Synthesis of Bis(phosphinomethyl)amines *via* Bis(hydroxymethyl)phosphonium Salts. Isolation of 9,9-Bis(hydroxymethyl)-9-phosphoniabicyclo[3.3.1]nonane Hydrogensulfate and Chloride Salts, and the Crystal Structures of $[PPh_2(CH_2OH)_2]^+Cl^-$ and $[(C_6H_{11})_2PCH_2]_2NCHMePh$†

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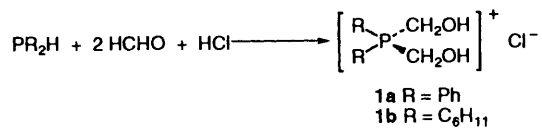
Phosphines of the type PR_2H reacted readily with formaldehyde in the presence of acid to afford high yields of bis(hydroxymethyl)phosphonium salts $[PPh_2(CH_2OH)_2]^+X^-$, $[P(C_6H_{11})_2(CH_2OH)_2]^+X^-$, $[CH_2CH_2CH_2CH_2CHP(CH_2OH)_2CHCH_2CH_2]^+X^-$, and $[CH_2CH_2CH_2CHP(CH_2OH)_2CHCH_2CH_2CH_2]^+X^-$ (X = Cl or HSO_4). Treatment of the mixed isomers of the bicyclononane phosphonium cation $[P(C_8H_{14})(CH_2OH)_2]^+$ in boiling H_2SO_4 gave a [3.3.1] isomer, the [4.2.1] isomer undergoing decomposition. A single-crystal X-ray diffraction study has been carried out on the phosphonium salt $[PPh_2(CH_2OH)_2]^+Cl^-$. The geometry around phosphorus is essentially tetrahedral, and there is hydrogen bonding between the hydroxyl groups and the chloride anion. Treatment of these phosphonium salts with triethylamine and a primary or secondary amine afforded aminomethylphosphines $(R_2PCH_2)_2NR'$ (R = Ph, R' = CHMePh, $CHMeCO_2Me$, $CHMeCO_2Et$, $CHCH_2CHCH_2CH_2CMeCMe_2$, CH_2CH_2OH or $CH_2CH{=}CH_2$; R = C_6H_{11}, R' = CHMePh or $CHMeCO_2H$; R_2 = C_8H_{14}, R' = CHMePh) or $C_8H_{14}PCH_2NEt_2$ in good yields. A single-crystal X-ray diffraction study has been carried out on $[(C_6H_{11})_2PCH_2]_2NCHMePh$.

Aminomethylphosphines have been known for some 30 years since the discovery by Coates and Hoye[1] that hydroxymethylphosphines react with primary and secondary amines to give aminomethylphosphines. Since then aminomethylphosphines have been used in various commercial applications such as flame retardants[2,3] and metal sequestrants.[4,5] Various aminomethylphosphines have been prepared to date,[6–8] including compounds with cage structures[9] and with chiral centres at phosphorus.[10] Despite this interest almost all published aminomethylphosphine chemistry concentrates on phenyl- and diphenyl-substituted phosphines, and characterisation details have been minimal with almost no elemental analysis or phosphorus NMR data. The most favoured route to aminomethylphosphines has been the modified Mannich reaction using hydroxymethylphosphines or hydroxymethylphosphonium salts as the key starting materials. The reaction of new hydroxymethylphosphonium salts, having alkyl or aryl substituents on phosphorus, with a variety of primary amines leads to new functionalised phosphines.

Results and Discussion

Bis(hydroxymethyl)phosphonium chloride salts **1** were prepared in quantitative yields (95–99%) by treatment of a secondary phosphine, PPh_2H or $P(C_6H_{11})_2H$, with aqueous formaldehyde and concentrated hydrochloric acid, Scheme 1. The compounds are highly crystalline white solids which are



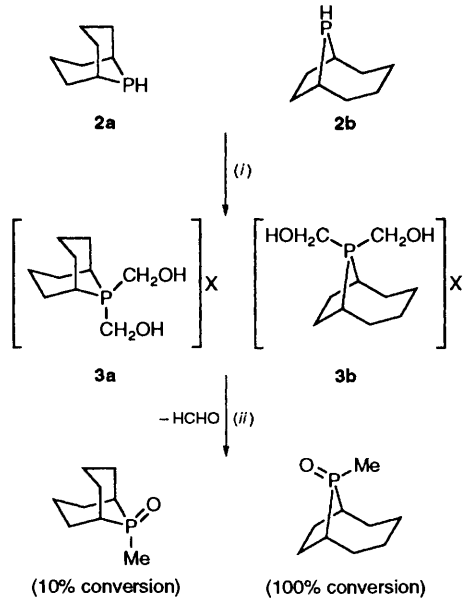
1a R = Ph
1b R = C_6H_{11}

Scheme 1

soluble only in polar solvents such as water or methanol. The phenyl derivative **1a** has been reported previously[11] although only the melting point and phosphorus analysis were given for characterisation. The melting point obtained for **1a** is in agreement with that previously obtained; 162 °C (lit.,[11] 165 °C). The bis[bis(hydroxymethyl)phosphonium] sulfate and [bis(hydroxymethyl)phosphonium] hydrogensulfate salts **3a** and **3b** were also prepared by treating the mixed isomers of $C_8H_{14}PH$ **2** with aqueous formaldehyde and concentrated sulfuric acid, Scheme 2. Despite the presence of both HSO_4^- and SO_4^{2-} salts, the ^{31}P NMR spectrum shows only two signals corresponding to the [3.3.1] and [4.2.1] isomers. Interestingly, the chemical shifts following quaternisation are significantly different for each isomer, δ −54.6 (**2a**), −49.2 (**2b**), +23.4 (**3a**) and +55.7 (**3b**). The chemical shift differences between the isomers **3a** and **3b** were taken to indicate a difference in the properties of the two isomeric species. Work by Hoye[12] has shown that phosphonium sulfate/hydrogen sulfate salts can be decomposed to give methylphosphine oxide compounds by refluxing in sulfuric acid and removal of formaldehyde. Using this method the phosphonium salts **3a** and **3b** were refluxed at 150 °C in 36% sulfuric acid, Scheme 2. The reaction mixture was monitored by ^{31}P NMR spectroscopy, revealing the formation of the [3.3.1] and [4.2.1] isomers of the decomposition product $(C_8H_{14})P(O)Me$ at δ 56.0 and 88.0

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

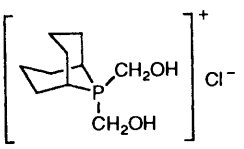
Non-SI unit employed: mmHg ≈ 133 Pa.



Scheme 2 X = HSO_4^- or $\frac{1}{2}SO_4^{2-}$. (*i*) HCHO, 98% H_2SO_4; (*ii*) 36% H_2SO_4, 150 °C, 13 h

Table 1 Selected bond lengths (Å), angles (°) and non-bonded contacts (Å) with estimated standard deviations (e.s.d.s) in parentheses for the phosphonium salt $[PPh_2(CH_2OH)_2]^+Cl^-$

C(2)–P–C(1)	107.8(3)	C(21)–P–C(2)	110.6(2)
C(21)–P–C(1)	108.8(2)	C(31)–P–C(21)	111.3(2)
C(31)–P–C(1)	111.2(2)	O(1)–C(1)–P	110.6(4)
C(31)–P–C(2)	107.1(2)	O(2)–C(2)–P	112.1(4)
C(1)–P	1.822(5)	C(1)–O(1)	1.400(7)
C(2)–P	1.838(6)	C(2)–O(2)	1.409(7)
C(21)–P	1.786(3)	H(1)–O(1)	0.79(7)
C(31)–P	1.781(3)	H(2)–O(2)	0.68(8)
H(1) · · · Cl	2.227	O(1) · · · Cl	3.020
H(2) · · · Cl	2.367	O(2) · · · Cl	3.030



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respectively. After a reaction time of 13 h the spectrum of the mixture showed total conversion of **3b** into the corresponding methylphosphine oxide and only about 10% conversion of **3a**. Compound **3a** was then isolated by recrystallisation in a 79.4% yield based on the original isomer ratio of [3.3.1]:[4.2.1] = 58.5:41.5. It was thought, from molecular models, that the [4.2.1] isomer **3b** would be less stable than typical hydroxymethylphosphonium sulfate salts due to apparent bond strain about phosphorus. However, the present studies show that it has similar reactivity to other hydroxymethylphosphonium sulfate salts under the given conditions, whereas isomer **3a** appears less reactive than was predicted. This is probably due to the stability of the two six-membered heterocyclic rings present in the symmetrical isomer of $C_8H_{14}PH$. Various derivatives of the [3.3.1] and [4.2.1] isomers of $C_8H_{14}PH$ have been reported over the past 25 years.[13] In all these studies the compounds are a mixture of isomers. The present work thus provides the first example of a derivative of 9-phosphabicyclo[3.3.1]nonane being isolated from its [4.2.1]

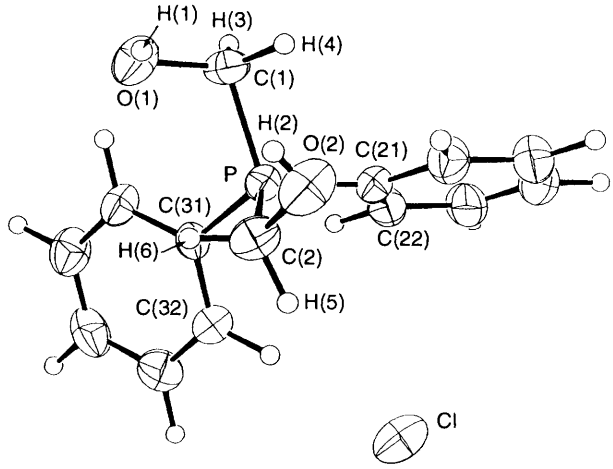
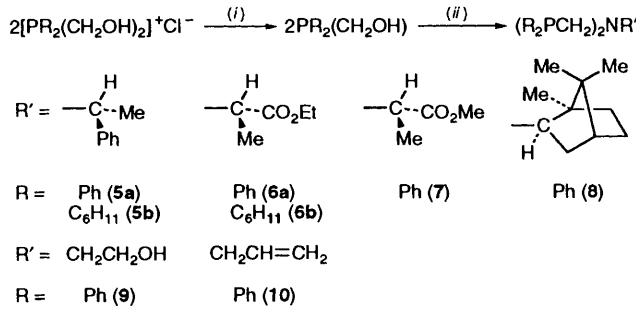


Fig. 1 Molecular structure of $[PPh_2(CH_2OH)_2]^+Cl^-$

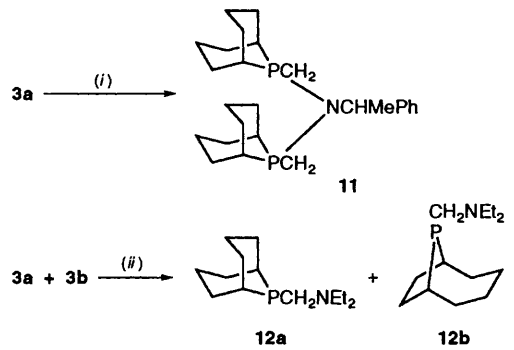


Scheme 3 (*i*) NEt_3; (*ii*) $NR'H_2$, water–methanol, 60 °C, 1–3 h

isomer. By treating a hot aqueous solution of the salt **3a** with barium chloride the corresponding chloride salt **4** was readily obtained.

As the phosphonium salts **1a**, **1b**, **3a**, **3b** and **4** were so highly crystalline, an X-ray diffraction study was carried out on $[PPh_2(CH_2OH)_2]^+Cl^-$ **1a**. The molecular structure is shown in Fig. 1 and selected bond lengths and angles in Table 1. The compound exists as a quaternary phosphonium cation with a chloride anion. Intermolecular contacts are indicated by the short distances of the H(1) · · · Cl and H(2) · · · Cl non-bonded contacts (Table 1). The O · · · Cl distances are also typical for OH · · · Cl hydrogen bonds of 2.99–3.05 Å.[14] The geometry around phosphorus is essentially tetrahedral, with the C–P–C angles in the range 107.1–111.3°. The P–C(1) and P–C(2) bond lengths of 1.822(5) and 1.838(6) Å are comparable to those reported for tertiary phosphonium alkyls of 1.800(15) Å.[15] The P–C(21) and P–C(31) bond distances of 1.786(3) and 1.781(3) Å also compare with those typical for tertiary phosphonium aryl compounds of 1.793(11) Å.[15] The C(1)–O(1) and C(2)–O(2) bond lengths of 1.400(7) and 1.409(7) Å appear slightly short when compared to typical CH_2–OH bond distances of 1.426(11) Å,[15] but this is presumably a consequence of the presence of the positively charged phosphonium ion which would have the effect of shortening these bonds.

The phosphines **5a**, **6a** and **7**–**10** were prepared by treating the phosphonium salt **1** with triethylamine followed by addition of a primary amine NRH_2, and gentle reflux for 1 h in a methanol–water solution, Scheme 3. The amines used were (*R*)-(+)-1-methylbenzylamine (**5a**), L-alanine ethyl ester (**6a**), L-alanine methyl ester (**7**), (*R*)-(+)-bornylamine (**8**), ethanolamine (**9**) and allylamine (**10**). The phosphines **5b** and **6b** were prepared in a similar fashion by treating the phosphonium salt **1b** with triethylamine and a primary amine $NR'H_2$. The compounds were mainly isolated as highly viscous oils with yields in the range 61–95%. Triethylamine and solvents evident in the ^1H NMR spectra of the crude oils required long periods (10–100 h)



Scheme 4 (*i*) NEt_3, then $H_2NCHMePh$; (*ii*) NEt_3, then NEt_2H

under high vacuum, with warming, for complete removal. The phosphine **6a**, however, was isolated as a white solid after several days under high vacuum. The phosphine **5b** was isolated by addition of methanol to a solution of it in toluene at 15 °C to give large colourless crystals in 56% yield. Attempts to recrystallise **6a**, or to induce crystallisation in **5a**, **6b** and **7**–**10** using the solvents dichloromethane–light petroleum, toluene–methanol and boiling Pr^iOH, were unsuccessful. The mass spectrum of **5b** showed peaks at *m*/*z* 541, corresponding to the molecular ion, and at 211, assigned to the fragment $[(C_6H_{11})_2PCH_2]^+$. The phosphine **11** was prepared by treating the pure [3.3.1] isomer of the phosphonium salt **3a** with triethylamine to form the hydroxymethylphosphine $(C_8H_{14})PCH_2OH$. This was extracted with toluene and refluxed for 3 h in the presence of (*R*-(±)-1-phenylethylamine, Scheme 4. Significantly more forcing conditions were required to prepare **11** than for the other isostructural aminophosphines **5a**–**10**. This may be due to the presence of bulky $C_8H_{14}P$ and NCH(Me)Ph units. In contrast the mixed-phosphine isomers **12a** and **12b** were readily prepared by treating the mixed phosphonium salt isomers **3a** and **3b** with tri- and di-ethylamine in a water–methanol solution at 60 °C, to give [3.3.1] and [4.2.1] isomers **12a** and **12b** in 84% yield with an isomeric ratio of 3 : 5, Scheme 4. The hydroxymethylphosphine intermediates $PPh_2(CH_2OH)$, $P(C_6H_{11})_2(CH_2OH)$ and $P(C_8H_{14})(CH_2OH)$, [3.3.1] isomer were monitored in their respective reaction mixtures by ^{31}P NMR spectroscopy using single peaks at δ −12.0, −0.4 and +1.0 respectively. The phosphines **5a**, **6a** and **7** have been reported previously[7,16–18] although not in any detail, **5a** only in metal complexes with no NMR or analytical data being given.[17] Phosphine **7** has been reported in rhodium(I) complexes but no data for the free phosphine were cited.[18]

The ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectra of the aminomethylphosphines are given in the Experimental section. In phenyl-substituted phosphines there is a deshielding of the PCH_2N protons as compared to the cyclohexyl derivatives, which can be attributed to the deshielding effect of the phenyl rings as has been observed previously in organophosphines.[19] The ^1H NMR spectra of phosphines **5**–**8** also showed interesting features. In particular, the diastereotopic CH_2 groups appeared as an AB pattern[20] with the low-frequency side exhibiting a larger coupling to phosphorus; the phosphorus–proton coupling was confirmed by ^{31}P-{^1H} heteronuclear shift correlation NMR spectra. Asymmetric ABX spin systems have been previously observed in aminophosphines,[16,17,21] and in these and other organophosphorus compounds $^2J(PH)$ is much larger when the coupled proton lies close to the orbital of the phosphorus(III) lone pair and is small when remote.[19,21] In view of the availability of crystals of **5b** it was therefore of interest to investigate its structure to determine the orientation of the α-methylene protons with respect to phosphorus.

The molecular structure of compound **5b** is illustrated in Fig. 2, and selected bond lengths and angles are shown in Table 2. Fig. 2 gives a view looking down onto the nitrogen lone pair. The diagram clearly shows the geometry of the bulky

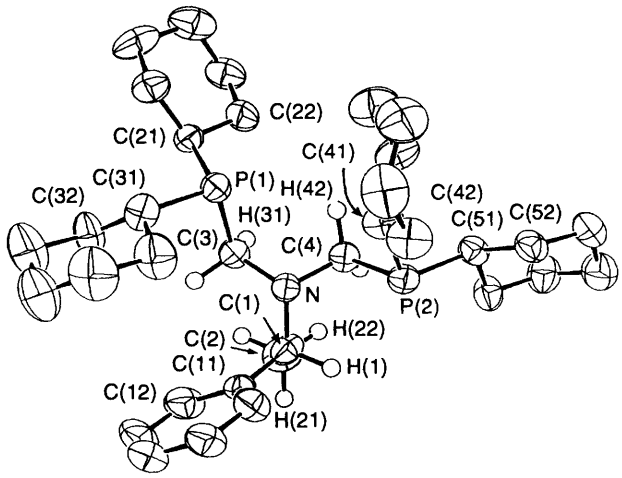


Fig. 2 Molecular structure of $[(C_6H_{11})_2PCH_2]_2NCHMePh$. All cyclohexyl and phenyl H atoms have been omitted

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for $[(C_6H_{11})_2PCH_2]_2NCHMePh$

C(21)–P(1)–C(3)	100.1(2)	C(41)–P(2)–C(4)	97.8(2)
C(31)–P(1)–C(3)	101.5(2)	C(3)–N–C(1)	113.7(4)
C(31)–P(1)–C(21)	104.2(2)	C(4)–N–C(1)	112.7(4)
C(51)–P(2)–C(4)	99.9(2)	C(4)–N–C(3)	110.8(4)
C(51)–P(2)–C(41)	106.8(2)		
C(3)–P(1)	1.856(5)	P(1)–C(21)	1.850(5)
C(4)–P(2)	1.861(4)	P(1)–C(31)	1.862(6)
C(4)–N	1.477(6)	P(2)–C(41)	1.875(5)
C(3)–N	1.483(5)	P(2)–C(51)	1.865(5)
C(1)–N	1.475(6)		

substituents about the central atom. The C–N–C bond angles [110.8(4)–113.7(4)°] reflect the presence of bulky substituents about nitrogen as compared to NH_3, with H–N–H bond angles (106.8°),[22] but are far from the near planarity of the extremely bulky $N(SiMe_3)_3$, Si–N–Si 119.6°.[23] The C–P–C angles between phosphorus cyclohexyl groups are large [104.2(2)–106.8(2)°], typically comparable to those in PBu^t_3 (105.7°).[24] The other C–P–C angles between cyclohexyl groups and PCH_2N carbon atoms C(3) and C(4) are more moderate [97.8(2)–101.5(2)°], being only slightly larger than in PMe_3 (98.9°).[24] The distances P(1)–C(3) and P(2)–C(4) appear within the typical range for P–C single bonds of 1.87(2) Å,[14] as are the phosphorus–cyclohexyl bond distances. The distances N–C(3) and N–C(4) also compare favourably with the N–C bond lengths in NMe_3 (1.47 Å).[23,25] The approximate dihedral angles between the theoretical position of the phosphorus lone pair for P(1) and the methylene protons H(31) and H(32) are 145 and 107° respectively. For the phosphorus atom P(2) and the methylene protons H(41) and H(42) the dihedral angles are 161 and 87° respectively. It is therefore apparent that in the solid state the methylene protons do occupy different positions with respect to the lone pair on phosphorus. In solution, however, the conformation of the phosphine may be different and we note that on cooling a CD_2Cl_2 solution of **5b** to −40 °C the resonances due to the PCH_2 protons broaden, but at this temperature the phosphine crystallises from solution preventing further studies. From 0 to 100 °C there is no apparent change in the PCH_2 signals.

Experimental

Melting points were measured in air on a Gallenkamp apparatus and are uncorrected. Hydrogen-1 NMR spectra were recorded on a Bruker AM 300 spectrometer at 300.13 MHz or on a JEOL EM 390 spectrometer at 90 MHz, with $SiMe_4$ (δ 0.0) as internal

reference, positive values being to high frequency. The ^{13}C-{^1H} spectra were recorded in [$^2H_1$]chloroform, unless otherwise stated, on a Bruker AM 300 spectrometer operating at 75.47 MHz with $SiMe_4$ as internal reference,[26] ^{31}P-{^1H} spectra on a JEOL JNM-FX60 spectrometer at 24.15 MHz with $[P(OH)_4]^+$ in [$^2H_2$]water (δ 0.0) as external reference and ^{31}P–^1H heteronuclear shift correlation spectra on a Bruker AM 300 spectrometer at 120.06 MHz with the same reference. Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using solvents dried and distilled under nitrogen prior to use. The compounds diphenylphosphine, diethylamine, D(+)-α-methylbenzylamine, L-alanine ethyl ester hydrochloride, ethanolamine and allylamine were used as supplied by Aldrich. L-Alanine methyl ester hydrochloride and *endo*-(1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylamine were used as supplied from Fluka. Dicyclohexylphosphine and the mixed isomers of phosphabicyclononane ($C_8H_{14}PH$) were used as supplied by Albright & Wilson Ltd. Microanalyses were carried out by Butterworth Laboratories Ltd.

Preparation of Bis(hydroxymethyl)phosphonium Salts.—(*i*) $[PPh_2(CH_2OH)_2]^+Cl^-$ **1a**. Solutions of formaldehyde (9 cm^3, 40%) and of HCl (5 cm^3, 36%) were added to stirred diphenylphosphine (10 g, 54 mmol). The mixture became hot and homogeneous. On cooling a white solid crystallised out. This was filtered off and recrystallised from boiling methanol to give the compound **1a** (15.0 g, 99%) (Found: C, 59.5; H, 5.8; P, 10.6. Calc. for $C_{14}H_{16}ClO_2P$: C, 59.6; H, 5.8; P, 11.0%), m.p. 160–162 °C. ^{31}P-{^1H} NMR (CD_3OD): δ 16.7. X-Ray quality crystals were grown slowly from methanol–diethyl ether at −15 °C in air.

(*ii*) $[P(C_6H_{11})_2(CH_2OH)_2]^+Cl^-$ **1b**. Solutions of formaldehyde (96 cm^3, 40%) and of HCl (47.5 cm^3, 36%) were added to stirred dicyclohexylphosphine (100.0 g, 0.5 mol). The mixture became hot, and upon cooling a white solid crystallised out. This was filtered off and recrystallised from boiling Pr^iOH to give the required compound **1b** (144.3 g, 98%) (Found: C, 57.2; H, 9.5; P, 10.2. $C_{14}H_{28}ClO_2P$ requires C, 57.0; H, 9.6; P, 10.5%), m.p. 170–173 °C. NMR (CD_3OD): ^1H(90 MHz), δ 0.9–2.3 (m, 22 H, C_6H_{11}), 4.3 [d, 4 H, CH_2, ^2J(PH) 3.0 Hz] and 4.5 (br s, 2 H, OH); ^{31}P-{^1H} (24 MHz), δ 28.3.

(*iii*) $2[P(C_8H_{14})(CH_2OH)_2]^+SO_4^{2-}/[P(C_8H_{14})(CH_2OH)_2]^+HSO_4^-$, *mixed isomers* **3a** *and* **3b**. Solutions of formaldehyde (405 cm^3, 40%) and of H_2SO_4 (180 cm^3, 98%) were added to a stirred sample of $C_8H_{14}PH$ (mixture of [3.3.1] and [4.2.1] isomers, 58.5:41.5) (365.3 g, 2.51 mol). The temperature rose to 60 °C over 1 h. On cooling two layers separated. The lower aqueous phase was decanted, washed with toluene and filtered through Dicalite. The solvent was removed under reduced pressure yielding a white solid which was recrystallised from boiling methanol to give the required compounds **3a** and **3b** (969 g, 81.3%), m.p. 190–200 °C. ^{31}P-{^1H} NMR (D_2O, 24 MHz): δ 23.0 (s, 1P, [3.3.1] isomer) and 55.7 (s, 1P, [4.2.1] isomer).

(*iv*) *Isolation of compound* **3a** *from the isomeric mixture of* **3a** *and* **3b**. A sample of compounds **3a** and **3b** (125 g, 0.26 mol) was dissolved in H_2SO_4 (70 cm^3, 36%) in a flask fitted with a dropping funnel, thermometer and a Dean and Stark condenser. The solution was heated to a constant 150 °C. Distillate (about 10 cm^3) was removed at regular intervals and replaced by distilled water (10 cm^3). This procedure was continued for 13 h, samples being monitored by ^{31}P NMR spectroscopy. The reaction mixture was then diluted with distilled water (60 cm^3) and refluxed at 105–110 °C. Further distillate was collected to remove any remaining formaldehyde. The solution was then filtered hot through carbon to remove discolourations and neutralised with calcium carbonate (100 g, 1.0 mol). It was filtered and the solvent removed under reduced pressure. The resulting solid was recrystallised from boiling methanol to give isomer **3a** (58.1 g, 46.5% recovery, based on the [3.3.1] isomer), m.p. 208–210 °C. ^{31}P-{^1H} NMR (D_2O): δ 21.8 (s, 1P, [3.3.1] isomer) (Found: P, 11.0. Requires 10.3–12.3%, ratio 35:65, mono-:di-anion).

(*v*) $[P(C_8H_{14})(CH_2OH)_2]^+Cl^-$ **4**. The phosphonium salt **3a** (5 g) was dissolved in hot distilled water (30 cm^3) and barium chloride (2.5 g, 10 mmol) in distilled water (30 cm^3) was added. The solution was allowed to cool and filtered through Celite. The solvent was removed under reduced pressure and the resulting solid recrystallised from boiling methanol to yield the required compound **4** (3.56 g, 84%), m.p. 248–250 °C (Found: C, 50.5; H, 8.3; P, 12.8. $C_{10}H_{20}ClO_2P$ requires C, 50.3; H, 8.4; P, 13.0%). ^{31}P-{^1H} NMR (D_2O): δ 23.4 (s, 1P, [3.3.1] isomer).

Preparation of Bis(diphenylphosphinomethyl)amines: General Method.—A slight excess of triethylamine was added to a stirred solution of $[PPh_2(CH_2OH)_2]Cl$ **1a** in water–methanol (2:1, *ca.* 50 cm^3). To this solution was added 1 equivalent of primary amine. The mixture was heated to reflux for 1 h. On cooling two layers separated. The product was extracted with dichloromethane (40 cm^3), dried over magnesium sulfate and filtered. The solvent was then removed under high vacuum over a minimum of 24 h to give the products as either a highly viscous oil or a white solid, depending on the amine.

(*i*) $(Ph_2PCH_2)_2NCHMePh$ **5a**. The phosphonium salt **1a** (10 g, 35 mmol) with triethylamine (5.2 cm^3, 35 mmol) and D(+)-α-methylbenzylamine (2.3 cm^3, 18 mmol) gave compound **5a** as a highly viscous oil (8.27 g, 91.4%) (Found: C, 79.8; H, 6.8; N, 2.3. $C_{34}H_{33}NP_2$ requires C, 79.4; H, 6.2; N, 2.6%). NMR: ^1H, δ 1.55 [d, 3 H, Me, ^3J(HH) 6.8], 3.8 [*A*B*X*, 2 H, PCH_2, ^2J(HH) 13.2, ^2J(PH) 6.0], 4.05 [A*B*X, 2 H, PCH_2, ^2J(HH) 13.2, ^2J(PH) 0], 5.0 (m, 1 H, CH) and 7.35–7.8 (m, 25 H, Ph); ^{13}C-{^1H}, δ 15.9 (s, Me), 56.2 [d, PCH_2, *J*(PC) 5.0], and 61.3 [t, NCH, ^3J(PC) 9.0 Hz]; ^{31}P-{^1H}, δ −27.8 (s).

(*ii*) $(Ph_2PCH_2)_2NCHMeCO_2Et$ **6a**. The phosphonium salt **1a** (10 g, 35 mmol) with triethylamine (5.2 cm^3, 36 mmol) and L-alanine ethyl ester hydrochloride (4.44 g, 29 mmol) neutralised with triethylamine (5.2 cm^3, 36 mmol) gave **6a** as a white air-sensitive solid (5.58 g, 61.5%) (Found: C, 71.5; H, 6.5; N, 2.9. Calc. for $C_{31}H_{33}NO_2P_2$: C, 72.5; H, 6.5; N, 2.9%), m.p. 76–77 °C. NMR: ^1H, δ [d, 3 H, Me, ^3J(HH) 7.1], 1.15 [t, 3 H, CH_2Me, ^3J(HH) 7.1], 3.5 [*A*B*X*, 2 H, PCH_2, ^2J(HH′) 13.2, ^2J(PH′) 9.3], 3.9 [A*B*X, 2 H, PCH_2, ^2J(HH′) 13.2, ^2J(PH) 0.0], 4.05 [m, 2 H, OCH_2Me, ^2J(HH′) 12.0, ^3J(HH) 7.1, ^5J(HH) 3.6], 4.3 [m, 1 H, NCH, ^5J(HH) 3.6, ^3J(HH) 7.1, ^4J(PH) 11.0] and 7.1–7.6 (m, 20 H, Ph); ^{13}C-{^1H}, δ 14.0 (s, Me), 14.5 (s, Me), 54.9 [d, PCH_2, *J*(PC) 4.9], 58.3 [t, NCH, ^3J(PC) 9.4 Hz], 59.9 (s, OCH_2) and 172.7 (s, C=O); ^{31}P-{^1H}, δ −26.4 (s).

(*iii*) $(Ph_2PCH_2)_2NCHMeCO_2Me$ **7**. The phosphonium salt **1a** (5 g, 17.7 mmol), triethylamine (2.5 cm^3, 34 mmol) and L-alanine methyl ester hydrochloride (1.24 g, 8.9 mmol) gave compound **7** as an air-sensitive sticky white solid (3.56 g, 80.5%) (Found: C, 72.0; H, 6.2; N, 2.7. $C_{30}H_{31}NO_2P_2$ requires C, 72.1; H, 6.3; N, 2.8%). NMR: ^1H, δ 1.0 [d, 3 H, CH*Me*, ^3J(HH) 7.1], 3.5 [*A*B*X*, 2 H, PCH_2, ^2J(HH) 13.2, ^2J(PH′) 9.0], 3.55 (s, 3 H, OMe), 3.85 [A*B*X, 2 H, PCH_2, ^2J(HH′) 13.2, ^2J(PH) 0], 4.3 (m, 1 H, CH) and 7.2–7.5 (m, 20 H, Ph), ^{13}C-{^1H}, δ 14.7 (s, Me), 50.9 (s, OMe), 54.9 [d, PCH_2, *J*(PC) 4.7], 58.5 [t, NCH, ^3J(PC) 9.2 Hz] and 173.0 (s, CO_2Me); ^{31}P-{^1H}, δ −26.6 (s).

(*iv*) $(Ph_2PCH_2)_2NCHCH_2CHCH_2CH_2C(Me)CMe_2$ **8**. The phosphonium salt **1a** (3.7 g, 13 mmol) with triethylamine (1.8 cm^3, 13 mmol) and *endo*-(1*R*)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-ylamine (1.0 g, 6.5 mmol) gave compound **8** as a highly viscous oil (3.39 g, 9.5%) (Found: C, 78.5; H, 7.4; N, 2.4. $C_{36}H_{41}NP_2$ requires C, 78.7; H, 7.5; N, 2.6%). NMR spectra: ^1H, δ 0.55 (s, 3 H, Me), 0.67 (s, 3 H, Me), 0.81 (s, 3 H, Me), 0.9–1.05 (m, 2 H, CH_2), 1.37 [t, 1 H, CH, ^3J(HH) 4.2], 1.4–1.55 (m, 2 H, CH_2), 3.0m (1 H, NCH), 3.85 [AB, 4 H, PCH_2, ^2J(HH′) 13.5] and 7.2–7.5 (m, 20 H, Ph); ^{13}C-{^1H}, δ 16.1 (s, Me), 18.3 (s, Me), 19.7 (s, Me), 27.0 (s, CH_2), 28.3 (s, CH_2), 44.2 (s, CH), 48.9 (s, C), 49.5 (s, C), 57.4 [t, PCH_2, *J*(PC) 11.8] and 68.3 [t, NCH, ^3J(PC) 7.2 Hz]; ^{31}P-{^1H}, δ −28.6.

(*v*) $(Ph_2PCH_2)_2NCH_2CH_2OH$ **9**. The phosphonium salt **1a** (2.0 g, 7.0 mmol) with triethylamine (1 cm^3, 7.0 mmol) and ethanolamine (0.21 cm^3, 3.5 mmol) gave compound **9** as a highly viscous oil (1.54 g, 96%) (Found: C, 72.4; H, 6.6; N, 3.8. $C_{28}H_{29}NOP_2$ requires C, 73.5; H, 6.4; N, 3.0%). NMR: ^1H, δ 3.0 [t, 2 H, CH_2N, ^3J(HH) 5.2], 3.27 [br s, exchange D_2O, 1 H, OH], 3.45 [t, 2 H, CH_2O, ^3J(HH) 5.2], 3.85 [d, 4 H, PCH_2, ^2J(PH) 3.3 Hz] and 7.2–8.0 (m, 20 H, Ph); ^{13}C-{^1H}, δ 56.0 (s, CH_2O) and 57.7–58.2 (m, PCH_2, NCH_2); ^{31}P-{^1H}, δ −28.2 (s).

(*vi*) $(Ph_2PCH_2)_2NCH_2CH{=}CH_2$ **10**. The phosphonium salt **1a** (2.0 g, 7 mmol) with triethylamine (1 cm^3, 7 mmol) and allylamine (0.26 cm^3, 3.5 mmol) gave compound **10** as a highly viscous oil (1.49 g, 94%) (Found: C, 75.8; H, 6.4; N, 3.5. $C_{29}H_{29}NP_2$ requires C, 76.8; H, 6.4; N, 3.1%). NMR: ^1H, δ 3.48–3.57 (m, 2 H, NCH_2), 3.6 [d, 4 H, PCH_2, ^2J(PH) 2.9], 5.04–5.1 (m, 2 H, $=CH_2$), 5.63–5.9 (m, 1 H, =CH) and 7.1–7.5 (m, 20 H, Ph); ^{31}P-{^1H}, δ −28.8 (s).

Preparation of Bis(dicyclohexylphosphinomethyl)amines.—(*i*) $[(C_6H_{11})_2PCH_2]_2NCHMePh$ **5b**. Triethylamine (8.5 cm^3, 84 mmol) was added to a stirred solution of compound **1b** (24.3 g, 82.5 mmol) in water–methanol (2:1, 100 cm^3) followed by D(+)-α-methylbenzylamine (5.3 cm^3, 46 mmol). The mixture became highly viscous and toluene (50 cm^3) was added. The reaction was heated to reflux on an oil-bath for 45 min and then allowed to cool. The organic layer was decanted, dried over magnesium sulfate and filtered. Methanol was then added to the solution until it began to cloud. The solution was placed in a freezer at −15 °C. Large colourless crystals of **5b** were collected, washed with methanol, and dried *in vacuo* (12.5 g, 56%) (Found: C, 75.2; H, 10.8; N, 2.5. $C_{34}H_{57}NP_2$ requires C, 75.3; H, 10.5; N, 2.6%), m.p. 87–89 °C. NMR: ^1H, δ 1.0–1.85 (m, 47 H, $4C_6H_{11}$ + Me), 2.6 [*A*BX, 2 H, PCH_2, ^2J(HH) 12.9, ^2J(PH) 3.82], 2.8 [A*B*X, 2 H, PCH_2, ^2J(HH) 12.9, *J*(PH)0], 4.85 [m, 1 H, CH, ^3J(HH) 6.9] and 7.15–7.4 (m, 5 H, Ph); ^{13}C-{^1H}, δ 11.1 (s, Me), 47.9 (m, PCH_2) and 57.3 [t, CH, ^3J(PC) 9.9 Hz] (cyclohexyl region omitted); ^{31}P-{^1H}, δ −18.4 (s). Mass spectrum *m/z* 541 (M^+, 541), 211 [100, $(C_6H_{11})_2PCH_2$] and 105 [28%, CH(Me)Ph].

(*ii*) $[(C_6H_{11})_2PCH_2]_2NCHMeCO_2Et$ **6b**. Triethylamine (1.5 cm^3, 20 mmol) was added to a stirred solution of compound **1b** (3.15 g, 10.7 mmol) in water–methanol (2:1, 30 cm^3). L-Alanine ethyl ester hydrochloride (0.82 g, 5.3 mmol) and triethylamine (4.44 cm^3, 6 mmol) in water–methanol (2:1, 30 cm^3) were then added. The mixture was heated to 60 °C for 3 h and allowed to cool. The product was extracted with dichloromethane (30 cm^3) and dried over magnesium sulfate. The solvent was then removed under reduced pressure to yield **6b** as a highly viscous oil (2.53 g, 90%) (Found: C, 70.1; H, 10.4; N, 2.9. $C_{31}H_{57}NO_2P_2$ requires C, 70.9; H, 10.9; N, 2.7%). NMR: ^1H, δ 1.1–1.9 (m, 50 H, $4C_6H_{11}$ + 2Me), 2.7 [*A*BX, 2 H, PCH_2, ^2J(HH) 14.0, ^2J(PH) 6.8], 3.2 [*A*BX, 2 H, PCH_2, ^2J(HH) 14.0, ^2J(PH) 0.0], 4.3 [q, 2 H, OCH_2, ^3J(HH) 7.1] and 4.5 (m, 1 H, CH); ^{13}C-{^1H}, δ 13.5 (s, Me), 13.8 (s, Me), 29.5 [d, PCH, *J*(PC) 12.6], 47.7 (unresolved, PCH_2), 56.7 [t, NCH, ^3J(PC) 10.2 Hz], 59.2 (s, OCH_2) and 172 (s, CO_2Et); ^{31}P-{^1H}, δ −18.2 (s).

Preparation of $[(C_8H_{14})PCH_2]_2NCHMePh$ **11**.—Triethylamine was added to a solution of the phosphonium salt **3a** ([3.3.1] isomer) in water–methanol (2:1, 40 cm^3). The compound $C_8H_{14}PCH_2OH$ was then extracted from the mixture with toluene (100 cm^3). D(+)-α-Methylbenzylamine (1.5 cm^3, 13 mmol) was added to the solution and the mixture refluxed for 3 h. The solvent was removed under reduced pressure. After 3 d at < 1 mmHg a white solid **11** formed (2.6 g, 48.5%) (Found: C, 72.5; H, 9.7; N, 3.2. $C_{26}H_{41}NP_2$ requires C, 72.7; H, 9.6; N, 3.4%). NMR: ^1H, δ 1.35 [d, 3 H, Me, ^3J(HH) 6.8], 1.5–2.2 (m, 28 H, C_8H_{14}), 3.0 [*A*BX, 2 H, PCH_2, ^2J(HH) 13.8, ^2J(PH) 2.9], 3.25 [A*B*X, 2 H, PCH_2, ^2J(HH) 13.8, ^2J(PH) 2.0], 4.35 (m, 1 H, CH) and 7.15–7.4 (m, 5 H, Ph); ^{13}C-{^1H}, δ 16.4 (s, Me), 48.0 [dd, PCH_2, ^3J(PC) 13.1, ^3J(PC) 9.5] and 60.3 [t, NCH, ^3J(PC) 9.7] (C_8H_{14} moiety omitted); ^{31}P-{^1H}, δ −46.6 (s).

Preparation of $(C_8H_{14})PCH_2NEt_2$ **12** (*mixed isomers*).—The phosphonium salts **3a** and **3b** ([4.2.1] and [3.3.1] isomers) (10 g, 45 mmol) were dissolved in water–methanol (2:1, 40 cm^3) and a solution of Na_2SO_3 (11 g, 87 mmol) in water (25 cm^3) followed by diethylamine (5 cm^3, 97 mmol) were then added. The mixture was heated to about 60 °C for 1 h. On cooling the mixture separated into two layers. The organic layer was decanted and the product distilled under high vacuum to give a mixture of the isomers **12a** and **12b** as a clear liquid (8.65 g, 84%) (Found: C, 68.5; H, 11.7; N, 6.4. $C_{13}H_{26}NP$ requires C, 68.7; H, 11.5; N, 6.2%), b.p. 124–127 °C at 2.5 mmHg. NMR: ^1H, δ 0.88 [t, 6 H, Me, ^3J(HH) 7.1], 0.9 [t, 6 H, ^3J(HH) 7.1], 1.3–2.3 [m, 28 H, $2C_8H_{14}$], 2.4 [d, 2 H, PCH_2, ^2J(PH) 2.2], 2.46 [dq, 4 H, CH_2CH_3, ^3J(HH) 7.1, ^4J(PH) 0.85], 2.52 [dq, 4 H, $2CH_2CH_3$, ^3J(HH) 7.1, ^4J(PH) 0.85] and 2.8 [d, PCH_2, ^2J(PH) 1.5]; ^{13}C-{^1H}, δ 12.7 (s, Me), 25.2 [d, PCH_2, *J*(PC) 10.5], 39.7 [d, PCH, *J*(PC) 11.8], 49.0 (m, PCH_2N), 50.5 [d, NCH_2, ^3J(PC) 15.1] and 51.9 [d, NCH_2, ^3J(PC) 9.1 Hz]; ^{31}P-{^1H}, δ −9.9 (s, 1P, [3.3.1] isomer) and −49.0 (s, 1P, [4.2.1] isomer).

X-Ray Crystallography.—(*a*) $[PPh_2(CH_2OH)_2]Cl$ **1a**. A crystal with dimensions 0.6 × 0.16 × 0.12 mm was glued to the end of a thin glass fibre using epoxy resin. Unit-cell parameters were determined by least-squares refinement of ω angles from 294 centred reflections with $15 < 2\theta < 30°$.[27] Intensities of 1416 reflections in the range $7 < 2\theta < 50°$ and $0 < h < 18$, $0 < k < 8$, $0 < l < 15$ were measured on a Stoe STADI-2 Weissenberg diffractometer using an ω-scan technique and graphite-monochromated Mo-Kα radiation. No crystal decay was detected from periodically measured check reflections. The data were corrected for Lorentz and polarisation effects, but not for absorption, and merged to give 1270 unique reflections with 994 having $I > 3\sigma(I)$.

Crystal data. $C_{14}H_{16}ClO_2P$, $M = 282.71$, orthorhombic, space group $Pna2_1$, $a = 14.615(10)$, $b = 6.476(4)$, $c = 15.126(2)$ Å, $U = 1432(2)$ Å^3, $Z = 4$, $\mu = 3.2$ cm^{-1}, λ(Mo-Kα) = 0.7107 Å, $F(000) = 592$, $D_c = 1.31$ g cm^{-3}, $T = 293$ K.

All calculations were performed on a VAX 8650 computer. The structure was solved by Patterson techniques using SHELXS 86.[28] All subsequent calculations were carried out using the computer program SHELX 76.[29] Phenyl rings, including H atoms, were included as rigid groups with D_{6h} symmetry, C–C 1.395 and C–H 1.08 Å. The remaining hydrogen atoms were located on Fourier difference maps and refined as normal atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters during the later cycles of refinement; hydrogen atoms were refined with group isotropic thermal parameters. Final cycles of least-squares refinement used a weighting scheme $w = 0.5/[\sigma^2(F_o) + gF_o^2]$, $g = 0.0054$, and gave final residual indices of R [$=\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$] = 0.038 and R' {$=[\Sigma w(|F_o| - |F_c|)/\Sigma w|F_o|]$} = 0.044, the average shift/e.s.d. = 0.02 (maximum = 0.209). An analysis of the final weighting scheme over $|F_o|$ and (sin θ)/λ was satisfactory. The final difference electron density had maximum and minimum values of +0.38 and −0.20 e Å^{-3} respectively. The atomic coordinates for the structure are given in Table 3.

(*b*) $[(C_6H_{11})_2PCH_2]_2NCHMePh$ **5b**. The analysis was carried out as for compound **1a**. Intensities were measured from a crystal with dimensions 0.64 × 0.64 × 0.20 mm. Cell parameters were obtained by refinement of 334 centred reflections in the range $7 < 2\theta < 30°$. A total of 7886 reflections was measured in the range $7 < 2\theta < 50°$ with $-34 < h < 34$, $0 < k < 15$, $0 < l < 11$ which merged to 6435 unique reflections, 3597 having $I > 3\sigma(I)$.

Crystal data. $C_{34}H_{57}NP_2$, $M = 541.8$, orthorhombic, space group $P2_12_12_1$, $a = 27.925(8)$, $b = 12.531(6)$, $c = 9.520(11)$ Å, $U = 3331.3$ Å^3, $Z = 4$, $D_c = 1.08$ g cm^{-3}, Mo-Kα, λ = 0.710 73 Å, $\mu = 1.2$ cm^{-1}, $F(000) = 1192$, $T = 293$ K.

Table 3 Fractional atomic coordinates for $[PPh_2(CH_2OH)_2]^+Cl^-$

Atom	x	y	z
Cl	0.280 89(9)	−0.188 66(21)	0.004 88(19)
P	0.016 51(7)	0.108 87(17)	0.000 00(0)
O(1)	−0.158 32(27)	0.116 3(8)	−0.048 7(3)
O(2)	−0.016 8(4)	−0.286 4(7)	0.047 6(4)
C(1)	−0.102 6(3)	0.173 6(9)	0.022 4(4)
C(2)	0.022 6(4)	−0.170 1(8)	−0.021 3(5)
C(21)	0.083 90(23)	0.175 7(5)	0.094 28(21)
C(22)	0.140 30(23)	0.349 3(5)	0.092 10(21)
C(23)	0.190 93(23)	0.404 2(5)	0.166 69(21)
C(24)	0.185 19(23)	0.285 6(5)	0.243 47(21)
C(25)	0.128 81(23)	0.111 9(5)	0.245 68(21)
C(26)	0.078 15(23)	0.057 0(5)	0.171 09(21)
C(31)	0.056 75(21)	0.236 0(5)	−0.096 98(20)
C(32)	0.147 32(21)	0.200 7(5)	−0.121 88(20)
C(33)	0.181 37(21)	0.287 3(5)	−0.199 69(20)
C(34)	0.124 85(21)	0.409 3(5)	−0.252 62(20)
C(35)	0.034 27(21)	0.444 6(5)	−0.227 71(20)
C(36)	0.000 24(21)	0.357 9(5)	−0.149 88(20)
H(1)	0.176(4)	0.006(11)	−0.033(4)
H(2)	−0.061(6)	−0.273(13)	0.036(6)
H(3)	−0.107(3)	0.314(8)	0.031(3)
H(4)	−0.108(5)	0.071(12)	0.084(6)
H(5)	0.092(4)	−0.213(8)	−0.024(3)
H(6)	−0.007(4)	−0.168(9)	−0.074(5)

Table 4 Fractional atomic coordinates for $[(C_6H_{11})_2PCH_2]_2$-NCHMePh

Atom	x	y	z
P(1)	0.134 30(4)	0.203 78(10)	0.238 26(15)
P(2)	0.114 15(5)	−0.122 15(10)	0.038 63(15)
N	0.069 38(13)	0.058 0(3)	0.133 3(4)
C(1)	0.018 93(16)	0.024 2(4)	0.121 4(6)
C(2)	−0.010 41(20)	0.087 7(5)	0.013 3(7)
C(3)	0.075 46(16)	0.174 2(4)	0.156 3(6)
C(4)	0.099 00(17)	0.021 3(3)	0.014 2(5)
C(11)	−0.003 50(12)	0.020 31(28)	0.265 3(3)
C(12)	−0.034 98(12)	0.098 55(28)	0.313 6(3)
C(13)	−0.052 96(12)	0.093 18(28)	0.450 1(3)
C(14)	−0.039 45(12)	0.009 54(28)	0.538 3(3)
C(15)	−0.007 96(12)	−0.068 70(28)	0.490 0(3)
C(16)	0.010 02(12)	−0.063 32(28)	0.353 5(3)
C(21)	0.145 93(16)	0.337 6(4)	0.163 5(6)
C(22)	0.162 45(19)	0.324 6(4)	0.013 9(6)
C(23)	0.177 59(20)	0.429 5(5)	−0.053 2(7)
C(24)	0.215 28(22)	0.484 0(5)	0.028 8(9)
C(25)	0.199 47(24)	0.501 8(5)	0.179 8(9)
C(26)	0.184 13(18)	0.394 8(4)	0.251 3(7)
C(31)	0.116 60(20)	0.231 0(4)	0.423 4(6)
C(32)	0.078 90(22)	0.316 2(5)	0.449 4(6)
C(33)	0.070 58(29)	0.332 6(6)	0.607 6(8)
C(34)	0.059 37(29)	0.233 2(7)	0.678 6(8)
C(35)	0.096 0(3)	0.148 4(6)	0.651 1(7)
C(36)	0.105 11(25)	0.130 6(5)	0.497 0(6)
C(41)	0.168 36(18)	−0.103 5(5)	0.152 2(6)
C(42)	0.180 99(20)	−0.200 1(5)	0.230 2(7)
C(43)	0.221 91(24)	−0.180 6(6)	0.335 0(7)
C(44)	0.265 33(21)	−0.134 1(6)	0.261 6(9)
C(45)	0.253 02(25)	−0.037 0(6)	0.187 4(8)
C(46)	0.212 33(19)	−0.053 1(5)	0.079 8(7)
C(51)	0.136 34(17)	−0.154 8(4)	−0.141 0(5)
C(52)	0.164 81(18)	−0.259 3(4)	−0.140 1(6)
C(53)	0.179 21(19)	−0.294 7(5)	−0.285 3(6)
C(54)	0.136 43(21)	−0.304 3(5)	−0.381 8(7)
C(55)	0.108 60(21)	−0.200 8(5)	−0.386 1(6)
C(56)	0.092 94(17)	−0.168 1(4)	−0.239 0(6)

All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included in calculated positions (C–H 1.08 Å), with a common fixed isotropic parameter. The final $R = 0.0611$ and $R' = 0.0595$ ($g = 0.002$) for 147 parameters refined. Maximum and minimum peak heights in the final Fourier difference map were 0.47 and −0.32 e Å^{-3}. The atomic coordinates for the structure are given in Table 4.

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

Acknowledgements

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