated with the monomer. The metallocene 3 (6.25 × 10^{–6} mol in 10 cm³ of toluene) was added to MAO (50 mg) and the mixture stirred for 15 min for pre-activation and then quickly added via a cannula to the Fischer–Porter reactor. The reaction mixture was stirred vigorously at 30°C under 2 bar (absolute pressure) of ethene for 1 h. After 1 h the polymerisation was quenched by venting the ethylene and adding a small amount of ethanol. The contents of the reactor were transferred to a conical flask and 300 cm³ of a 20% (by volume) solution of conc. HCl in ethanol was added and the resulting mixture stirred at room temperature overnight. The polymer was then separated from the solution by filtration and washed with water, ethanol and diethyl ether, then dried in vacuo at 50°C to constant weight. 2.0075 g of polymer were obtained (activity 3.2 × 10⁵ g of PE/M × h).

3.5.2. Polymerisation of propene

The polymerisation was performed under the same conditions and using essentially the same procedure as for ethene.

MAO (2 g) was weighed into a Fischer–Porter apparatus, the reactor was evacuated and filled with propene. Toluene was then added (130 cm³), the propene pressure increased to 2 bar and the mixture stirred at 30°C until saturated with the monomer. Meanwhile, 5.0 × 10^{–5} mol of the metallocene in 80 cm³ of toluene was added to 400 mg of MAO, stirred for 15 min for pre-activation and quickly added via a cannula to the Fischer–Porter reactor. The reaction mixture was stirred vigorously at 30°C under 2 bar (absolute pressure) of ethylene for 6 h. After 6 h the polymerisation was quenched by venting the propene and then adding a small amount of ethanol. The contents of the reactor

Table 3
Atomic coordinates for $C_{32}H_{50}Cl_2Zr$ (3)

Atom	x	y	z
Zr	0.0000	-0.14580(7)	0.2500
Cl	-0.01037(7)	-0.3983(2)	0.30907(4)
C(1)	0.1402(2)	-0.0399(6)	0.2978(1)
C(2)	0.1641(2)	-0.1634(6)	0.2624(1)
C(3)	0.1430(3)	-0.0660(7)	0.2209(1)
C(4)	0.1033(3)	0.1146(6)	0.2298(1)
C(5)	0.1009(2)	0.1306(6)	0.2771(1)
C(6)	0.1673(2)	-0.0670(6)	0.3482(1)
C(7)	0.2458(2)	0.0743(7)	0.3582(1)
C(8)	0.2769(3)	0.1126(7)	0.4081(1)
C(9)	0.1981(3)	0.1766(8)	0.4328(2)
C(10)	0.1154(3)	0.0510(7)	0.4269(1)
C(11)	0.0939(3)	0.0037(7)	0.3763(1)
C(12)	0.1935(3)	-0.2868(6)	0.3572(2)
C(13)	0.3282(3)	-0.0619(9)	0.4308(2)
C(14)	0.3396(3)	0.2904(8)	0.4091(2)
C(15)	0.1191(4)	-0.1383(9)	0.4561(2)
C(16)	0.0415(3)	0.1787(9)	0.4422(2)

were transferred to a conical flask and 300 cm³ of a 20% (by volume) solution of conc. HCl in ethanol was added and the resulting mixture stirred at room temperature overnight. Since the polypropylene was soluble in toluene, the organic layer was separated, washed well with water (5 × 100 cm³) and dried with MgSO₄. After filtration, the solvent was removed under reduced pressure leaving the polymer as a highly viscous material,

Table 4
Selected bond lengths (Å) and angles (°) for $C_{32}H_{50}Cl_2Zr$ (3)

Zr–C(2)	2.547(4)	Zr–C(1)	2.597(3)
Zr–C(4)	2.475(4)	Zr–C(3)	2.507(4)
C(1)–C(2)	1.410(6)	Zr–C(5)	2.511(4)
C(1)–C(6)	1.532(5)	C(1)–C(5)	1.409(5)
C(3)–C(4)	1.391(6)	C(2)–C(3)	1.407(6)
C(6)–C(7)	1.551(5)	C(4)–C(5)	1.412(6)
C(6)–C(12)	1.542(6)	C(6)–C(11)	1.542(6)
C(8)–C(9)	1.541(6)	C(7)–C(8)	1.542(6)
C(8)–C(14)	1.535(7)	C(8)–C(13)	1.536(7)
C(10)–C(11)	1.544(6)	C(9)–C(10)	1.532(7)
C(10)–C(16)	1.531(7)	C(10)–C(15)	1.533(7)
Cl–Zr–Cl'	92.9(1)	Cl–Zr–Cp	109.4(1)
Cp–Zr–Cp'	129.9(1)	C(7)–C(8)–C(14)	107.2(3)
C(5)–C(1)–C(6)	126.5(3)	C(7)–C(8)–C(13)	113.9(4)
C(2)–C(1)–C(6)	126.3(3)	C(7)–C(8)–C(9)	107.8(3)
C(2)–C(1)–C(5)	106.3(3)	C(9)–C(8)–C(14)	107.6(3)
C(1)–C(2)–C(3)	109.0(4)	C(9)–C(8)–C(13)	113.9(4)
C(2)–C(3)–C(4)	108.0(4)	C(8)–C(9)–C(10)	119.0(4)
C(3)–C(4)–C(5)	107.7(4)	C(9)–C(10)–C(16)	107.6(4)
C(1)–C(5)–C(4)	108.9(4)	C(9)–C(10)–C(15)	113.3(4)
C(1)–C(6)–C(12)	109.2(3)	C(9)–C(10)–C(11)	109.6(3)
C(1)–C(6)–C(11)	109.7(3)	C(11)–C(10)–C(12)	113.2(3)
C(1)–C(6)–C(7)	105.2(3)	C(11)–C(10)–C(16)	107.2(3)
C(6)–C(7)–C(8)	117.6(3)	C(11)–C(10)–C(15)	112.1(3)
C(6)–C(11)–C(10)	118.6(3)	C(13)–C(8)–C(14)	106.0(4)
C(7)–C(6)–C(12)	110.8(3)	C(15)–C(10)–C(16)	106.6(4)
C(7)–C(6)–C(11)	108.3(3)		

which was dried in vacuo at 50 °C to constant weight. 0.66 g of polymer was obtained (activity 2.3×10^3 g of PP/M × h).

3.6. Crystal data and structure determination of compound 3

$C_{32}H_{50}Cl_2Zr$, $M_r = 596.88$, white prism ($0.20 \times 0.22 \times 0.38$ mm³), monoclinic, space group $C2/c$, $a = 15.534(3)$, $b = 6.685(2)$, $c = 29.697(5)$ Å, $\beta = 94.78(3)^\circ$; $U = 3073(1)$ Å³, $Z = 4$, $D_x = 1.29$ Mg m⁻³, λ (Mo $K\alpha$) = 0.71069 Å, μ (Mo $K\alpha$) = 5.50 cm⁻¹, $F(000) = 1264$, $T = 293$ K.

X-ray diffraction data were recorded on a four-circle Philips PW1100 (Febo System) [15] diffractometer operating in $\theta/2\theta$ scan mode with graphite-monochromated (Mo $K\alpha$) radiation ($\lambda = 0.71069$ Å), following standard procedures. 3708 reflections were measured ($2\theta_{max} = 52^\circ$). There were no significant fluctuations of intensity other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption, as described by North et al. [16].

The structure was solved by heavy-atom methods [17]. Refinement was carried out by full-matrix least-squares; the function minimised was $\sum w(F_o^2 - F_c^2)^2$, with weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 15.94P]$, where $P = \max(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located from difference Fourier maps and refined isotropically, except for those belonging to the methyl groups which were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U_{eq}$ of the parent carbon atom). For a total of 205 parameters, $wR' = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.104$ (on F^2), $S = 1.124$, and conventional $R = 0.045$, based on F values of 2590 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. Scattering factors were taken from Ref. [18]. Structure refinement and final geometrical calculations were carried out with SHELXL 93 [19] and PARST [20] programs, drawings were produced using ORTEP II [21]. The atomic coordinates are reported in Table 3 and selected bond lengths and angles are given in Table 4.

Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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