Acylation and Esterification of the Aryloxide Ligand in [AlMe(dbmp)$_2$]. Crystal Structures of [AlMe(dbmp)(bhmap)], Hbhmap and O=C(dbmp)Bu^t (Hdbmp = 2,6-di-*tert*-butyl-4-methylphenol, Hbhmap = 3-*tert*-butyl-2-hydroxy-5-methylacetophenone)†

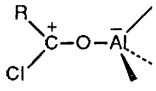
Michael B. Power,[a] Simon G. Bott,[b] Elizabeth J. Bishop,[b] Kelli D. Tierce,[b] Jerry L. Atwood[b] and Andrew R. Barron*[,a]

[a] *Department of Chemistry and Materials Research Laboratory, Harvard University, Cambridge, Massachusetts 02138, USA*

[b] *Department of Chemistry, University of Alabama, Tuscaloosa, Alabama 35486, USA*

The reaction of [AlMe(dbmp)$_2$] (Hdbmp = 2,6-di-*tert*-butyl-4-methylphenol) with O=C(Cl)Me leads to acylation of one of the dbmp ligands and affords [AlMe(dbmp)(bhmap)] **1** (Hbhmap = 3-*tert*-butyl-2-hydroxy-5-methylacetophenone). Hydrolysis of **1** yields uncomplexed Hbhmap **5**. The Et, Pr^i and Ph analogues of **1** and **5** have been obtained by the use of the appropriate acyl chloride. By contrast, the interaction of [AlMe(dbmp)$_2$] with O=C(Cl)Bu^t results in the formation of O=C(dbmp)Bu^t **12** and [AlCl$_2$(dbmp){O=C(Me)Bu^t}] **13**. The molecular structures of **1**, **5** and **12** have been confirmed by X-ray crystallography.

The interaction of acyl chlorides, O=C(Cl)R, with aluminium chloride, $AlCl_3$, results in the formation of an addition complex for which two structures are commonly proposed. Although structure **I** was first suggested by Pfeiffer,[1] upon noting that the addition compounds of aluminium halides with acid halides are similar to the addition compounds formed with ketones, ethers and other oxygen donor compounds, it was structure **II**, proposed by Meerwein,[2] that was accepted for many years. Structural and spectroscopic investigations have now confirmed that both are indeed correct, that is, in some instances the compounds exist as acylium salts (**II**) and in others the



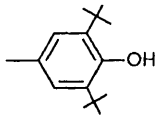
I

II

aluminium is bonded to the carbonyl oxygen (**I**).[3] In fact, mixtures are sometimes obtained. The distribution is dependent on whether the material is in the solid state or in solution, and even on the nature of the solvent.[4] In contrast, the interaction of acyl halides with organoaluminium compounds has been reported to result in alkyl–halide exchange [equation (1)].[5]

$$O{=}C(Cl)R + R'AlCl_2 \longrightarrow AlCl_3[O{=}C(R')R] \quad (1)$$

Recent work in our laboratory[6] has been concerned with the structure, bonding and reactivity of monomeric aluminium compounds derived from the sterically hindered phenol, 2,6-di-*tert*-t-butyl-4-methylphenol (Hdbmp) **III**.[6]



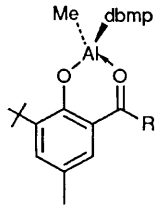
III

As part of this work we have studied the interaction of these compounds with organic carbonyls,[7,8] in particular with respect to the formation of stable Lewis acid–base adducts.[8] We report here our results pertaining to the reaction of [AlMe(dbmp)$_2$] with O=C(Cl)R, where R = Me, Et, Pr^i, Bu^t or Ph.

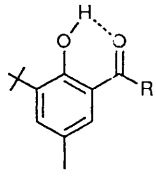
Results and Discussion

The interaction of [AlMe(dbmp)$_2$] with acetyl chloride, O=C(Cl)Me, results in the Friedel–Craft acylation of one of the aryloxide ligands, with the concurrent elimination of Bu^{t}Cl, to give [AlMe(dbmp)(bhmap)] **1** (Hbhmap = 3-*tert*-butyl-2-hydroxy-5-methylacetophenone) as the major aluminium-containing product [equation (2)]. Compound **1** has been fully characterised by ^1H and ^{13}C-{^1H} NMR and IR spectroscopy (see Experimental). Hydrolysis of **1** yields, in addition to one molar equivalent of Hdbmp, the uncomplexed ligand Hbhmap **5** as a bright yellow crystalline solid.

$$[AlMe(dbmp)_2] + O{=}C(Cl)Me \longrightarrow [AlMe(dbmp)(bhmap)] + Bu^tCl \quad (2)$$



R
1 Me
2 Et
3 Pr^i
4 Ph



R
5 Me
6 Et
7 Pr^i
8 Ph

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

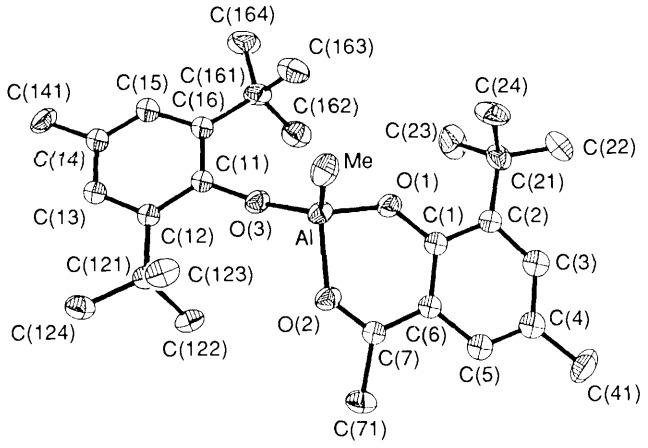


Fig. 1 The molecular structure of [AlMe(dbmp)(bhmap)] **1**. Thermal ellipsoids are drawn at the 30% level, and the hydrogen atoms are omitted for clarity.

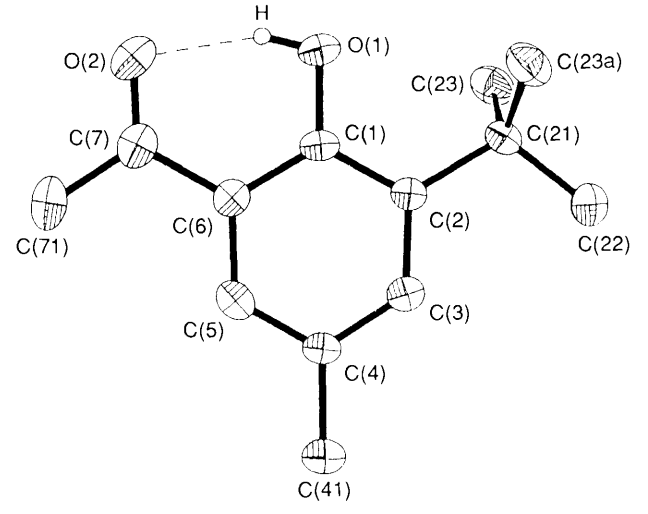


Fig. 2 The molecular structure of Hbhmap **5**. Thermal ellipsoids are drawn at the 30% level. Only the hydrogen atom attached to O(1) is depicted; the remainder are omitted for clarity.

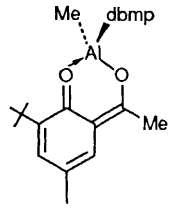
Table 1 Selected bond lengths (Å) and angles (°) for [AlMe(dbmp)(bhmap)] **1**

Al–O(1)	1.765(5)	Al–O(2)	1.836(4)
Al–O(3)	1.706(4)	Al–Me(1)	1.933(7)
O(1)–C(1)	1.332(7)	O(2)–C(7)	1.283(7)
O(3)–C(11)	1.363(7)	C(6)–C(7)	1.418(8)
C(7)–C(71)	1.489(8)	C(1)–C(6)	1.421(8)
O(1)–Al–O(2)	94.2(2)	O(1)–Al–O(3)	111.2(2)
O(1)–Al–Me(1)	113.1(3)	O(2)–Al–O(3)	105.6(2)
O(2)–Al–Me(1)	110.0(3)	O(3)–Al–Me(1)	119.1(3)
Al–O(1)–C(1)	129.6(4)	Al–O(2)–C(7)	127.9(4)
Al–O(3)–C(11)	158.0(4)	O(1)–C(1)–C(6)	119.9(6)
C(1)–C(6)–C(7)	122.9(6)	O(2)–C(7)–C(6)	122.7(6)
C(2)–C(7)–C(71)	113.1(6)		

Table 2 Selected bond lengths (Å) and angles (°) for Hbhmap **5**

O(1)–C(1)	1.358(7)	O(2)–C(7)	1.234(8)
C(1)–C(6)	1.409(8)	C(6)–C(7)	1.468(8)
C(7)–C(71)	1.497(8)		
O(1)–C(1)–C(6)	120.2(5)	C(1)–C(6)–C(7)	120.4(6)
O(2)–C(7)–C(6)	121.5(6)		

The molecular structures of **1** and **5** have been confirmed by X-ray crystallography and are shown in Figs. 1 and 2 respectively. Selected bond lengths and angles are given in Tables 1 and 2. The structure of **1** is monomeric with the near planar bhmap ligand co-ordinated to the aluminium *via* both the phenolic oxygen and the acyl group. The geometry around the aluminium is distorted from tetrahedral, with the most acute angle [94.2(2)°] associated with the bhmap bite. The terminal aryloxide Al–O(3) distance [1.706(4) Å] and Al–O(3)–C(11) angle [158.0(4)°] are consistent with some degree of Al–O π-donation of electron density from the oxygen lone pair into the aluminium-centred σ antibonding orbitals.[6a,b] The aryloxide Al–O distance for the bhmap ligand [1.765(5) Å] is longer than that associated with the dbmp ligand, however, it is shorter than that observed in $[AlMe_2(OC_6F_5)\{N(C_2H_4)_3CH\}]$ [1.787(1) Å] in which no Al–O π-interaction is present.[6e] Within the bhmap ligand in **1**, the C–O bond [O(2)–C(7) 1.283(7) Å] is significantly longer, and the acyl–aryl C–C distance [C(6)–C(7) 1.418(8) Å] shorter, than the analogous distances for uncomplexed Hbhmap [1.234(8) Å and 1.468(8) Å respectively]. In fact, the acyl–aryl C–C distance in **1** is within the range found for the aromatic C–C bonds in both **1** and **2**, 1.344(9)–1.437(8) Å, indicating that resonance form **IV** is a significant contributor to the structure of **1**.

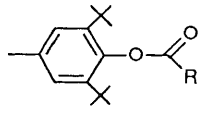


IV

The molecular structure of **5** shows that it is monomeric in the solid state, with an intramolecular hydrogen bond between the phenol and the acyl groups. The low-field ^1H NMR signal for the hydroxy proton in **5** (δ 13.52) is consistent with the existence of hydrogen bonding in solution while solution relative molecular mass measurements show that **5** is monomeric. Thus the structure observed in the solid state is retained in solution. Similar results are seen for non-sterically hindered hydroxyacetophenone derivatives.[9]

The Et, Pr^i and Ph analogues of **1**, [AlMe(dbmp)(bhmpp)] **2**, [AlMe(dbmp)(bhmibp)] **3** and [AlMe(dbmp)(bhmbp)] **4** (Hbhmpp = 3-*tert*-butyl-2-hydroxy-5-methylpropiophenone, Hbhmibp = 3-*tert*-butyl-2-hydroxy-5-methylisobutyrophenone, Hbhmbp = 3-*tert*-butyl-2-hydroxy-5-methylbenzophenone), have been obtained by the reaction of $[AlMe(dbmp)_2]$ with the appropriate acyl chloride. Hydrolysis of compounds **2**, **3** and **4** yields the free ligands Hbhmpp **6**, Hbhmibp **7** and Hbhmbp **8** respectively (see Experimental).

Although **1** is seen to be the major product from the reaction of $[AlMe(dbmp)_2]$ and O=C(Cl)Me, a side product, **9**, may also



R	
9	Me
10	Et
11	Pr^i
12	Bu^t

be isolated, in *ca.* 5% yield, from the reaction mixture. Compound **9** has been identified by ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopy to be the sterically hindered ester O=C(dbmp)Me (see Experimental).

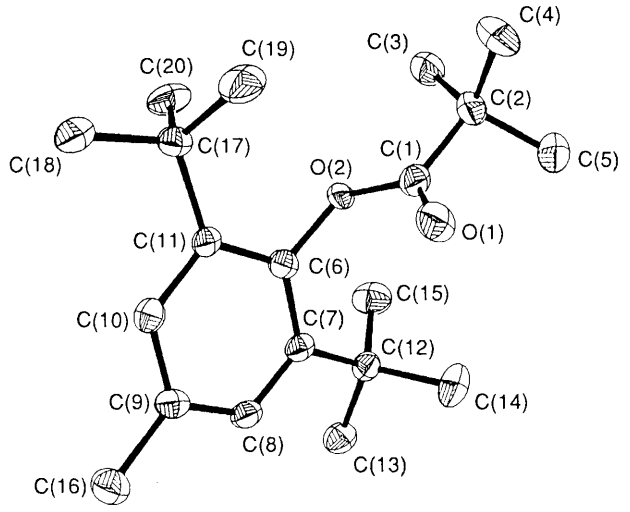


Fig. 3 The molecular structure of O=C(dbmp)Bu^t **12**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for O=C(dbmp)Bu^t **12**

O(1)–C(1)	1.207(2)	O(2)–C(1)	1.362(2)
O(2)–C(6)	1.420(2)	C(1)–C(2)	1.523(3)
C(1)–O(2)–C(6)	117.0(1)	O(1)–C(1)–O(2)	122.9(2)
O(1)–C(1)–C(2)	124.1(2)	O(2)–C(1)–C(2)	113.1(2)

The esters O=C(dbmp)Et **10** and O=C(dbmp)Pr^i **11** have been characterised as side products in the synthesis of **2** and **3** respectively. The ratio of esters **9–11** to the acylation product **1–3** increases with the increasing steric bulk of the alkyl substituent, R, *i.e.*, Me < Et < Pr^i. In fact, when the steric bulk of the alkyl substituent is sufficiently large, *i.e.*, Bu^t, then no acylation of the aryloxide ligand is observed.

Reaction of [AlMe(dbmp)$_2$] with two equivalents of O=C(Cl)Bu^t results in the quantitative formation of O=C(dbmp)Bu^t **12**, with [AlCl$_2$(dbmp){O=C(Me)Bu^t}] **13** isolated as the aluminium-containing product [equation (3)].

$$[AlMe(dbmp)_2] + 2O{=}C(Cl)Bu^t \longrightarrow [AlCl_2(dbmp)\{O{=}C(Me)Bu^t\}] + O{=}C(dbmp)Bu^t \quad (3)$$

If only one equivalent of the acyl chloride is employed an equimolar mixture of **12**, **13** and [AlMe(dbmp)$_2$] is formed. Although they are undoubtedly formed, we have not attempted to isolate the Me, Et and Pr^i derivatives of **13** from their respective reaction mixtures. Compound **13** may also be prepared directly from [AlCl$_2$(dbmp)(OEt$_2$)][6e] and O=C(Me)Bu^t (see Experimental).

The molecular structure of compound **12** is shown in Fig. 3; selected bond lengths and angles are given in Table 3. It has been observed in the X-ray structural determination of aromatic esters that the phenyl ring and the carbonyl group are coplanar, resulting in the conjugation of the π systems.[10] The presence of the sterically hindering *ortho*-Bu^t groups of the dbmp moiety in **12** forces the ester carbonyl group to be oriented perpendicular to the phenyl ring, eliminating the possibility of an extended π system. Thus, the phenol oxygen is conjugated with the carbonyl [O(2)–C(1) 1.362(2) Å] but not the aromatic ring [O(2)–C(6) 1.420(2) Å].

Friedel–Craft Acylation versus *Esterification*.—In the reaction described above, as with any mechanistic discussion of Friedel–Craft acylation there is a dilemma as to whether the effective electrophile is the acylium ion **II** or a polarised complex **I**.[11] Although we have no direct evidence for either structure, the presence of a steric effect[12] on the ratio of acylation *versus* esterification products, and the use of a non-polar solvent, suggests that a polarised complex **I** is the more likely intermediate.

The significant difference in reactivity between O=C(Cl)R (R = Me, Et, Pr^i or Ph) and O=C(Cl)Bu^t is that the steric bulk of the electrophile in the latter is sufficient to inhibit completely electrophilic attack at the *tert*-butyl substituted *ortho*-carbons, and thus acylation does not occur. Instead electrophilic attack occurs at the dbmp oxygen resulting in aryloxide substitution [equation (4)]. The subsequent reaction of the resulting alkyl

$$[AlMe(dbmp)_2] + O{=}C(Cl)Bu^t \longrightarrow [AlMe(Cl)(dbmp)] + O{=}C(dbmp)Bu^t \quad (4)$$

$$[AlMe(Cl)(dbmp)] + O{=}C(Cl)Bu^t \longrightarrow [AlCl_2(dbmp)\{O{=}C(Me)Bu^t\}] \quad (5)$$

chloride, [AlMe(Cl)(dbmp)], with a second equivalent of O=C(Cl)Bu^t gives the dichloro compound, [AlCl$_2$(dbmp)], which complexes with the O=C(Me)Bu^t produced [equation (5)]. The ester formation reaction [equation (4)] can also be described as nucleophilic attack on the co-ordinated acyl chloride by the oxygen lone pair of dbmp.

Experimental

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, New York. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra (4000–600 cm^{-1}) were recorded on a Nicolet DX-5 FTIR spectrometer as Nujol mulls; NMR spectra, in C_6D_6 unless otherwise stated, were recorded on Bruker AM-400 and -500 spectrometers relative to $SiMe_4$. Solution relative molecular mass measurements were made with the use of an instrument similar to that described by Clark.[13] All manipulations were carried out under nitrogen. Solvents were dried, distilled and degassed before use. The compounds [AlMe(dbmp)$_2$][6a] and [AlCl$_2$(dbmp)(OEt$_2$)][14] were prepared as previously described.

[AlMe(dbmp)(bhmap)] **1**.—To a pentane (40 cm^3) solution of [AlMe(dbmp)$_2$] (5.0 g, 10.4 mmol) was added O=C(Cl)Me (0.74 cm^3, 10.39 mmol) *via* a syringe. The resulting yellow solution was allowed to warm to room temperature, at which point a yellow precipitate formed which was filtered and then dried under vacuum. X-Ray quality crystals were obtained after recrystallisation from pentane–Et$_2$O, m.p. 183–184 °C. Yield: 3.39 g, 70%. {Found: C, 73.90; H, 8.90. [AlMe(dbmp)(bhmap)] requires C, 74.65; H, 9.30%}. IR: 1619m, 1579s, 1537s, 1326m, 1298s, 1285s, 1263s, 1249s, 1221m, 1208m, 1197m, 1127w, 1108w, 1027w, 992m, 954w, 944w, 925w, 903s, 874w, 865m, 857m, 845s, 808w, 789m, 778m, 707m, 676m and 660s cm^{-1}. NMR: ^{1}H, δ 7.29 (1 H, s, C_6H, bhmap), 7.27 (2 H, s, C_6H_2, dbmp), 6.72 (1 H, s, C_6H, bhmap), 2.36 (3 H, s, CH_3, dbmp), 1.94 [3 H, s, O=C(CH_3), bhmap], 1.86 (3 H, s, CH_3, bhmap), 1.70 [18 H, s, C(CH_3)$_3$, dbmp], 1.46 [9 H, s, C(CH_3)$_3$] and −0.166 (3 H, s, Al–CH_3): ^{13}C, δ 206.91 (O=C, bhmap), 167.14 (OC, bhmap), 154.39 (OC, dbmp), 143.24, 140.34 (C_6, bhmap), 138.84 (*o*-C, dbmp), 129.82, 126.35 (C_6, bhmap), 126.15 (*m*-C, dbmp), 126.06 (*p*-C, dbmp), 120.94, (C_6, bhmap), 35.32 [*C*(CH_3)$_3$, bhmap], 35.18 [*C*(CH_3)$_3$, dbmp], 31.38 [C(*C*H_3)$_3$, dbmp], 29.64 [C(*C*H_3)$_3$, bhmap], 26.04 [O=C(*C*H_3), bhmap], 21.52 (CH_3, dbmp), 20.57 (CH_3, bhmap) and −10.50 ppm (Al–CH_3).

[AlMe(dbmp)(bhmpp)] **2**.—To a pentane solution (40 cm^3, −78 °C) of [AlMe(dbmp)$_2$] (4.0 g, 8.32 mmol) was added O=C(Cl)Et (0.72 cm^3, 8.32 mmol) *via* a syringe. As the mixture was warmed (*ca.* −40 °C), a large quantity of yellow precipitate

formed. On further warming (0 °C) this precipitate redissolved and a clear yellow solution resulted. On reaching room temperature a second bright yellow precipitate formed. This was filtered, washed once with pentane (15 cm^3) and then dried *in vacuo*, m.p. 169–171 °C. Yield: 2.79 g, 70% {Found: C, 74.45; H, 9.20. [AlMe(dbmp)(bhmpp)] requires C, 74.95; H, 9.45%}. IR: 1620m, 1578s, 1535s, 1310(sh), 1296s, 1274s, 1248s, 1197s, 1125w, 1095w, 1050m, 1024w, 1012w, 990w, 952w, 940w, 930w, 920w, 900s, 860s, 850m, 815m, 770m, 725w, 695(sh), 675s, 655m and 605w cm^{-1}. NMR ^1H, δ 7.31 (1 H, s, C_6H, bhmpp), 7.27 (2 H, s, C_6H_2, dbmp), 6.82 (1 H, s, C_6H, bhmpp), 2.36 (3 H, s, CH_3, dbmp), 2.29 (2 H, m, O=CC$H_2$$CH_3$, bhmpp), 1.98 (3 H, s, CH_3, bhmpp), 1.72 [18 H, s, $C(CH_3)_3$, dbmp], 1.48 [9 H, s, $C(CH_3)_3$, bhmpp], 0.876 [3 H, t, J(H–H) = 7.25 Hz, O=CCH$_2$CH_3, bhmpp] and −0.226 (3 H, s, Al–CH_3); ^{13}C, δ 210.15 (O=C, bhmpp), 166.97 (OC, bhmpp), 154.52 (OC, dbmp), 143.34, 140.0 (C_6, bhmpp), 138.95 (*o*-C, dbmp), 128.98, 128.29 (C_6, bhmpp), 126.32 (*p*-C, dbmp), 126.17 (C_6, bhmpp), 126.07 (*m*-C, dbmp), 120.43 (C_6, bhmpp), 35.39 [$C(CH_3)_3$, bhmpp], 35.20 [$C(CH_3)_3$, dbmp], 31.73 (O=CCH_2, bhmpp), 31.45 [C(CH_3)$_3$, dbmp], 29.66 [C(CH_3)$_3$, bhmpp], 21.54 (CH_3, dbmp), 20.68 (CH_3, bhmpp), 9.13 (O=CCH$_2$$CH_3$, bhmpp) and −10.54 ppm (Al–CH_3).

[AlMe(dbmp)(bhmibp)] **3**.—To a pentane solution (40 cm^3, −78 °C) of [AlMe(dbmp)$_2$] (4.0 g, 8.32 mmol) was added O=C(Cl)Pr^i (0.87 cm^3, 8.32 mmol) *via* a syringe. A beige colour formed. As the reaction mixture warmed slowly a large quantity of beige precipitate formed (*ca.* −40 °C). On further warming this precipitate disappeared and a clear orange solution resulted (*ca.* 0 °C), which lightened to yellow at room temperature. After stirring for a further 1 h, the solution was evaporated to dryness *in vacuo* to leave an oily residue. This was redissolved in the minimum of pentane (*ca.* 20 cm^3) and set aside in the freezer overnight (−20 °C), to give yellow crystals. Colourless crystals of O=C(dbmp)Pr^i were observed, by ^1H NMR, as a minor product. Compound **3**, m.p. 140–142 °C. Yield: *ca.* 2.46 g, 60% {Found: C, 75.65; H, 9.35. [AlMe(dbmp)(bhmibp)] requires C, 75.25; H, 9.55%}. IR: 1621m, 1573s, 1535s, 1314m, 1294m, 1264s, 1247s, 1216s, 1198s, 1157m, 1124w, 1093w, 1055w, 1023w, 1001w, 954w, 927(sh), 919w, 891s, 847s, 832(sh), 801m, 776w, 720m, 675s, 650m, 610w and 460m cm^{-1}. NMR: ^1H, δ 7.33 (1 H, s, C_6H, bhmibp), 7.28 (2 H, s, C_6H_2, dbmp), 7.00 (1 H, s, C_6H, bhmibp), 3.04 [1 H, heptet., J(H–H) = 6.77 Hz, O=CCH(Me)$_2$, bhmibp], 2.36 (3 H, s, CH_3, dbmp), 1.99 (3 H, s, CH_3, bhmibp), 1.73 [18 H, s, $C(CH_3)_3$, dbmp], 1.48 [9 H, s, $C(CH_3)_3$, bhmibp], 0.912 [6 H, d, J(H–H) = 6.7 Hz, O=CH(CH_3)$_2$, bhmibp] and −0.27 (3 H, s, Al–CH_3); ^{13}C, δ 213.67 (O=C, bhmibp), 167.98 (OC, bhmibp), 154.56 (OC, dbmp), 143.62, 140.36 (C_6, bhmibp), 138.96 (*o*-C, dbmp), 128.92 (C_6, bhmibp), 126.52 (*m*-C, dbmp), 126.21 (*p*-C, dbmp), 126.06, 119.43 (C_6, bhmibp), 35.48 [$C(CH_3)_3$, dbmp], 35.25 [$C(CH_3)_3$, bhmibp], 31.49 [C(CH_3)$_3$, dbmp], 29.62 [C(CH_3)$_3$, bhmibp], 21.56 (CH_3, dbmp), 20.57 (CH_3, bhmibp), 20.25 [H$C(CH_3)_2$, bhmibp], 19.75 [HC(CH_3)$_2$, bhmibp] and −10.66 ppm (Al–CH_3).

[AlMe(dbmp)(bhmbp)] **4**.—To a pentane solution (40 cm^3, −78 °C) of [AlMe(dbmp)$_2$] (3.0 g, 6.24 mmol) was added O=C(Cl)Ph (0.72 cm^3, 6.23 mmol) *via* a syringe. As the resulting solution was warmed to room temperature a deep brown colour formed which paled gradually in colour to red and then to bright orange, with some orange precipitate forming. The resulting solution was reduced in volume and cooled (−20 °C) to give more orange precipitate. The solution was filtered and the precipitate dried *in vacuo*, m.p. 176 °C. Yield: 2.30 g, 70% {Found: C, 76.00; H, 8.10. [AlMe(dbmp)(bhmbp)] requires C, 77.25; H, 8.55%}. IR: 1615w, 1596w, 1579w, 1557s, 1527s, 1379s, 1297m, 1273s, 1242s, 1204s, 1155w, 1124w, 1079w, 1036w, 1023w, 994w, 976w, 954w, 917w, 893s, 848s, 833(sh), 810w, 779m, 766(sh), 730m, 691s and 670s cm^{-1}. NMR: ^1H, δ 7.37 (3 H, m, C_6H, bhmbp), 7.26 (2 H, s, C_6H_2, dbmp), 7.04 (1 H, t, *p*-CH, bhmbp), 6.93 (3 H, m, C_6H, bhmbp), 2.35 (3 H, s, CH_3, dbmp), 1.85 (3 H, s, CH_3, bhmbp), 1.70 [18 H, s, $C(CH_3)_3$, dbmp] and −0.09 (3 H, s, Al–CH_3); ^{13}C, δ 202.01 (O=C, bhmbp), 168.57 (OC, bhmbp), 158.44 (OC, dbmp), 143.17, 140.22, 138.88 (*o*-C, dbmp), 136.77, 133.61, 133.21, 131.69, 128.32, 126.30, 126.07, 125.82, 120.88, 35.47 [$C(CH_3)_3$, bhmbp], 34.31 [$C(CH_3)_3$, dbmp], 31.38 [C(CH_3)$_3$, dbmp], 29.65 [C(CH_3)$_3$, bhmbp], 21.57 (CH_3, dbmp), 20.53 (CH_3, bhmbp) and −10.59 ppm (Al–CH_3).

Hbhmap **5**.—To a pentane (40 cm^3) solution of **1** (4.0 g, 8.57 mmol) was added a saturated aqueous solution of NH_4Cl (100 cm^3). The aqueous layer was separated and washed with CH_2Cl_2 (3 × 100 cm^3). Evaporation of the volatiles *in vacuo* and sublimation of the residue (58 °C, 10^{-3} mmHg, 0.133 Pa) gave pale yellow crystals, m.p. 58 °C. Yield: 1.15 g, 65%. (Found: C, 75.90; H, 8.90. Hbhmap requires C, 75.70; H, 8.80%). IR: 1629s, 1552m, 1541m, 1385s, 1359s, 1327s, 1289m, 1269s, 1234s, 1199s, 1181(sh), 1102w, 1043w, 1020m, 968m, 941w, 930m, 855s, 808s, 794s, 774w, 654s, 621w, 583m, 575m, 531m, 507w, 469w and 450w cm^{-1}. NMR: ^1H, δ 13.52 (1 H, s, HO), 7.23, 6.99 (2 H, s, C_6H_2), 2.06 (3 H, s, CH_3), 2.02 [3 H, s, O=C(CH_3)] and 1.50 [9 H, s, $C(CH_3)_3$]; ^{13}C, δ 204.83 (O=C), 160.74, 138.74, 134.69, 128.55, 126.64, 119.74, (C_6H), 35.07 [$C(CH_3)_3$], 29.63 [C(CH_3)$_3$], 26.35 (O=CCH_3) and 20.77 ppm (CH_3). Relative molecular mass (Et_2O): 173 (calc. 194).

Hbhmpp **6**.—Prepared as for **5** but using **2**. NMR: ^1H, δ 13.60 (1 H, s, OH), 7.24 (1 H, s, C_6H), 7.06 (1 H, s, C_6H), 2.41 [2 H, q, J(H–H) = 7.24, C$H_2$$CH_3$], 2.11 (3 H, s, CH_3), 1.51 [9 H, s, $C(CH_3)_3$] and 0.95 [3 H, t, J(H–H) = 7.2 Hz, CH_2CH_3]; ^{13}C, δ 204.11 (O=C), 160.66, 138.65, 134.42, 128.40, 127.66, 119.15 (C_6), 35.09 [$C(CH_3)_3$], 31.56 (O=C$H_2$$CH_3$), 29.60 [C($CH_3$)$_3$], 20.94 ($CH_3$) and 8.28 ppm (O=$CH_2CH_3$).

Hbhmibp **7**.—Prepared as for **5** but using **3**. NMR: ^1H, δ 13.92 (1 H, s, OH), 7.23 (1 H, s, C_6H), 7.07 (1 H, s, C_6H), 3.12 [1 H, m, CH(CH_3)$_2$], 2.17 (3 H, s, CH_3), 1.53 [9 H, s, $C(CH_3)_3$] and 0.97 [6 H, d, J(H–H) = 6.83 Hz, CH(CH_3)$_3$]; ^{13}C, δ 204.22 (O=C), 168.91, 137.02, 134.65, 128.44, 127.89, 118.34 (C_6), 35.39 [$C(CH_3)_3$], 31.63 [C(CH_3)$_3$], 21.15 (CH_3), 19.41 [H$C(CH_3)_2$] and 18.88 ppm [HC(CH_3)$_3$].

Hbhmbp **8**.—To a pentane (40 cm^3) solution of **4** (5.0 g, 9.45 mmol) was added a saturated aqueous solution of NH_4Cl (100 cm^3). The aqueous layer was separated and washed with Et_2O (5 × 100 cm^3). The combined organic fractions were dried with anhydrous $MgSO_4$, filtered and then reduced in volume to *ca.* 150 cm^3. An orange precipitate formed which was filtered off, washed with pentane (2 × 50 cm^3) and dried *in vacuo*, m.p. >240 °C. Yield: *ca.* 1.90 g, 75% (Found: C, 79.35; H, 7.25. Hbhmbp requires C, 80.55; H, 7.50%). IR: 3675m, 1615s, 1575s, 1540s, 1500s, 1260s, 1210w, 1185w, 1160w, 1150w, 1075w, 1035m, 1010s, 1000(sh), 945w, 855w, 830w, 790w, 730s, 690s, 635m and 555m cm^{-1}. NMR: ^1H, δ 12.67 (1 H, s, HO), 7.62 [2 H, d, J(H–H) = 7.25, *o*-CH], 7.55 [1 H, t, J(H–H) = 7.25, *p*-CH], 7.47 [2 H, t, J(H–H) = 7.25 Hz, *m*-CH], 7.30, 7.18 (1 H, s, C_6H_2), 2.21 (3 H, s, CH_3) and 1.43 [9 H, s, $C(CH_3)_3$]; ^{13}C, δ 202.49 (O=C), 160.87, 138.67, 138.41, 134.83, 131.47, 131.25, 129.04, 128.20, 126.47, 118.65 (C_6H), 34.91 [$C(CH_3)_3$], 29.36 [C(CH_3)$_3$] and 20.82 ppm (CH_3). Relative molecular mass (tetrahydrofuran): 296 (calc. 268).

O=C(dbmp)Me **9**.—A solution of **1** (16.0 g, 34.28 mmol), prepared as described above, was hydrolysed with a saturated aqueous solution of NH_4Cl (200 cm^3). The aqueous layer was extracted with Et_2O (5 × 100 cm^3) and the organic layers combined. These were dried with anhydrous $MgSO_4$, filtered and then reduced in volume to leave a green oil. Thin-layer chromatography (silica plates with pentane as eluent) showed the presence of Hdbmp **5** and a third species. Column

Table 4 Summary of X-ray diffraction data

Compound	**1**	**5**	**12**
Formula	$C_{29}H_{43}AlO_3$	$C_{13}H_{18}O_2$	$C_{20}H_{32}O_2$
M	466.64	206.28	304.47
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	*Pnma*	$P2_1/n$
a/Å	15.698(5)	9.3136(4)	9.239(5)
b/Å	9.613(2)	7.1177(3)	21.735(7)
c/Å	19.420(3)	17.7719(7)	9.294(3)
β/°	101.70(2)		96.43(4)
U/Å^3	2870(1)	1178.12(8)	1854(1)
Z	4	4	4
D_c/g cm^{-3}	1.084	1.167	1.090
F(000)	1016	448	672
Crystal dimensions	0.18 × 0.22 × 0.72	0.31 × 0.32 × 0.98	0.15 × 0.33 × 0.21
T/°C	25	25	−78
Radiation	Mo-Kα	Cu-Kα	Mo-Kα
λ/Å	0.710 73	1.5418	0.710 73
μ/cm^{-1}	0.91	5.76	6.30
2θ limits/°	2.0–50.0	2.0–110.0	4.0–55.0
No. of collected data	5680	927	2689
No. of unique data	5473	927	2425
Observed data	1994	704	2197
Criterion for observed data	$F > 6\sigma(F)$	$F > 6\sigma(F)$	$F > 4\sigma(F)$
R^a	0.0657	*0.0695*	0.0668
R'^b	0.0664	*0.0788*	0.1069
Maximum final residual/e Å^{-3}	0.34	*0.26*	0.20

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = [(\sigma F)^2]$ for **1** and **5**; $w^{-1} = \sigma^2(|F_o|) + 0.027\,01(|F_o|^2)$ for **12**.

Table 5 Fractional atomic coordinates for [AlMe(dbmp)(bhmap)] **1**

Atom	X/a	Y/b	Z/c
Al	0.8367(1)	0.2520(2)	0.0352(1)
O(1)	0.8058(3)	0.3594(5)	0.0996(2)
O(2)	0.9503(3)	0.2371(5)	0.0822(2)
O(3)	0.8399(3)	0.3435(5)	−0.0395(2)
C(1)	0.8454(4)	0.3811(7)	0.1661(3)
C(2)	0.7976(4)	0.4381(7)	0.2133(3)
C(3)	0.8432(5)	0.4614(8)	0.2823(4)
C(4)	0.9313(5)	0.4277(8)	0.3060(4)
C(5)	0.9760(4)	0.3743(7)	0.2601(3)
C(6)	0.9344(4)	0.3448(7)	0.1888(3)
C(7)	0.9844(4)	0.2837(6)	0.1435(3)
C(11)	0.8276(4)	0.3707(7)	−0.1097(3)
C(12)	0.8910(4)	0.3360(7)	−0.1473(3)
C(13)	0.8757(4)	0.3705(7)	−0.2195(3)
C(14)	0.8011(4)	0.4397(7)	−0.2520(3)
C(15)	0.7405(4)	0.4735(7)	−0.2138(3)
C(16)	0.7508(4)	0.4459(7)	−0.1421(3)
C(21)	0.7021(5)	0.4771(8)	0.1915(4)
C(22)	0.6651(5)	0.5313(9)	0.2523(4)
C(23)	0.6897(6)	0.5892(9)	0.1345(4)
C(24)	0.6492(5)	0.3448(9)	0.1633(5)
C(41)	0.9736(6)	0.461(1)	0.3816(4)
C(71)	1.0803(4)	0.2630(8)	0.1624(4)
C(121)	0.9761(4)	0.2612(7)	−0.1147(3)
C(122)	1.0288(4)	0.3517(7)	−0.0551(3)
C(123)	0.9586(5)	0.1182(7)	−0.0874(4)
C(124)	1.0361(4)	0.2402(9)	−0.1668(3)
C(141)	0.7890(5)	0.4793(9)	−0.3283(3)
C(161)	0.6834(4)	0.4932(8)	−0.1011(4)
C(162)	0.7261(5)	0.6020(9)	−0.0460(4)
C(163)	0.6443(5)	0.379(1)	−0.0658(4)
C(164)	0.6068(5)	0.569(1)	−0.1492(4)
Me(1)	0.7806(5)	0.0721(7)	0.0274(4)

chromatography (pentane) removed the Hdbmp; subsequent elution with increasingly polar solvent mixtures (pentane–CH_2Cl_2) removes **5** and finally the ester O=C(dbmp)Me. Sublimation of the crude material (67 °C, 10^{-3} mmHg, 0.133 Pa) yielded pure white crystals, m.p. 67 °C. Yield: 1.8 g, 20% [Found: C, 78.15; H, 10.20. O=C(dbmp)Me requires C, 77.80;

Table 6 Fractional atomic coordinates for Hbhmap **5**

Atom	X/a	Y/b	Z/c
O(1)	0.8585(4)	0.2500	0.4718(2)
O(2)	0.7661(6)	0.2500	0.3371(3)
C(1)	0.7192(6)	0.2500	0.4944(3)
C(2)	0.6896(6)	0.2500	0.5717(3)
C(3)	0.5461(6)	0.2500	0.5919(3)
C(4)	0.4325(6)	0.2500	0.5412(3)
C(5)	0.4649(6)	0.2500	0.4666(3)
C(6)	0.6078(6)	0.2500	0.4408(3)
C(7)	0.6411(8)	0.2500	0.3601(4)
C(21)	0.8111(6)	0.2500	0.6307(4)
C(22)	0.7538(8)	0.2500	0.7111(4)
C(23)	0.9051(5)	0.0722(7)	0.6204(3)
C(41)	0.2779(6)	0.2500	0.5670(4)
C(71)	0.5232(9)	0.2500	0.3028(4)

Table 7 Fractional atomic coordinates for O=C(dbmp)Bu^t **12**

Atom	X/a	Y/b	Z/c
O(1)	0.2420(2)	0.2307(1)	1.0327(1)
O(2)	0.1904(1)	0.1309(1)	0.9829(1)
C(1)	0.1701(2)	0.1925(1)	0.9627(2)
C(2)	0.0497(2)	0.2076(1)	0.8422(2)
C(3)	−0.0348(2)	0.1515(1)	0.7805(3)
C(4)	−0.0541(3)	0.2536(1)	0.9020(3)
C(5)	0.1225(3)	0.2393(1)	0.7214(3)
C(6)	0.3026(2)	0.1124(1)	1.0914(2)
C(7)	0.4444(2)	0.1054(1)	1.0527(2)
C(8)	0.5523(2)	0.0934(1)	1.1663(2)
C(9)	0.5229(2)	0.0851(1)	1.3071(2)
C(10)	0.3786(2)	0.0858(1)	1.3357(2)
C(11)	0.2651(2)	−0.0994(1)	1.2295(2)
C(12)	0.4863(2)	0.1081(1)	0.8956(2)
C(13)	0.6246(2)	0.0697(1)	0.8842(2)
C(14)	0.5185(3)	0.1746(1)	0.8540(2)
C(15)	0.3689(2)	0.0795(1)	0.7866(2)
C(16)	0.6445(2)	0.0746(1)	1.4276(2)
C(17)	0.1053(2)	0.0951(1)	1.2658(2)
C(18)	0.0987(2)	0.0732(1)	1.4215(2)
C(19)	0.0271(3)	0.1565(1)	1.2506(3)
C(20)	0.0238(2)	0.0468(1)	1.1655(3)

H, 10.00%]. IR: 1807m, 1766s, 1754(sh), 1598m, 1270s, 1223s, 1202s, 1186s, 1138m, 1108s, 1040m, 1004m, 948w, 925m, 904s, 889s, 860s, 817m, 802m, 741w, 640s, 623w, 585m, 568m, 496m and 468w cm^{-1}. NMR: ^1H, δ 7.08 (2 H, s, C_6H_2), 2.16 (3 H, s, CH_3), 1.94 (3 H, s, O=CCH$_3$) and 1.32 [18 H, s, C(CH$_3$)$_3$]; ^{13}C, δ 170.16 (O=C), 146.55, 142.30, 134.35, 127.12 (C_6H), 35.34 [*C*(CH$_3$)$_3$], 31.72 [C(*C*H$_3$)$_3$], 22.25 [O=C(*C*H$_3$)] and 21.50 ppm (CH_3).

O=C(dbmp)Et **10**.—Prepared as for **9**. NMR: ^1H ($CDCl_3$), δ 7.13 (2 H, s, C_6H_2, dbmp) 2.83 [1 H, heptet., J(H–H) = 7.0 Hz, C*H*(CH$_3$)$_2$], 2.30 (3 H, s, CH_3, dbmp), 1.35 [6 H, d, CH(C*H*$_3$)$_2$] and 1.30 [18 H, s, C(CH$_3$)$_3$, dbmp].

O=C(dbmp)Pr^i **11**.—Prepared as for **9**. NMR: ^1H ($CDCl_3$), δ 7.03 (2 H, s, C_6H_2, dbmp), 2.63 [2 H, q, J(H–H) = 7.0, C*H*$_2$CH$_3$], 2.28 (3 H, s, CH_3, dbmp), 1.30 [3 H, t, J(H–H) = 7.0 Hz, CH$_2$C*H*$_3$] and 1.00 [18 H, s, C(CH$_3$)$_3$, dbmp].

Reaction of [AlMe(dbmp)$_2$] *with* O=C(Cl)Bu^t.—The compound O=C(Cl)Bu^t (2.0 cm^3, 16.94 mmol) was added *via* a syringe to [AlMe(dbmp)$_2$] (4.0 g, 8.32 mmol) in pentane (*ca.* 30 cm^3) at room temperature. A light orange colour formed. The resulting solution was allowed to stir overnight after which the solvent was removed *in vacuo*. The residue was redissolved in pentane (30 cm^3) and set aside in the freezer (−20 °C). Crystalline O=C(dbmp)Bu^t **12** was obtained and dried *in vacuo*. The filtrate was reduced in volume to *ca.* 10 cm^3 and cooled (−20 °C) to give white crystals of [AlCl$_2$(dbmp){O=C(Me)Bu^t}] **13** (see below).

O=C(dbmp)Bu^t **12**.—M.p. 116–118 °C. Yield: 1.77 g, 70% [Found: C, 78.55; H, 10.40. O=C(dbmp)Bu^t requires C, 78.90; H, 10.60%]. IR: 1781w, 1738s, 1723(sh), 1696w, 1631w, 1597m, 1267s, 1231m, 1216s, 1199s, 1182s, 1119s, 1103s, 1033s, 977w, 942m, 924w, 890s, 857s, 832w, 810w, 768m, 761s, 743s, 722w, 641w, 598m, 569m, 528m, 470m, 447w and 429w cm^{-1}. NMR ^1H, δ 7.08 (2 H, s, C_6H_2, dbmp), 2.12 (3 H, s, CH_3, dbmp) and 1.32 [27 H, s, C(C*H*$_3$)$_3$]; ^{13}C, δ 177.44 (O=C), 147.85 (OC, dbmp), 142.48 (*o*-C, dbmp), 134.33 (*p*-C, dbmp), 127.19 (*m*-C, dbmp), 39.55 [*C*(CH$_3$)$_3$], 35.50 [*C*(CH$_3$)$_3$, dbmp], 31.68 [C(*C*H$_3$)$_3$, dbmp], 28.15 [C(*C*H$_3$)$_3$] and 21.42 ppm (*C*H$_3$, dbmp).

[AlCl$_2$(dbmp){O=C(Me)Bu^t}] **13**.—To a suspension of [AlCl$_2$(dbmp)(OEt$_2$)] (2.0 g, 4.79 mmol) in pentane (40 cm^3) was added O=C(Me)Bu^t (0.66 cm^3, 5.7 mmol) *via* a syringe. The resulting suspension was stirred for 0.5 h, after which time the solvent was removed under vacuum. The resulting white solid was washed with pentane (30 cm^3) and then dried *in vacuo*, m.p. 110–112 °C. Yield: 1.5 g, 75% (Found: C, 61.30; H, 8.50. [AlCl$_2$(dbmp){O=C(Me)Bu^t}] requires C, 60.40; H, 8.45%). IR: 1640s, 1300(sh), 1270(sh), 1250s, 1230m, 1215s, 1200(sh), 1135m, 1050w, 965w, 936w, 900(sh), 885s, 870m, 825w, 785w, 720m, 672s, 648(sh) and 592w cm^{-1}. NMR: ^1H, δ 7.19 (2 H, s, C_6H_2, dbmp), 2.29 (3 H, s, CH_3, dbmp), 2.17 [3 H, s, O=C(CH$_3$)], 1.61 [18 H, s, C(CH$_3$)$_3$, dbmp] and 0.65 [9 H, s, C(CH$_3$)$_3$]; ^{13}C, δ 242.83. (O=C), 152.94 (OC, dbmp), 139.10 (*o*-C, dbmp), 126.28 (*m*-C, dbmp), 126.16 (*p*-C, dbmp), 47.39 [O=C(*C*H$_3$)], 35.00 [*C*(CH$_3$)$_3$, dbmp], 31.61 [C(*C*H$_3$)$_3$, dbmp], 27.67 [*C*(CH$_3$)$_3$], 25.68 [C(*C*H$_3$)$_3$, dbmp] and 21.42 ppm (CH$_3$, dbmp).

Crystallography.—Crystals of compounds **1** or **5** were sealed in a glass capillary under argon and mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Final lattice parameters, as determined from a least-squares fit of the setting angles of 25 accurately centred reflections (2θ > 35° for **1** and > 70° for **5**) are given in Table 4. Typical data collection procedures in our laboratory have been described previously.[15] Examination of the data, which was corrected for Lorentz and polarization effects, but not for absorption, revealed the space groups to be $P2_1/n$ for **1** and either $Pn2_1a$ or $Pnma$ for **5** (the latter was chosen on the basis of intensity statistics and refinement).

Structure solution was accomplished readily by using the direct methods option of SHELXS,[16] through which the bulk of the molecules were located. The remaining atomic coordinates were determined through the generation of difference Fourier maps using SHELX-76.[17]

Treatment of all non-aromatic non-hydrogen atoms for **1** and all non-hydrogen atoms for **5** with anisotropic thermal parameters permitted the location of all the hydrogens. These were included in the final model with fixed thermal parameters and constrained to 'ride' upon the appropriate atoms. Final residuals are also listed in Table 4. Scattering factors were taken from ref. 18. Final atomic positional parameters are given in Tables 5 and 6.

A crystal of compound **12** was mounted directly onto the goniometer with silicon grease. Unit-cell parameters and intensity data were obtained, by following previously detailed procedures,[6a] using a Nicolet R3m/v diffractometer operating in the θ−2θ scan mode. Empirical absorption corrections were applied to the data using the program PSICOR.[16] Further experimental data are given in Table 4.

The structure was solved using the direct methods program SHELXS,[16] which revealed the positions of the carbon and oxygen atoms. Most, but not all of the hydrogens were visible in the final difference map. Hydrogens were included as fixed atom contributors in the final cycle (C–H 0.96 Å).

Details of the refinement are given in Table 4. Atomic scattering factors and anomalous scattering parameters are as given in ref. 18. Final atomic positional parameters are given in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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