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Synthesis of new bis(cyclopentadienyl)yttrium complexes with ether functionalized cyclopentadienyl ligands.

Crystal structure of $[(C_5H_4CH_2CH_2OMe)_2Y(\mu-H)_2BH_2]^*$

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Abstract

Treatment of $C_5H_4CH_2CH_2OMe \cdot Li(TMEDA)$ ($TMEDA = N, N, N', N'$ tetramethylethylenediamine) with half an equivalent of $YCl_3(THF)_{3.5}$ in toluene afforded the salt- and solvent-free dimeric biscyclopentadienyl yttrium chloride $[(C_5H_4CH_2CH_2OMe)_2Y(\mu-Cl)_2]$ (1). Reaction of 1 with one equivalent of $LiAlH_4$ in THF gave the yttrium alumohydride complex $[(C_5H_4CH_2CH_2OMe)_2Y(\mu-H)_2YAlH_4]$ (2), which was transformed into $[(C_5H_4CH_2CH_2OMe)_2Y(\mu-H)_2]$ (4) by expulsion of AlH_3 with NEt_3 . Reaction of 1 with an excess of $LiBH_4$ gave the yttrium borohydride complex $[(C_5H_4CH_2CH_2OMe)_2Y(\mu-H)_2BH_2]$ (3), whose crystal structure has been shown to be monomeric species with yttrium-coordinated ether functions and a η^2 -bonded borohydride ligand.

1. Introduction

Salt and solvent free hydrides of Group 3 metals and the lanthanides $[Cp'_2Ln(\mu-H)_2]$ ($Cp' = C_5H_5-nR_n$, R = alkyl) are extremely interesting because of their potential as catalysts for olefin polymerization, hydrogenation, hydrosilylation, and hydroamination, and have therefore been widely investigated [1–4]. A frequently used method to synthesize these hydrides involves hydrogenolysis of the corresponding carbyls Cp'_2LnR , but this route is cumbersome [5]. A more attractive, direct, route is through reaction of Cp'_2LnCl and $LiAlH_4$ to give Cp'_2LnAlH_4 , which on treatment with Et_3N produces $[Cp'_2Ln(\mu-H)_2]$ [6].

The compounds Cp'_2LnX (X = halide, hydride, carbyl) are normally so strongly Lewis acidic that they tend to incorporate salt (e.g. $LiCl$ or $MgCl_2$) or solvent

molecules. These are generally very difficult to remove, and greatly reduce the (catalytic) reactivity of the metal centre. On the other hand a Lewis base function on each of the spectator ligands can prevent inclusion of salt and solvent and enhance the activity and selectivity of the metal centre. We therefore planned a series of dicyclopentadienyl derivatives of yttrium, in which the cyclopentadienyl ligand carries a pending ether function, and chose the system $C_5H_5CH_2CH_2OMe$. During our investigations analogous derivatives were reported for La, Pr and Nd [7], and this has prompted us to present our results on yttrium.

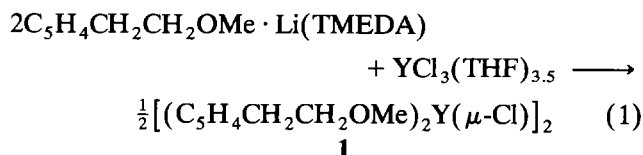
2. Results and discussion

Convenient amounts (50 mmol scale) of the starting material $[(C_5H_4CH_2CH_2OMe)_2Y(\mu-Cl)_2]$ (1) were obtained by treatment of a solution of $C_5H_4CH_2CH_2OMe \cdot Li(TMEDA)$ in toluene at $-80^\circ C$ with half an equivalent of $YCl_3(THF)_{3.5}$ followed by overnight stirring at room temperature. Filtration, concentration

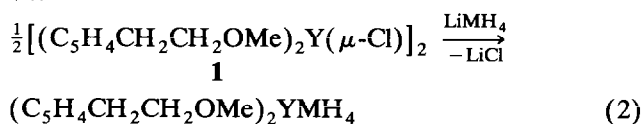
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* This paper is dedicated to Professor M.F. Lappert F.R.S. on the occasion of his 65th birthday.

and cooling of the solution gave white crystals of **1** (eqn. (1)).

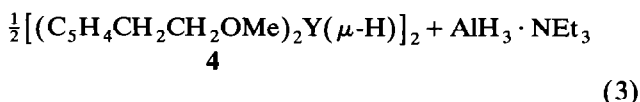


Reaction of **1** with one equivalent of LiAlH_4 gave the yttrium alumohydride complex $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2\text{YAlH}_4$ (**2**) as white crystals (eqn. (2)). The borohydride derivative **3** was prepared analogously (eqn. (2)).



2 M = Al;

3 M = B



Treatment of **2** with an excess of NEt_3 in a mixture of toluene and pentane (1 : 3) led to expulsion of AlH_3 [8*] and formation of the symmetric yttrium hydride dimer $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2\text{Y}(\mu\text{-H})]_2$ (**4**) in moderate yield (eqn. (3)) [9*]. Direct conversion of **1** into **4** can be easily carried out by *in situ* reaction and this presents an excellent route for the synthesis of hydride **4**. No attempt to obtain monometallic hydrides by the well-known treatment of borohydrides with triethylamine (*e.g.* for $\text{Cp}_2\text{Zr}(\text{BH}_4)_2$ this procedure yields triethylaminoborane and zirconium monohydride or zirconium dihydride [10*]) succeeded in displacing BH_3 from **3** to give **4** (similar reactions of samarocene borohydrides $\text{Cp}'_2\text{SmBH}_4$ ($\text{Cp}' = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4^t\text{Bu}$, $\text{C}_5\text{H}_3^t\text{Bu}_2$) with triethylamine were also unsuccessful [6b]).

The crystal structure of **3** was determined (Fig. 1). The molecular structure is disordered in that for C17 there are two possible positions, each with *ca.* 50% occupancy (for the sake of clearness one position is shown in Fig. 1). The bond parameters (see Table 1) indicate that the molecule has a pseudo-octahedral coordination geometry around yttrium if the η^5 -bonded cyclopentadienyl ligand is regarded as occupying a single polyhedral vertex. The yttrium atom appears to be electronically saturated, since all the ligand contribu-

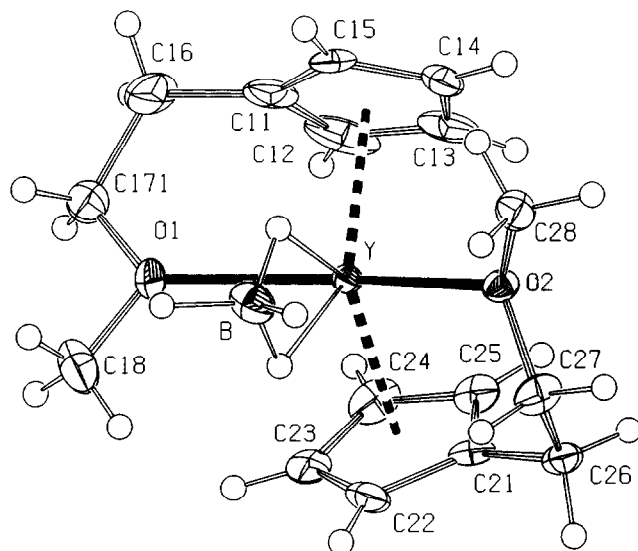


Fig. 1. Atomic displacement ellipsoid plot (50% probability level) of $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2\text{Y}(\mu\text{-H})_2\text{BH}_2$ (**3**).

tions, when accounted for in the regular way, add up to 18 electrons on the metal. The Y–Cent1 (2.386(3) Å) and Y–Cent2 (2.393(5) Å) distances are similar to those in $[(\text{MeC}_5\text{H}_4)_2\text{Y}(\mu\text{-H})\text{THF}]_2$ (2.397, 2.414 Å) [11]. Two hydride atoms bridge between yttrium (Y–H3 = 2.26(5), Y–H4 = 2.27(5) Å) and boron, and the latter also bears two terminal hydrides. The borohydride acts as a bidentate ligand, which is common for analogous compounds in which the metal is smaller than or comparable with yttrium (Ti, Yb), whereas for

TABLE 1. Selected bond distances (Å) and angles (°) for $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2\text{Y}(\mu\text{-H})_2\text{BH}_2$ (**3**)

Bond distances			
Y–O1	2.438(5)	Y–O2	2.419(4)
Y–C11	2.659(8)	Y–C21	2.649(6)
Y–C12	2.639(8)	Y–C22	2.694(10)
Y–C13	2.668(6)	Y–C23	2.716(10)
Y–C14	2.695(9)	Y–C24	2.671(11)
Y–C15	2.678(6)	Y–C25	2.631(10)
Y–H3	2.26(5)	Y–H4	2.27(5)
B–H1	1.16(5)	B–H2	1.15(6)
B–H3	1.11(5)	B–H4	1.11(5)
C16–C171	1.54(2)	C16–C172	1.27(3)
O1–C171	1.394(14)	O1–C172	1.53(2)
Y–Cent1 ^a	2.386(3)	Y–Cent2 ^a	2.393(5)
Bond angles			
H3–Y–H4	43.8(18)	H3–B–H4	99 (4)
Y–H4–B	108 (3)	H1–B–H2	103 (4)
Y–H3–B	109 (3)	O2–C27–C26	108.6(5)
Y–O1–C171	128.3(6)	Y–O1–C172	116.0(9)
O1–C171–C16	109.2(10)	O1–C172–C16	117.0(17)

* Reference number with an asterisk indicates a note in the list of references.

^a Cent1, Cent2 are the centres of gravity of the cyclopentadienyl rings.

larger metals (Sm) tridentate complexation is generally observed [12]. The structure clearly shows that the ether functions of both cyclopentadienyl ligands are coordinated to yttrium. The Y–O bond distances (2.438(5), 2.419(4) Å) are typical, and close to those found in complexes of other yttrium compounds with coordinated ether molecules (MeC_5H_4)₂Y(THF)(μ -H)₂ (Y–O = 2.460(8)) [11]; (Y(BH₄)₃(THF)₃ (Y–O = 2.350(6), 2.412(7)) [13]; [(1,3-Me₂C₅H₃)(THF)Y(μ -H)₂ (Y–O = 2.46(1)) [14]. The ¹H NMR spectrum of **3** shows a quartet (1:1:1:1) at δ = 0.62 ppm (¹J(B–H) = 83 Hz) for the terminal and bridging hydrides. ¹H NMR spectra of **3** at various temperatures (cooling to –80°C in intervals of 10°C) did not reveal any splitting of the quartet into separate resonances for bridging and terminal hydrides, indicating a fast fluxional behaviour of the hydrides, as expected for this type of compound.

Compounds **2**, **3** and **4** show a strong ν (C–O) absorption at 1044 cm^{–1}, shifted by 75 cm^{–1} to lower wave number from the values for the stretching vibration of the free ethers [15*], so indicating a coordinated ether function. The ¹H NMR resonances of the methoxy group are shifted to higher field for **2**, **3** and **4** compared with those for the free cyclopentadiene (3.09, 3.11 and 3.06 ppm, respectively; free cyclopentadiene: OMe = 3.36 ppm). Normally, coordination of the ether to a Lewis acid metal centre causes a shift to low field, as in [(C₅H₄CH₂CH₂OMe)₂LaCl]₂ [7] and (C₅H₄CH₂CH₂OMe)₂TiCl₂ [16]. Since the yttrium centre is a very strong Lewis acid and coordination of the ether function is obvious from the solid state structure we assume that this coordination is maintained in benzene solution. The reason for the high field shift remains unclear for the present.

In the ¹H NMR spectrum of hydride **4** the hydride ligands give a triplet at δ 2.09 ppm (¹J(Y–H) = 28 Hz), indicating a symmetric yttrium hydride dimer, as has been observed for other systems such as [(C₅H₄Me)₂Y(μ -H)(THF)]₂ (¹J(Y–H) = 27 Hz) [11], [(C₅Me₅)₂Y(μ -H)]₂ (¹J(Y–H) = 38 Hz) [17*], [(C₅Me₅)(OC₆H₃Bu^t)₂Y(μ -H)]₂ (¹J(Y–H) = 35 Hz) [18] and [(C₆H₅C(NSiMe₃)₂)₂Y(μ -H)]₂ (¹J(Y–H) = 28 Hz) [19]. Symmetrically bridged hydride ligands appear to be characteristic for yttrium and the lanthanides. Up to now only one asymmetric bridged hydride complex, (C₅Me₅)₂Lu(H)(μ -H)Lu(C₅Me₅)₂, has been reported [20].

3. Experimental section

All operations were performed under an inert atmosphere by use of Schlenk or glovebox techniques. Solvents (THF, ether, pentane, toluene) were distilled from Na/K alloy prior to use. YCl₃(THF)_{3.5} was pre-

pared from YCl₃ by continuous extraction with THF; YCl₃ was obtained by dissolving Y₂O₃ in hydrochloric acid and dehydrating the product with SOCl₂ [21]. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR as Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WH-90, Varian Gemini 200 or Varian VXR 300. Chemical shifts are reported in ppm, ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances (benzene-*d*₆: 7.15 ppm, THF-*d*₈: 3.57 ppm, toluene-*d*₈: 7.09 ppm). Elemental analyses were carried out at the Microanalytical Department of this university. All values given are the average of at least two independent determinations.

3.1. [(C₅H₄CH₂CH₂OMe)₂Y(μ -Cl)]₂ (**1**)

To a solution of 24.8 g (24 ml, 0.2 mol) of C₅H₅CH₂CH₂OMe in 840 ml of toluene at 0°C were added, 30 ml of TMEDA and 78.5 ml (2.5 M, 0.2 mol) of n-BuLi, the mixture becoming orange. At –50°C 36.1 g (0.081 mol) of YCl₃(THF)_{3.5} was added in portions and the mixture then allowed to warm to room temperature and stirred overnight (during the warming the mixture became bright yellow). Filtration, concentration, and subsequent cooling to –20°C yielded white crystals of **1** (19 g, 0.051 mol, 63%). ¹H NMR (THF-*d*₈, 200 MHz): δ 2.65 (t, 4 H, CpCH₂); 3.52 (s, 6H, MeO); 3.91 (t, 4H, CH₂OMe); 5.85 (t, 4H, C₅H₄); 5.97 (t, 4H, C₅H₄). ¹³C NMR (THF-*d*₈, 75.429 MHz): δ 29.74 (t, CpCH₂, ¹J(C–H) 144 Hz); 79.40 (t, CH₂OMe, ¹J(C–H) 142 Hz); 110.31 (d, CH ring, ¹J(C–H) 165 Hz); 110.70 (d, CH ring, ¹J(C–H) 165 Hz); 125.93 (s, C ring). IR (cm^{–1}): 3081m, 3023m, 2924vs, 2855vs, 1491m, 1460s, 1379m, 1335w, 1256w, 1229vw, 1202m, 1057vs, 1044vs, 993s, 966s, 918vw, 889vw, 833s, 816s, 781vs, 727w, 685m, 629w, 527m. Anal. found: C, 51.95; H, 5.92; Y, 23.92; Cl, 9.55. C₁₆H₂₂O₂YCl calc.: C, 51.83; H, 5.98; Y, 23.98; Cl, 9.56%.

3.2. (C₅H₄CH₂CH₂OMe)₂YAlH₄ (**2**)

To a solution of 1.53 g (4.1 mmol) of **1** in 50 ml of toluene at 0°C was added dropwise a solution of 2.4 ml (1.72 M, 4.1 mmol) of LiAlH₄ in THF. A white suspension was immediately formed. The suspension was allowed to warm to room temperature and stirred overnight. After filtration and concentration the solution was cooled to –20°C, affording 1.06 g (2.9 mmol) of **2** as white crystals (71%). ¹H NMR (benzene-*d*₆, 200 MHz): δ 2.27 (t, 4H, CpCH₂); 3.09 (s, 6H, MeO); 3.27 (t, 4H, MeOCH₂); 3.46 (s, 4H, AlH₄); 5.86 (t, 4H, C₅H₄); 5.98 (t, 4H, C₅H₄). ¹³C NMR (THF-*d*₈, 75.429 MHz): δ 29.45 (t, CpCH₂, ¹J(C–H) 127 Hz); 60.81 (q, MeO, ¹J(C–H) 144 Hz); 78.16 (t, CH₂OMe, ¹J(C–H) 145 Hz); 107.67 (d, CH ring, ¹J(C–H) 163 Hz); 108.03 (d, CH ring, ¹J(C–H) 163 Hz); 126.13 (s, C ring). IR

(cm^{-1}): 3069w, 2955vs, 2924vs, 2855vs, 2728m, 2689m, 2674m, 2361m, 2342m, 1730s, 1456s, 1377m, 1200w, 1055m, 1042m, 993m, 966m, 920w, 895w, 835m, 797s, 775s, 741s, 681m, 523w. Anal. found: C, 52.35; H, 7.51; Al, 7.44; Y, 23.9. Calc.: C, 52.46; H, 7.16; Al, 7.37; Y, 24.27%.

3.3. $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2\text{Y}(\mu\text{-H})_2\text{BH}_2$ (**3**)

To a mixture of 0.85 g (2.2 mmol) of **1** and 0.29 g (13.3 mmol) of LiBH_4 at room temperature was added 40 ml of THF. The white suspension was stirred for 2 days and the solvent was then removed *in vacuo* and 50 ml of toluene added. White crystals of **3** were obtained, after filtration, concentration, and cooling of the toluene solution to -20°C (0.48 g, 1.4 mmol, 62%). Recrystallization from hot toluene gave crystals suitable for an X-ray structural determination. ^1H NMR (benzene- d_6 , 200 MHz): δ 0.62 (q, 4H, BH_4 , $^1J(\text{B-H}) = 83$ Hz); 2.32 (t, 4H, CpCH_2); 3.11 (s, 6H, *MeO*); 3.29 (t, 4H, MeOCH_2); 5.90 (t, 4H, C_5H_4); 6.05 (t, 4H, C_5H_4). ^{13}C NMR (toluene- d_8 , 75.429 MHz): δ 28.99 (t, CpCH_2 , $^1J(\text{C-H})$ 128 Hz); 62.87 (q, *MeO*, $^1J(\text{C-H})$ 143 Hz); 78.67 (t, CH_2OMe , $^1J(\text{C-H})$ 143 Hz); 110.10 (d, CH ring, $^1J(\text{C-H})$ 164 Hz); 110.28 (d, CH ring, $^1J(\text{C-H})$ 165 Hz); 125.93 (s, C ring). IR (cm^{-1}): 3069w, 2953vs, 2924vs, 2855vs, 2726w, 2419w, 2367m, 2294w, 2226w, 2197w, 2174w, 1460vs, 1377s, 1304w, 1265vw, 1229vw, 1182vw, 1154vw, 1119w, 1055m, 1042m, 991w, 966w, 920vw, 837w, 812w, 785m, 762w, 723w, 681vw. Anal. found: C, 55.23; H, 7.50; Y, 24.93. $\text{C}_{16}\text{H}_{26}\text{O}_2\text{YB}$ calc.: C, 54.89; H, 7.49; Y, 25.39%.

3.4. $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2\text{Y}(\mu\text{-H})_2]$ (**4**)

To a solution of 0.64 g (1.7 mmol) of **2** in toluene/pentane (15/45 ml) was added 1.22 ml (8.7 mmol) of Et_3N , and the mixture was refluxed overnight during which metallic aluminium was formed. The solvent was removed *in vacuo* and the residue was extracted with toluene. Concentration of the extract and subsequent cooling to -20°C afforded **4** as white crystals (0.30 g, 0.9 mmol, 52%). ^1H NMR (benzene- d_6 , 200 MHz): δ 2.09 (t, H, $^1J(\text{Y-H}) = 28$ Hz); 2.56 (t, 4H, CpCH_2); 3.06 (s, 6H, *MeO*); 3.35 (t, 4H, MeOCH_2); 6.10 (t, 4H, C_5H_4); 6.22 (t, 4H, C_5H_4). ^{13}C NMR (benzene- d_6 , 75.429 MHz): δ 30.29 (t, CpCH_2 , $^1J(\text{C-H})$ 127 Hz); 60.73 (q, *MeO*, $^1J(\text{C-H})$ 142 Hz); 77.66 (t, CH_2OMe , $^1J(\text{C-H})$ 142 Hz); 107.25 (d, CH ring, $^1J(\text{C-H})$ 166 Hz); 108.06 (d, CH ring, $^1J(\text{C-H})$ 160 Hz); 123.87 (s, C ring). IR (cm^{-1}): 3069w, 2953vs, 2855vs, 2728vw, 1460s, 1377m, 1296m, 1262m, 1204w, 1184w, 1112m, 1061m, 1042m, 993vw, 968m, 881m, 866m, 829m, 812m, 768s, 752m, 704vw, 680vw, 635m, 615w, 526vw, 478vw. Anal. found: C, 57.26; H, 6.96; Y, 26.05. $\text{C}_{16}\text{H}_{23}\text{YO}_2$ calc.: C, 57.15; H, 6.89; Y, 26.44%.

3.5. X-ray structure determination

Crystals of $\text{C}_{16}\text{H}_{26}\text{O}_2\text{BY}$ are orthorhombic, space group $\text{Pna}2_1$, with $a = 12.2448(7)$, $b = 11.1701(5)$, $c = 11.7887(5)$ Å, $Z = 4$, $V = 1612.4(1)$ Å³, $\text{MW} = 350.10$, $F(000) = 728$, $\mu(\text{Mo K}\alpha) = 36.4$ cm^{-1} . X-ray data were collected at 100 K on an Enraf Nonius CAD4T/Rotating anode system [$\theta_{\text{max}} = 27.5^\circ$; $\omega/2\theta$ -scan; $\Delta\omega = 0.53 + 0.35 \text{ tg } \theta^\circ$; Mo $\text{K}\alpha$ monochromated $\lambda = 0.71073$ Å] for a crystal [$0.35 \times 0.35 \times 0.35$ mm] mounted in a Lindemann glass capillary. Unit cell dimensions were derived from the SET4 setting angles of 24 reflections in the range $10 < \theta < 14^\circ$. A total of 2161 reflections was scanned, corrected for L_p and absorption (DIFABS [22]) and averaged into a unique set of 1384 reflections with $I > 2.5\sigma(I)$. The structure was solved with DIRDIF-92 [23] and refined on F to a final $R = 0.031$, $R_w = 0.031$ with SHELX-76 [24]. A disorder model was used to describe the positional disorder C171/C172. Hydrogen atoms were taken into account at calculated positions (except for those on B, for which the positional parameters were refined). Weights were based on counting statistics. The absolute structure was checked by refinement with opposite $\Delta f''$ contributions to the scattering factors. Scattering factors were those of Cromer and Mann [25], corrected for anomalous dispersion (Cromer and Liberman [26]). All calculations were done on a DEC5000/ULTRIX system. Geometrical calculations and the illustration were made with PLATON-92 [27].

TABLE 2. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Y	0.22194(3)	0.05762(4)	0.0092	0.0146(1)
O(1)	0.1602(4)	0.2362(4)	0.1093(4)	0.0290(16)
O(2)	0.3507(3)	-0.1058(3)	-0.0064(4)	0.0190(13)
C(11)	0.2384(6)	0.2580(7)	-0.1113(6)	0.039(3)
C(12)	0.1659(6)	0.1837(8)	-0.1709(7)	0.047(3)
C(13)	0.2261(6)	0.0872(7)	-0.2153(5)	0.039(2)
C(14)	0.3355(8)	0.1014(8)	-0.1822(7)	0.028(3)
C(15)	0.3421(5)	0.2061(5)	-0.1182(6)	0.0257(19)
C(16)	0.2093(11)	0.3646(11)	-0.0450(12)	0.076(5)
C(18)	0.1224(7)	0.2392(7)	0.2244(6)	0.040(2)
C(21)	0.1310(4)	-0.1564(5)	0.0305(6)	0.019(2)
C(22)	0.0933(9)	-0.0948(9)	0.1254(7)	0.026(3)
C(23)	0.0215(8)	-0.0049(11)	0.0881(8)	0.029(3)
C(24)	0.0158(9)	-0.0086(12)	-0.0300(8)	0.030(3)
C(25)	0.0830(9)	-0.1042(9)	-0.0649(6)	0.025(3)
C(26)	0.2134(4)	-0.2556(5)	0.0281(8)	0.023(2)
C(27)	0.3261(5)	-0.2132(5)	0.0592(6)	0.0267(17)
C(28)	0.4677(5)	-0.0890(6)	-0.0121(5)	0.025(2)
C(171) *	0.1444(13)	0.3511(12)	0.0662(12)	0.029(3)
C(172) *	0.2007(18)	0.356(2)	0.0620(19)	0.029(3)
B(1)	0.3606(9)	0.0853(10)	0.1981(9)	0.028(3)

$U_{\text{eq}} = 1/3$ of the trace of the orthogonalized U . * Disordered.

Atom coordinates are given in Table 2. Tables of hydrogen atom coordinates and thermal parameters, and a full list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Lists of structure factors are available from A.L.S.

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