# Synthesis and structural studies of selected multifunctional phosphonate and phosphonic acid ligands

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**Abstract**

The carbanion $[(RO)_2P(O)][C(O)NEt_2]CH^-$ is used to prepare several new carbamoylmethyl phosphonates of the general type $[(RO)_2P(O)][C(O)NEt_2]CH(X)$, $X = CH_3$, $C_2H_5$, $(CH_2)_2CN$, $CH_2CH[(RO)_2P(O)][C(O)NEt_2]$, $(CH_2)_3OH$ and $CH_2C(O)OCH_3$. In addition, an interesting intramolecular transesterification process for the molecule with $X = (CH_2)_3OH$ and novel hydrolysis chemistry that produces useful phosphonic acids are described. The molecular structure determinations of two compounds, $\{[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CH\}_2CH_2$ (**4b**) and $[\overline{NH_2C(CH_3)_2CH_2C(O)CH_2C(CH_3)_2}^+][(HO)PO_2CH_2C(O)NEt_2^-]$ (**11**) are outlined. Compound **4b** crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.0996(24)$, $b = 12.6604(31)$, $c = 16.5711(48)$ Å, $\alpha = 68.655(20)$, $\beta = 78.714(22)$, $\gamma = 70.742(19)°$ and $Z = 2$. The molecular structure confirms that two carbamoylmethyl phosphonate fragments are bonded to a central methyl group. Compound **11** crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.2384(21)$, $b = 9.8404(21)$, $c = 11.0702(25)$ Å, $\alpha = 85.276(18)$, $\beta = 74.477(17)$, $\gamma = 78.644(17)°$ and $Z = 2$. The molecular structure contains a 2,2,6,6-tetramethyl piperidone cation and a carbamoylmethyl phosphonic acid anion.

## Introduction

We have previously reported that carbamoylmethyl phosphonates [1, 2], $[(RO)_2P(O)][C(O)NEt_2]CH_2$ (CMP), and carbamoylmethyl phosphine oxides [3], $[R_2P(O)][C(O)NEt_2]CH_2$ (CMPO), can be efficiently deprotonated with a strong base (e.g. NaH) at the central methylene carbon atom. The resulting carbanions are useful synthons for the production of more complex, multifunctional ligands [4–9], and the coordination chemistry of the multifunctional ligands is particularly interesting [5–9]. These results and long-range goals directed at immobilizing phosphonate ligands on solid chromatographic supports have encouraged us to explore additional carbanion addition reaction chemistry on CMP and CMPO fragments. In this report, syntheses of new carbamoylmethyl phosphonates $[(RO)_2P(O)][C(O)NEt_2]CH(X)$, $X = CH_3$, $C_2H_5$, $C_2H_4CN$ and $C_3H_6OH$, the bis-CMP derivative $\{[(RO)_2P(O)][C(O)NEt_2]CH\}_2CH_2$ and the phosphonic acids $[(HO)_2P(O)][C(O)NEt_2]CH_2COOH$ and $(HO)_2P(O)CH_2C(O)NEt_2$ are described.

## Experimental

*General information*

Trimethylsilyl bromide, methylbromoacetate, methyl iodide, ethyl bromide, bromopropylnitrile, bromopropanol, chloropropanol and dihydropyran were purchased from Aldrich Chemical Co. and used as freshly distilled reagents. The CMP ligands, $(RO)_2P(O)CH_2C(O)NEt_2$, R = Et (**1a**), i-Pr (**1b**), Hx (**1c**)**, were prepared as described in the literature [2]. All reactions were performed under dry nitrogen in Schlenk-type reaction flasks, and dried solvents were used throughout unless specified otherwise. IR spectra were recorded from Nicolet model 6000 or Matteson 2020 Fourier transform spectrometers, and NMR spectra were recorded on Varian FT-80A, Nicolet/GE-360 and JEOL GSX-400 NMR spectrometers. Standards were $Me_4Si$ ($^1H$ and $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). Analytical data were obtained from the UNM microanalytical facility and Galbraith Laboratories.

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**Abbreviations used in the text include Me = $CH_3$, Et = $C_2H_5$, i-Pr = i-$C_3H_7$, Hx = n-$C_6H_{13}$, THF = tetrahydrofuran, TSA = *p*-toluene sulfonic acid, TMS = trimethylsilyl.

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*Synthesis of phosphonate ligands*

*$Na^+\{[(RO)_2P(O)][C(O)NEt_2]CH^-\}$ ($R = C_2H_5$ (**2a**), $i\text{-}C_3H_7$ (**2b**), $C_6H_{13}$ (**2c**))*

The carbanions **2** were prepared in the same manner and used without isolation. Typically 100 mmol of the neutral CMP precursor **1** was dissolved in 100 ml of dry THF, and the solution was added to excess NaH (~125 mmol). The slurry was vigorously stirred overnight, with the flask vented through a mercury bubbler to relieve the evolved hydrogen. The resulting mixture was filtered under nitrogen and the filtrate added directly to substrates, as described below.

*$[(RO)_2P(O)][C(O)NEt_2]CH(R')$ ($R = Et$, $R' = Me$ (**3a**); $R = Hx$, $R' = Me$ (**3c**); $R = Et$, $R' = Et$ (**3a'**))*

Alkyl halide (100 mmol) was slowly dripped into rapidly stirred THF solutions containing **2a** or **2c** (100 mmol). Heat was evolved and the addition rate was controlled so that the solvent refluxed gently. After addition was complete, the mixture was stirred for 1 h and then filtered to remove sodium halide. The colorless products were recovered by vacuum evaporation of the solvent, followed by vacuum distillation. Yield: **3a**, 88%; **3c**, 72%; **3a'**, 85%. Derivatives with R = i-Pr and R' = Me and Et may also be prepared in a similar fashion; however, these compounds were not isolated and fully characterized.

*$\{[(RO)_2P(O)][C(O)NEt_2]CH\}_2CH_2$ ($R = i\text{-}Pr$ (**4b**))*

As described in the synthesis of **3**, 50 mmol of $CH_2Br_2$ was added slowly with vigorous stirring to a THF solution containing 100 mmol of **2b**. The reaction mixture was refluxed at 52 °C during addition. Following addition, the mixture was held at this temperature for an additional 2 h. The mixture was centrifuged to remove NaBr, and the supernatant was distilled at 120–126 °C (5 mTorr). Higher distillation pressures result in significant decomposition. The colorless distillate solidifies upon standing overnight. Yield: 54%.

*$[(RO)_2P(O)][C(O)NEt_2]CH(CH_2CH_2CN)$ ($R = i\text{-}Pr$ (**5b**), $Hx$ (**5c**))*

Bromopropionitrile (110 mmol) in dry THF (100 ml) was dripped into THF solutions of **2b** or **2c** (110 mmol) held at 0 °C. After reagent addition, the mixture was warmed to 25 °C and stirred for 1 h. The NaBr was removed by centrifugation, and the resulting supernatant was vacuum evaporated to dryness. **5b** was distilled at 120–140 °C (10 mTorr) and isolated as a colorless oil. Yield: 34%. **5c** was distilled at 155–180 °C (10 mTorr) and isolated as a colorless oil. Yield: 17%.

*$[(RO)_2P(O)][C(O)NEt_2]CH(CH_2CH_2CH_2OH)$ ($R = Et$ (**6a**), $i\text{-}Pr$ (**6b**))*

A protected form of bromopropanol was prepared by a modification of a published procedure [10]. 3-Bromopropanol (72 mmol, 10 g) was added to 300 ml of dry $CH_2Cl_2$. The solution was cooled to 0 °C, and dihydropyran (180 mmol, 15.1 g) was added with vigorous stirring. A catalytic amount of *p*-toluene sulfonic acid (0.20 mmol, 35 mg) was added slowly in order to avoid superheating, and the mixture was warmed to 25 °C and stirred for 1 h. The reaction mixture was then transferred to a separatory funnel and combined with 200 ml of diethyl ether, 120 ml of saturated aqueous brine, 120 ml of saturated aqueous $NaHCO_3$ and 240 ml of water. The ether layer was removed, the aqueous layer washed with fresh ether (2×50 ml), and the combined ether fractions were dried over $MgSO_4$. The ether was vacuum evaporated, and the residue was vacuum distilled at 50–54 °C (10 mTorr). The colorless product is the known tetrahydropyranyl ether, $THPOC_3H_6Br$. Yield: 14.8 g (92%).

A sample of $THPOC_3H_6Br$ (48 mmol) was dissolved in 100 ml THF and combined with **2a** or **2b** (43 mmol) in 100 ml of THF. The mixture was stirred at 23 °C for 4 h, filtered to remove NaBr, and a light yellow oil in near quantitative yield was isolated. The protected alcohol was deprotected by addition of 100 ml of 0.1 M HCl, and the mixture was heated to 70 °C for 3 h. The mixture was saturated with NaCl and extracted with 50 ml portions (3×) with $CH_2Cl_2$. The combined organic layers were dried with $MgSO_4$ and evaporated to dryness. Coextracted pyranol was removed by vacuum distillation at 90 °C (10 mTorr). The remaining oils, **6a** or **6b**, were recovered in pure form without further distillation. Yield: 85–88%.

*$[(RO)\overline{P(O)][C(O)NEt_2]CH(CH_2CH_2CH_2O)}$ ($R = Et$ (**7a**), $i\text{-}Pr$ (**7b**))*

The cyclized products were obtained from two reactions. Prolonged heating of **6a** or **6b** under vacuum at 90–100 °C did not result in internal transesterification. However, a reaction took place when **6** in 50 ml of the respective alcohol, ROH, was combined at 0 °C with excess sodium, and the resulting solution was stirred and warmed to 25 °C for 1 h. The excess alcohol was removed by vacuum evaporation, and the residue was stirred with 100 ml of saturated aqueous NaCl solution. The solution was extracted with $CH_2Cl_2$ (2×50 ml) and the organic layer dried over $MgSO_4$. The remaining oils were distilled *in vacuo*; **7a**: 110–125 °C (10 mTorr), yield 85%; **7b**: 115–130 °C (10 mTorr), yield 65%.

In a second approach, chloropropanol (84 mmol, 7.9 g) was added dropwise to a stirred solution of **2a** or **2b** (80 mmol) in 100 ml of THF maintained at 0 °C. The mixture was warmed to 25 °C and stirred for 1 h. The NaCl was separated by centrifugation, and the supernatant was vacuum evaporated. The resulting oils

were distilled as described above. Yields: **7a**, 65%; **7b**, 18%.

*Syntheses of phosphonic acids*

*$[(HO)_2P(O)][C(O)NEt_2]CHCH_2C(O)OH$ (8)*

The phosphonate $[(EtO)_2P(O)][C(O)NEt_2]$-$CH(CH_2C(O)OMe)$ was prepared as described in the literature [8]. This ligand (31 mmol, 10 g) was added to 6 M HCl (50 ml) and refluxed for 3 h. The product was evaporated to dryness (70 °C under vacuum) until a semisolid of constant weight was obtained. Yield: 95%.

*$[\overline{NH_2C(CH_3)_2CH_2C(O)CH_2C(CH_3)_2}^+]$-$[(HO)P(O)_2CH_2C(O)NEt_2^-]$ (11)*

A sample of $(EtO)_2P(O)CH_2C(O)NEt_2$ (43 mmol, 11 g) was weighed into a Schlenk flask, cooled to 0 °C, and freshly distilled $Me_3SiBr$ (86 mmol, 11.5 ml) was dripped into the flask. Ethyl bromide was rapidly evolved and swept from the flask by a nitrogen purge. The flask was then warmed to 25 °C and stirred for 1 h. The contents of the flask were vacuum evaporated, leaving a clear liquid identified as $[(Me_3SiO)_2P(O)][C(O)NEt_2]CH_2$ (**9**). Yield: 99%.

The sample of $[(Me_3SiO)_2P(O)][C(O)NEt_2]CH_2$ was dissolved in 15 ml of $Et_2O$ and transferred to a separatory funnel. A 20 ml sample of distilled water was added to the funnel, and the mixture was vigorously shaken for 30 min. The aqueous phase was collected, and the ether layer was exposed to another sample of fresh water. The aqueous layers were combined and evaporated under vacuum at 40 °C. The acid $[(HO)_2P(O)][C(O)NEt_2]CH_2$ (**10**) was isolated as a sticky, white solid. Yield: 95%.

The aqueous wash layers obtained above were combined and the solution made basic with $NH_4OH$ (pH 7–9). After vacuum evaporation, colorless crystals were obtained and identified as the monoammonium salt. These crystals, however, were not of satisfactory quality for single crystal X-ray diffraction analysis. The crystals were subsequently dissolved in MeOH, and acetone was carefully layered over the solution. After standing overnight, X-ray quality single crystals of **11** were obtained.

*Characterization data*

*$[(RO)_2P(O)][C(O)NEt_2]CH(R')$ (3)*

**3a**. Solubility: benzene, toluene, THF. *Anal.* Calc. for $PO_4NC_{11}H_{24}$: C, 49.80; H, 9.12; N, 8.30. Found: C, 49.67; H, 9.01; N, 8.18%. Mass spectrum: $[M^+]$ 265. IR spectrum (neat, $cm^{-1}$): 2970(s), 2930(m), 2900(sh), 1645(s), 1450(w), 1432(m), 1248(m), 1069(m), 1020(w), 965(w), 955(m), 944(w). NMR spectra ($C_6D_6$, 22 °C): $^{31}P\{^1H\}$ $\delta$ 27.9; $^{13}C\{^1H\}$ $\delta$ 169.9 ($C$(O) $^2J_{PC}=3.1$ Hz), 63.9 ($OCH_2$, $^2J_{PC}=5.6$ Hz), 43.6 ($NCH_2$), 43.5 ($NCH_2$), 35.2 ($CH$, $^1J_{PC}=140.7$ Hz), 16.4 ($CH_3$, $^3J_{PC}=6.3$ Hz), 14.9 ($CH_3$), 14.7 ($CH_3$), 13.1 ($CHCH_3$); $^1H$ $\delta$ 4.2 ($OCH_2$, $^3J_{HH}=6.5$ Hz), 3.3 ($CH$, $NCH_2$), 1.2 ($J_{HH}=6.5$ $CH_3$).

**3a'**. Solubility: benzene, toluene, THF, *Anal.* Calc. for $PO_4NC_{12}H_{26}$: C, 51.60; H, 9.38; N, 5.01. Found: C, 51.41; H, 9.64; N, 5.00%. Mass spectrum $[M^+]$ 279. IR spectrum (neat, $cm^{-1}$): 2975(s), 2934(m), 1638(s), 1483(m), 1461(s), 1450(s), 1381(m), 1363(m), 1272(s), 1251(s), 1220(m), 1095(m), 1054(s), 1025(s), 965(m). NMR spectra (22 °C, $C_6D_6$): $^{31}P\{^1H\}$ $\delta$ 23.7; $^{13}C\{^1H\}$ $\delta$ 166.6 ($C$(O), $^2J_{PC}=4.2$ Hz), 61.9 ($OCH_2$, $^2J_{PC}=6.4$ Hz), 60.7 ($OCH_2$, $^2J_{PC}=6.4$ Hz), 43.7 ($CH$, $^1J_{PC}=131.7$ Hz), 42.1 ($NCH_2$), 40.4 ($NCH_2$), 21.4 ($CHCH_2$), 15.9 ($OCH_2CH_3$, $^3J_{PC}=5.7$ Hz), 14.2 ($NCH_2CH_3$), 12.7 ($NCH_2CH_3$), 12.2 ($CH_2CH_3$, $^3J_{PC}=13.1$ Hz); $^1H$ $\delta$ 4.0 ($OCH_2$, $^3J_{HH}=7.0$ Hz), 3.2 ($NCH_2$, $^3J_{HH}=7.0$ Hz), 3.0 ($CHCH_2$), 2.9 ($CH$), 1.1 ($OCH_2CH_3$, $^3J_{HH}=7.0$ Hz), 1.0 ($NCH_2CH_3$, $^3J_{HH}=7.0$ Hz), 0.8 ($CH_2CH_3$, $^3J_{HH}=7.4$ Hz).

**3c**. Solubility: benzene, toluene, THF. Analyses were unsatisfactory due to ligand solvation of small amounts of NaBr. Mass spectrum $[M^+]$ 377. IR spectrum (neat, $cm^{-1}$): 1647(s), 1444(m), 1245(m), 1067(m), 1022(w). NMR spectrum (22 °C, $C_6D_6$): $^{31}P\{^1H\}$ $\delta$ 26.4.

*$\{[(RO)_2P(O)][C(O)NEt_2]CH\}_2CH_2$ ($R$=i-Pr (4b))*

Solubility: benzene, toluene, THF. *Anal.* Calc. for $P_2O_8N_2C_{25}H_{52}$: C, 52.12; H, 9.19; N, 4.91. Found: C, 51.87; H, 8.84; N, 4.82%. Mass spectrum: $[M^+]$ 571. IR spectrum (neat, $cm^{-1}$): 2978(m), 1638(s), 1449(m), 1433(m), 1248(m), 987(s). NMR spectra (22 °C, $C_6D_6$): $^{31}P\{^1H\}$ $\delta$ 21.7; $^{13}C\{^1H\}$ $\delta$ 165.1 ($C$(O), $^3J_{PC}=2.7$ Hz), 70.5 ($CHO$, $^2J_{PC}=3.3$ Hz), 69.8 ($CHO$, $^2J_{PC}=3.3$ Hz), 42.0 ($CHCH_2CH$, $^2J_{PC}=15.6$ Hz), 41.1 ($NCH_2$), 39.5 ($NCH_2$), 35.7 (P–$CH$), 22.9 ($CHCH_3$), 12.6 ($NCH_2CH_3$), 11.4 ($NCH_2CH_3$).

*$[(RO)_2P(O)][C(O)NEt_2]CH(CH_2CH_2CN)$ (5)*

**5b**. Solubility: benzene, toluene, $CHCl_3$, THF. *Anal.* Calc. for $PO_4N_2C_{15}H_{29}$: C, 54.21; H, 8.80; N, 8.43. Found: C, 53.98; H, 8.84; N, 8.68%. Mass spectrum: $[M^+]$ 332. IR spectrum (neat, $cm^{-1}$): 2980(m), 2245(w), 1640(s), 1450(m), 1250(s), 1106(m), 985(s). NMR spectra (22 °C, $CDCl_3$): $^{31}P\{^1H\}$ $\delta$ 11.8; $^{13}C\{^1H\}$ $\delta$ 165.2 ($C$(O), $^2J_{PC}=5.0$ Hz), 118.8 ($C{\equiv}N$), 71.6 ($CHO$, $^2J_{PC}=7.0$ Hz), 70.8 ($CHO$, $^2J_{PC}=7.1$ Hz), 42.3 ($NCH_2$), 40.7 ($PCH$, $^1J_{PC}=134.2$ Hz), 40.7 ($NCH_2$), 23.8 ($OCHCH_3$), 23.3 ($CHCH_2$, $^3J_{PC}=5.0$ Hz), 15.4 ($CH_2CN$), 14.0 ($NCH_2CH_3$), 12.5 ($NCH_2CH_3$); $^1H$ $\delta$ 4.44 ($CHO$), 3.51 ($NCH_2$, $J_{HH}=6.6$ Hz), 3.30 ($NCH_2$, $J_{HH}=6.5$ Hz), 3.0 ($CH_2CN$), 2.23 ($CHCH_2$), 2.10, 1.84 ($PCH$), 1.07 ($CH_3CH$), 0.99 ($NCH_2CH_3$), $^2J_{HH}=6.6$ Hz), 0.88 ($NCH_2CH_3$, $J_{HH}=6.4$ Hz).

**5c**. Solubility: benzene, toluene, $CHCl_3$, THF. Mass spectrum; $[M^+]$ 416. NMR spectrum (22 °C, $CDCl_3$): $^{31}P\{^1H\}$ $\delta$ 22.2.

*$[(RO)_2P(O)][C(O)NEt_2]CH(CH_2CH_2CH_2OH)$ (6)*

**6a**. Solubility: benzene, THF, $CHCl_3$, $CH_2Cl_2$. Mass spectrum: $[M^+]$ 309. NMR spectra (22 °C, $CDCl_3$): $^{31}P\{^1H\}$ $\delta$ 24.9; $^{13}C\{^1H\}$ $\delta$ 166.7 ($C$(O), $^2J_{PC}=5.5$ Hz), 80.7 ($NCH_2$), 79.7 ($NCH_2$), 61.9 ($POCH_2$, $^2J_{PC}=6.3$ Hz), 61.3 ($POCH_2$, $J_{PC}=6.3$ Hz), 60.7 ($CH_2OH$), 41.1 ($PCH$, $^1J_{PC}=133.2$ Hz), 30.4 ($CHCH_2$, $J_{PC}=15.6$ Hz), 23.5 ($CH_2CH_2OH$), 15.5 ($CH_3CH_2OH$), 15.5 ($CH_3CH_2O$, $J_{PC}=5.0$ Hz), 13.7 ($NCH_2CH_3$), 12.0 ($NCH_2CH_3$).

**6b**. Solubility: benzene, THF, $CHCl_3$, $CH_2Cl_2$. *Anal.* Calc. for $PO_5NC_{15}H_{32}$: C, 53.40; H, 9.56; N, 4.15. Found: C, 53.18; H, 9.59; N, 3.89. Mass spectrum: $[M^+ + H]$ 338. IR spectrum (neat, $cm^{-1}$): 3426(br), 2980(m), 1634(s), 1452(m), 1235(s), 1105(m), 987(s). NMR spectra (22 °C, $CDCl_3$): $^{31}P\{^1H\}$ $\delta$ 23.5; $^{13}C\{^1H\}$ 164.3 (C(O)), 68.1 ($OCH$, $J_{PC}=4.9$ Hz), 67.7 ($OCH$, $J_{PC}=5.1$ Hz), 58.2 ($CH_2OH$), 39.5 ($NCH_2$), 39.0 ($OCH$, $^1J_{PC}=134.6$ Hz), 37.9 ($NCH_2$), 28.1 ($CHCH_2$, $J_{PC}=14.8$ Hz), 21.3 ($CH_2CH_2OH$), 20.6 ($OCHCH_3$), 9.7 ($NCH_2CH_3$).

*$[(RO)\overline{P(O)][C(O)NEt_2]CH(CH_2CH_2CH_2O)}$ (7)*

**7a**. Solubility: benzene, THF, $CHCl_3$, $CH_2Cl_2$. *Anal.* Calc. for $PO_4NC_{11}H_{21}$: C, 50.38; H, 8.07; N, 5.34. Found: C, 50.05; H, 8.78; N, 5.24%. Mass spectrum: $[M^+]$ 263. IR spectrum (neat, $cm^{-1}$), 2975(m), 1641(s), 1266(s), 963(s). NMR spectra (22 °C, $CDCl_3$): $^{31}P\{^1H\}$ $\delta$ 15.4; $^{13}C\{^1H\}$ $\delta$ 165.5 (C(O), $^2J_{PC}=5.7$ Hz), 69.8 ($POCH_2$, $J_{PC}=7.5$ Hz), 62.2 ($CH_2O$, $J_{PC}=6.6$ Hz), 41.6 ($NCH_2$), 40.2 ($PCH$, $^1J_{PC}=117.7$), 40.2 ($NCH_2$), 26.0 ($CH_2CH_2O$, $J_{PC}=7.7$ Hz), 25.2 ($CH_2CH_2O$, $J_{PC}=5.1$ Hz), 15.8 ($CH_3CH_2O$, $J_{PC}=5.4$ Hz), 13.7 ($NCH_2CH_3$), 12.3 ($NCH_2CH_3$); $^1H$ $\delta$ 3.96 ($CH_3CH_2O$, $J_{PH}=7.1$ Hz), 3.86 ($CH_2CH_2O$, $J_{PH}=7.1$ Hz), 3.34 ($NCH_2$, $J_{HH}=6.8$ Hz), 3.00 ($NCH_2$, $J_{HH}=7.4$ Hz), 2.70 ($CHCH_2$), 2.05 ($PCH$), 1.62 ($CH_2CH_2CH_2O$), 1.14 ($CH_3CH_2O$), 0.97 ($NCH_2CH_3$), 0.91 ($NCH_2CH_3$).

**7b**. Solubility: benzene, THF, $CHCl_3$, $CH_2Cl_2$. *Anal.* Calc. for $PO_4NC_{12}H_{24}$: C, 51.98; H, 8.89; N, 5.05. Found: C, 52.02; H, 8.89; N, 4.88%. Mass spectrum: $[M^+]$ 277 not observed. IR spectrum (neat, $cm^{-1}$): 1642(s), 1264(s), 969(s). NMR spectra (22 °C, $CDCl_3$): $^{31}P\{^1H\}$ $\delta$ 14.4; $^{13}C\{^1H\}$ $\delta$ 164.7 (C(O), $^2J_{PC}=5.9$ Hz), 70.2 ($CH_2CH_2O$, $J_{PC}=6.9$ Hz), 69.0 ($CHO$, $^2J_{PC}=7.5$ Hz), 40.9 ($NCH_2$), 39.9 ($PCH$, $^1J_{PC}=118.3$ Hz), 39.4 ($NCH_2$), 25.4 ($CH_2CH_2O$, $J_{PC}=8.0$ Hz), 24.6 ($CHCH_2$, $J_{PC}=4.8$ Hz), 23.0 ($CH_3CH$), 13.1 ($NCH_2CH_3$), 11.7 ($NCH_2CH_3$); $^1H$ $\delta$ 4.22 ($CHO$), 3.82 ($CH_2CH_2O$). 3.56 ($NCH_2$, $J_{HH}=7.5$ Hz), 3.21 ($NCH_2$, $J_{HH}=6.7$ Hz), 2.78 ($CHCH_2$), 2.65 ($CHCH_2$), 1.9 ($PCH$), 1.65 ($CH_2CH_2CH_2O$), 1.39 ($CH_2CH_2CH_2O$), 0.88 ($OCHCH_3$, $J_{PH}=5.5$ Hz, $J_{HH}=6.2$ Hz), 0.72 ($NCH_2CH_3$, $J_{HH}=7.0$ Hz), 0.66 ($NCH_2CH_3$, $J_{HH}=7.0$ Hz).

*$[(HO)_2P(O)][C(O)NEt_2]CH(CH_2COOH)$ (8)*

Solubility: water. *Anal.* Calc. for $PO_6NC_8H_{16}$: C, 37.95; H, 6.37; N, 5.53. Found: C, 38.24; H, 6.31; N, 5.53%. NMR spectra (22 °C, $D_2O$): $^{31}P\{^1H\}$ $\delta$ 17.7; $^{13}C\{^1H\}$ $\delta$ 175.1 ($COOH$, $J_{PC}=19.2$ Hz), 172.8 ($C$(O), $J_{PC}=2.8$ Hz), 43.0 ($NCH_2$), 42.9 ($PCH$, $^1J_{PC}=126.9$ Hz), 32.0 ($CH_2COOH$), 11.4 ($NCH_2CH_3$).

*$[(Me_3SiO)_2P(O)][C(O)NEt_2]CH_2$ (9)*

Solubility: benzene, toluene, THF and $Et_2O$. IR spectrum (neat, $cm^{-1}$) 2960(m), 2940(sh), 2900(w), 1645(s), 1465(m), 1455(m), 1430(m), 1385(w), 1365(w), 1315(w), 1252(s), 1225(sh), 1100(m), 1020(s), 950(w), 920(w), 850(s), 810(sh), 710(m), NMR spectra (22 °C, $C_6D_6$): $^{31}P\{^1H\}$ $\delta$ 2.8; $^{13}C\{^1H\}$ $\delta$ 164.0 ($C$(O), $^2J_{PC}=6.4$ Hz), 42.9 ($NCH_2$), 40.2 ($NCH_2$), 36.1 ($PCH_2$, $J_{PC}=137.4$ Hz), 14.2 ($NCH_2CH_3$), 13.2 ($NCH_2CH_3$), 0.9 ($CH_3Si$); $^1H$ $\delta$ 3.3 ($NCH_2$, $J_{HH}=7.0$ Hz), 2.9 ($PCH_2$, $J_{PH}=22.8$ Hz), 1.0 ($NCH_2CH_3$, $J_{HH}=7.0$ Hz), 0.2 ($CH_3Si$).

*$[(HO)_2P(O)][C(O)NEt_2]CH_2$ (10)*

Solubility: water and ethanol. IR spectrum (KBr, $cm^{-1}$): 2985(m), 1559(s), 1478(m), 1456(m), 1177(m), 1102(m), 1034(s), 1019(s), 952(s). NMR spectra (22 °C, $CD_3CN/H_2O$): $^{31}P\{^1H\}$ $\delta$ 17.9; $^{13}C\{1H\}$ $\delta$ 166.6 ($C$(O), $J_{PC}=6.0$ Hz), 43.0 ($NCH_2$), 40.4 ($NCH_2$), 33.4 ($PCH_2$, $^1J_{PC}=129.1$ Hz), 12.9 ($NCH_2CH_3$), 11.8 ($NCH_2CH_3$); $^1H$ $\delta$ 3.35 ($NCH_2$, $J_{HH}=7.1$ Hz), 3.31 ($NCH_2$, $J_{HH}=7.1$ Hz), 2.93 ($PCH_2$, $J_{PH}=21.9$ Hz), 1.07 ($NCH_2CH_3$, $J_{HH}=6.8$ Hz), 0.98 ($NCH_2CH_3$, $J_{HH}=6.8$ Hz).

*$[\overline{NH_2C(CH_3)_2CH_2C(O)CH_2C}(CH_3)_2^+]$-*
*$[(HO)P(O)_2CH_2C(O)NEt_2^-]$ (11)*

Solubility: water. *Anal.* Calc. for $PO_5N_2C_{15}H_{31}$: C, 51.43; H, 8.92; N, 8.00; P, 8.84; O, 21.82. Found: C, 51.32; H, 8.92; N, 8.14; P, 8.62; O, 22.81%. NMR spectra (22 °C, $CD_3CN/H_2O$): $^{31}P\{^1H\}$ $\delta$ 12.1; $^{13}C\{^1H\}$ $\delta$ 168.2 ($PCH_2C$(O), $J_{PC}=5.3$ Hz), 61.3 (pip $C$ $CH_3$)$_2$, 51.5 (pip $CH_2$), 45.2 ($NCH_2$), 42.3 ($NCH_2$), 37.0 ($PCH_2$, $J_{PC}=120.4$ Hz), 29.0 (pip $CH_3$), 14.7 ($NCH_2CH_3$), 13.8 ($NCH_2CH_3$).

*X-ray diffraction studies*

The sample of **4b** was recrystallized from n-butanol, and a colorless crystal of dimensions $0.23\times0.34\times0.41$ mm was placed in a capillary and sealed off under an ambient atmosphere. The crystals of **11** were obtained as described in the synthesis section, and a crystal of dimension $0.14\times0.16\times0.62$ mm was lodged in a glass capillary and sealed under an ambient atmosphere. The crystals were centered on a Siemens R3M/V automated diffractometer, and determinations of crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner. Data were obtained with use of Mo K$\alpha$ radiation, a scintillation counter, and pulse height analyzer. Data collection parameters are

TABLE 1. X-ray data for {[i-Pr(O)$_2$P(O)][C(O)NEt$_2$]CH}$_2$CH$_2$ (**4b**) and [$\overline{NH_2C(CH_3)_2CH_2C(O)CH_2C(CH_3)_2}^+$][(HO)P(O)$_2$CH$_2$C(O)N(C$_2$H$_5$)$_2^-$] (**11**)

| | **4b** | **11** |
|---|---|---|
| *Crystal parameters* (T°) | 20(2) | 25(2) |
| Chemical formula | $P_2O_8N_2C_{25}H_{52}$ | $PO_5N_2C_{15}H_{31}$ |
| Crystal system | triclinic | triclinic |
| Space group | *P*1 | *P*1 |
| *a* (Å) | 9.0996(24) | 9.2384(21) |
| *b* (Å) | 12.6604(31) | 9.8404(21) |
| *c* (Å) | 16.5711(48) | 11.0702(25) |
| $\alpha$ (°) | 68.655(20) | 85.276(18) |
| $\beta$ (°) | 78.714(22) | 74.477(17) |
| $\gamma$ (°) | 70.742(19) | 78.644(17) |
| *V* (Å$^3$) | 1909.1 | 950.27 |
| *Z* | 2 | 2 |
| $D_{calc}$ (g Å$^{-3}$) | 1.13 | 1.22 |
| Molecular weight | 570.64 | 350.40 |
| $\mu$ (cm$^{-1}$) | 1.66 | 1.63 |
| *F*(000) | 620 | 380 |
| *Data collection* | | |
| Radiation | Mo K$\alpha$ ($\lambda$=0.71069 Å) | |
| Monochromator | highly oriented graphite crystal | |
| Reflections measured | $\pm h \pm k \pm l$ | $\pm h \pm k \pm l$ |
| 2$\theta$ range (°) | 3–53 | 2–50 |
| Scan type | $\omega$ | $\theta$–2$\theta$ |
| Scan speed (° min$^{-1}$) | 4–30 | 4–30 |
| Scan range (°) | $\omega(0)-1$ to $\omega(0)+1.25$ | $2\theta(K_{\alpha 1})-1.15$ to $2\theta(K_{\alpha 2})+1.25$ |
| Background measurements | Stationary crystal and counter; at the beginning and end of scan, each for 1/2 of total scan time | |
| Standard reflections | [3-2-2, 040, 004]<br>3 measured every 141 reflections | [300, 040, 003] |
| Total reflections collected | 14226 | 6884 |
| Unique reflections | 5882 | 3362 |
| Observed reflections used in refinement | 3203<br>$F>4\sigma(F)$ | 2573<br>$F>3\sigma(F)$ |
| Transmission (min./max.) | 0.409/0.466 | 0.754/0.838 |
| $R_F$ (%) | 8.49 | 7.49 |
| $R_{wF}$ (%) | 8.28 | 6.71 |
| Weighting scheme, $w=$ | $1/\sigma^2(F)+0.00115F^2$ | $1/\sigma^2(F)+0.0004F^2$ |
| No. parameters | 330 | 289 |
| Goodness of fit | 1.574 | 1.795 |

summarized in Table 1. In each case, an empirical adsorption correction was made, based on $\psi$ scans*. Redundant and equivalent data were averaged and converted to unscaled $|F_0|$ values, following corrections for Lorentz and polarization effects.

All calculations were performed with the R3/SHELXTL structure determination package [11]**. Least-squares refinements use a blocked-cascade algorithm with full matrix blocks of 103 parameters†. The structure of **4b** was solved by direct methods, and positions of 22 atoms were initially located. Fourier difference maps provided the positions of the remaining 15 atoms. Four atoms, C(12), C(14), C(24), and C(25), were found to have two-fold disorder, and each position was assigned an occupancy factor of 1/2. Final refinement with hydrogen atoms in idealized positions (riding model) led to $R_F=8.49\%$. The non-hydrogen atom

*The empirical absorption correction uses an ellipsoidal model fitted to azimuthal scans and then applied to the intensity data.

**SHELXTL uses absorption, anomalous dispersion, and scattering data compiled in ref. 12. Anomalous dispersion terms were included for all atoms with atomic numbers greater than 2.

†A general description of the least-squares algebra is found in ref. 13. The least-squares refinement minimizes $\Sigma w(|F_o|-|F_c|)^2$, where $w=1/[\sigma(F)^2+gF^2]$, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_{wF}=[\Sigma(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, and $GOF=[\Sigma w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$ where $NO$ = number of observations and $NV$ = number of variables.

TABLE 2. Atomic positions for {[(i-PrO)$_2$P(O)]-[C(O)NEt$_2$]CH}$_2$CH$_2$ (**4b**)

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| P(1) | 0.83859(18) | 0.18330(13) | 0.22966(10) |
| P(2) | 0.44727(17) | 0.58761(13) | 0.28204(10) |
| O(1) | 0.9958(5) | 0.1148(4) | 0.2074(3) |
| O(2) | 0.7111(4) | 0.2061(4) | 0.1695(3) |
| O(3) | 0.7557(5) | 0.1266(3) | 0.3193(3) |
| O(4) | 0.9194(5) | 0.3027(4) | 0.3627(2) |
| O(5) | 0.3361(4) | 0.5766(4) | 0.2363(3) |
| O(6) | 0.4322(4) | 0.5285(4) | 0.3841(3) |
| O(7) | 0.4466(5) | 0.7149(4) | 0.2693(3) |
| O(8) | 0.6812(5) | 0.5801(4) | 0.1001(2) |
| N(1) | 1.1001(5) | 0.3205(4) | 0.2480(3) |
| N(2) | 0.7786(7) | 0.6718(5) | 0.1593(3) |
| C(1) | 0.8319(6) | 0.3290(4) | 0.2286(3) |
| C(2) | 0.9548(6) | 0.3173(5) | 0.2847(4) |
| C(3) | 0.6686(6) | 0.3946(5) | 0.2571(4) |
| C(4) | 0.6513(6) | 0.5218(4) | 0.2541(3) |
| C(5) | 0.7041(6) | 0.5941(5) | 0.1652(4) |
| C(6) | 1.1556(7) | 0.3322(7) | 0.1560(4) |
| C(7) | 1.1509(10) | 0.4559(7) | 0.0996(5) |
| C(8) | 1.2156(8) | 0.3098(6) | 0.3028(4) |
| C(9) | 1.3303(9) | 0.1914(7) | 0.3284(6) |
| C(10) | 0.7471(9) | 0.2343(7) | 0.0758(5) |
| C(11) | 0.6122(11) | 0.3284(9) | 0.0327(5) |
| C(12) | 0.7376(24) | 0.1074(19) | 0.0709(13) |
| C(12a) | 0.8204(18) | 0.1236(14) | 0.0493(10) |
| C(13) | 0.8418(11) | 0.0385(8) | 0.3887(6) |
| C(14) | 0.7832(35) | −0.0762(26) | 0.3766(18) |
| C(14a) | 0.8589(24) | −0.0803(17) | 0.4025(12) |
| C(15) | 0.7623(14) | 0.0729(11) | 0.4685(7) |
| C(16) | 0.7967(9) | 0.7060(7) | 0.2326(5) |
| C(17) | 0.9464(10) | 0.6432(9) | 0.2650(6) |
| C(18) | 0.8316(10) | 0.7413(7) | 0.0714(4) |
| C(19) | 0.7062(14) | 0.8478(8) | 0.0268(6) |
| C(20) | 0.2994(8) | 0.4878(7) | 0.4331(4) |
| C(21) | 0.3647(12) | 0.3645(8) | 0.4935(6) |
| C(22) | 0.2067(9) | 0.5721(8) | 0.4804(5) |
| C(23) | 0.3043(8) | 0.8145(6) | 0.2608(4) |
| C(24) | 0.3572(21) | 0.9172(16) | 0.2716(11) |
| C(24a) | 0.3189(18) | 0.8812(14) | 0.3204(10) |
| C(25) | 0.2367(16) | 0.8617(12) | 0.1721(9) |
| C(25a) | 0.3194(23) | 0.8893(18) | 0.1638(12) |

positional parameters are listed in Table 2. See also 'Supplementary material'.

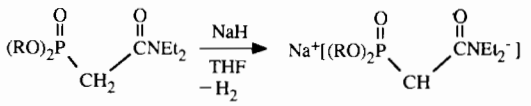
The structure of **11** was solved by direct methods, and positions for the atoms in the fragment $O_3PCC(O)NC_2$ were initially located. Subsequent Fourier difference maps located the remaining heavy atoms. Final refinements included all hydrogen atom positions on C and N atoms except C(6) and C(7). The well-behaved hydrogen atoms were allowed to vary in position with $U_{iso}$ set to 1.2 times the last $U_{eq}$ of the parent atom. The hydrogen positions on C(6) and C(7) were calculated using the riding model. The final agreement factor was $R_F = 7.49\%$. The non-hydrogen atom positional parameters are listed in Table 3.

TABLE 3. Atomic positions for [$\overline{NC(CH_3)_2CH_2C(O)CH_2C}$-$(CH_3)_2^+$][(HO)P(O)$_2$CH$_2$C(O)NEt$_2$] (**11**)

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| P(1) | 0.10559(11) | 0.16499(9) | 0.00289(9) |
| O(1) | 0.0912(4) | 0.1222(3) | −0.1249(3) |
| O(2) | 0.0948(3) | 0.3197(2) | −0.0017(2) |
| O(3) | −0.0072(3) | 0.1118(2) | 0.1122(2) |
| O(4) | 0.4036(3) | 0.2094(3) | 0.1216(3) |
| C(1) | 0.2957(4) | 0.0820(4) | 0.0079(4) |
| C(2) | 0.3424(4) | 0.1097(4) | 0.1220(4) |
| N(3) | 0.3195(4) | 0.0199(4) | 0.2200(4) |
| C(4) | 0.2468(6) | −0.1024(4) | 0.2320(5) |
| C(5) | 0.1090(7) | −0.0982(5) | 0.3392(5) |
| C(6) | 0.4025(10) | 0.0258(7) | 0.3217(6) |
| C(7) | 0.3080(8) | 0.1251(8) | 0.3957(7) |
| N(8) | −0.1578(3) | 0.4706(3) | 0.1701(2) |
| C(9) | −0.3113(4) | 0.4332(4) | 0.1737(3) |
| C(10) | −0.3324(4) | 0.3059(4) | 0.2617(4) |
| C(11) | −0.2968(5) | 0.3166(4) | 0.3834(4) |
| C(12) | −0.1393(5) | 0.3478(4) | 0.3685(4) |
| C(13) | −0.1146(4) | 0.4813(4) | 0.2912(3) |
| C(14) | −0.4413(5) | 0.5555(4) | 0.2149(4) |
| C(15) | −0.3050(4) | 0.3989(4) | 0.0414(4) |
| C(16) | −0.2074(5) | 0.6091(4) | 0.3628(4) |
| C(17) | 0.0528(5) | 0.4930(4) | 0.2561(4) |
| O(5) | −0.3826(4) | 0.2988(4) | 0.4843(3) |

## Results and discussion

Reactive carbanions **2** of the carbamoylmethyl phosphonates $(RO)_2P(O)CH_2C(O)NEt_2$, R = Et, i-Pr and n-Hex (**1**), are obtained from their reaction with NaH in THF, as described in eqn. (1).

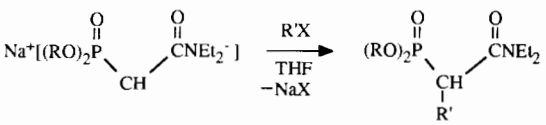



(1)

**1** **2**

| R | Et | i-Pr | n-Hex |
|---|---|---|---|
| | **1a** | **1b** | **1c** |

| R | Et | i-Pr | n-Hex |
|---|---|---|---|
| | **2a** | **2b** | **2c** |

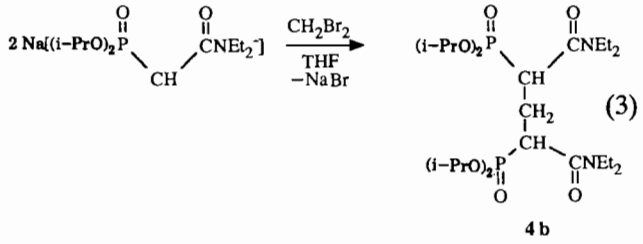



(2)

| R/R' | Et | n-Hex |
|---|---|---|
| Me | **3a** | **3c** |
| Et | **3a'** | |

Combinations of the carbanion **2a** with MeI and EtBr result in formation of 1-phosphono-1-carbamoylethanes (**3a** and **3c**) and -propane (**3a'**) as distillable liquids. In a related fashion, combination of **2b** with $CH_2Br_2$ in a 2:1 ratio results in elimination of two equivalents of NaBr and formation of 1,3-diphosphono-

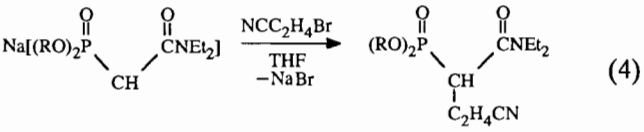
1,3-dicarbamoyl propane (**4b**), as shown in eqn. 3. This compound effectively links two carbamoylmethyl phosphonate ligand fragments on a short hydrocarbon backbone.



(3)

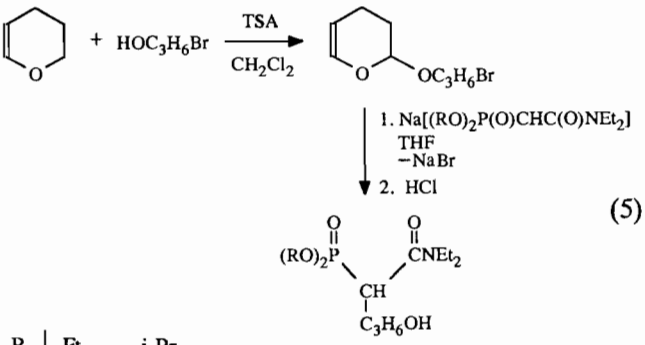
**4b**

The reactions of **2b** and **2c** with bromopropionitrile in a 1:1 ratio results in the formation of 1-phosphono-1-carbamoyl-3-cyanopropanes (**5b** and **5c**) as distillable, colorless oils, as described in eqn. (4). In both cases, the substitution reactions are sluggish, and the yields of products are unexpectedly low. On the other hand, the reactions of **2a** and **2b** with a tetrahydropyranyl protected form of bromopropanol readily leads to the respective 1-phosphono-1-carbamoyl-4-butanols (**6a** and **6b**), as shown in eqn. (5). It is interesting that prolonged heating of **6a** and **6b** at 90–100 °C (10 mTorr) does not result in intramolecular transesterification. Combinations of protected chloropropanol or chloroethanol with **2a** and **2b**, on the other hand, gave no reaction. Given these results, it is unexpected that combination of **2a** and **2b** with unprotected chloropropanol leads to intramolecular transesterification, as shown in eqn. (6). Alternatively, **7a** and **7b** are obtained by stirring **6a** and **6b** with Na in EtOH or i-PrOH.



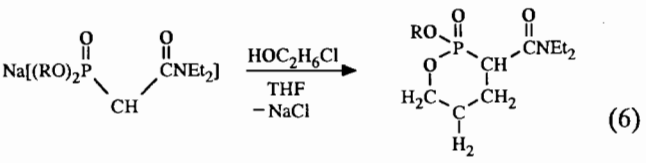
(4)

| R | i-Pr | n-Hex |
|---|---|---|
| | **5b** | **5c** |



(5)

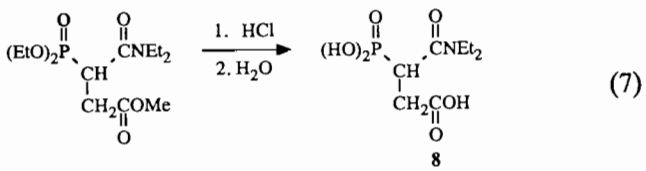
| R | Et | i-Pr |
|---|---|---|
| | **7a** | **7b** |



(6)

| R | Et | i-Pr |
|---|---|---|
| | **7a** | **7b** |

There is considerable interest in multifunctional phosphonic acid ligands, and the hydrolysis of two phosphonates, $[(EtO)_2P(O)][C(O)NEt_2]CHCH_2C(O)OMe$ and $(EtO)_2P(O)CH_2C(O)NEt_2$, was examined in this study. It is well known that both phosphono and carboxy esters undergo ready hydrolysis with strong mineral acids [14]. Indeed, when the trifunctional ligand $[(EtO)_2P(O)][C(O)NEt_2]CHCH_2C(O)OMe$ was exposed to 6 M HCl and refluxed for 3 h, hydrolysis ensued, as summarized in eqn. (7). The tri-acid **8** is obtained as a semi-solid in high yield. The hydrolysis of the CMP ligand $(EtO)_2P(O)CH_2C(O)NEt_2$, on the other hand, is much more sluggish. Attempts to effect hydrolysis with HCl resulted in formation of the mono-acid $(EtO)(HO)P(O)CH_2C(O)NEt_2$ in poor yield, and none of the di-acid was obtained.

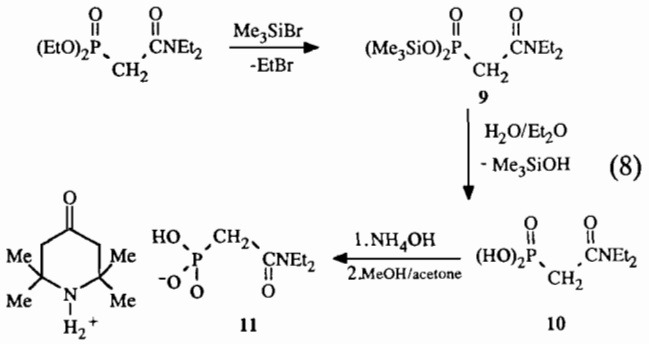


(7)

**8**

Several investigators [15–17] have reported that $Me_3SiCl$ and $Me_3SiBr$ react with organophosphonates $(RO)_2P(O)R'$ with formation of the respective organosilyl phosphonates $(Me_3SiO)_2P(O)R'$. In the present study, $(EtO)_2P(O)CH_2C(O)NEt_2$ was combined with $Me_3SiBr$ in a 1:2 ratio, and the disilyl ester **9** was obtained as a colorless liquid in quantitative yield. This compound was then hydrolyzed in diethyl ether solution, and the di-acid **10** was obtained as a sticky white solid. The di-acid character was confirmed by titrametric analysis with $Et_4NOH$, and the ionization constants were estimated as $pK_{a1} = 4.80$ and $pK_{a2} = 10.49$. Several attempts to recrystallize **10** in various solvents were unsuccessful. Consequently, efforts were made to recrystallize salts of the acid. In most cases, sticky solids were obtained; however, in one case, the acid was neutralized with $NH_4OH$ to pH 7–9, which resulted in formation of the monoammonium salt. Dissolution of this salt in MeOH, followed by addition of acetone, led to a Mannisch reaction between ammonium ion and acetone with formation of the 2,2,6,6-tetramethylpiperidone cation, as shown in eqn. (8). This

species serves as an excellent counter ion for the mono-acid $[(HO)PO_2CH_2C(O)NEt_2^-]$, and the salt **11** is isolated as colorless crystalline solid.




The new compounds were characterized by a combination of elemental analysis, mass spectrometry, and IR and NMR spectroscopy. In general, the compounds provide satisfactory composition analyses; however, the analyses for **3c** and **5c** were troubled by complexation of small amounts of NaBr by the ligands. All of the compounds except **7b** and the acids **8** and **10** display a parent ion in the mass spectra. IR spectra of the phosphonate esters display a strong absorption in the region 1647–1634 $cm^{-1}$ that can be assigned to $\nu$(C=O) and a strong absorption in the region 1266–1234 $cm^{-1}$ that is assigned to $\nu$(P=O). The acid **10** displays a $\nu$(C=O) band at 1559 $cm^{-1}$ and bands at 1034 and 1019 $cm^{-1}$ that correspond to $\nu$(P=O). The $^{31}P\{^1H\}$ NMR spectra for the new compounds display a single resonance in the expected regions for organophosphonate esters $\delta$ 30–5 and phosphonic acids $\delta$ 20–10 [18]. Further, the $^{13}C\{^1H\}$ and $^1H$ NMR spectra are fully consistent with the proposed structures of the compounds.

The molecular structures of the tetrafunctional ligand **4b** and the mono-acid **11** were of sufficient interest that they were determined by single crystal X-ray diffraction analyses. Views of the molecules are shown in Figs. 1 and 2, respectively, and selected bond distances and angles are summarized in Table 4. The structure of **4b** confirms that two CMP fragments have been linked at the central methylene carbon atoms C(1) and C(4) through a $-C(3)H_2-$ bridge. It is interesting that the P=O and C=O groups within each CMP fragment are twisted with respect to each other: dihedral angles between planes C(1)–C(2)–O(4) and C(1)–P(1)–O(1) and C(4)–C(5)–O(8) and C(4)–P(2)–O(5) are 104.5 and 111.4°, respectively. Further, the phosphoryl groups P(1)–O(1) and P(2)–O(5) are on the same side (pseudo *cis* relationship) of (C3), but the groups are approximately *anti* with respect to each other. The same is true for the relative orientation of the carbonyl groups C(2)–O(4) and C(5)–O(8). It might be expected, therefore, that this ligand could act as a P(O)–P(O), P(O)–C(O) or C(O)–C(O) bidentate ligand. In each case, the ligand would have to undergo some torsional distortion from the structure shown in Fig. 1 in order to accommodate bidentate chelation, but it would be expected that the barrier to reorientation would be small. Unfortunately, all attempts to date to isolate metal complexes of this ligand have been unsuccessful.

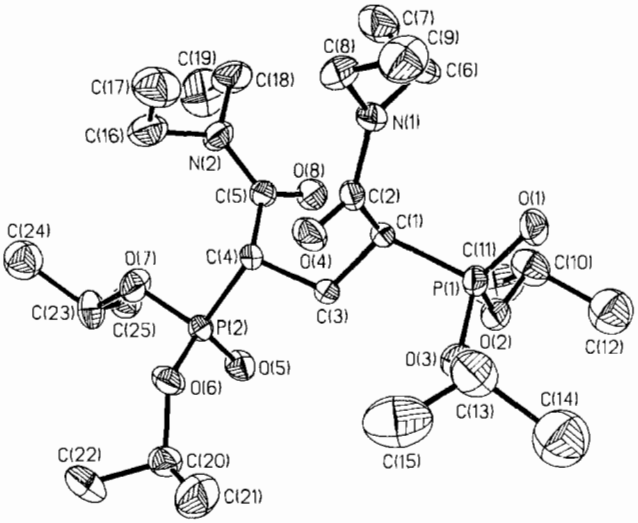



Fig. 1. Molecular structure and atom labeling scheme for **4b**.

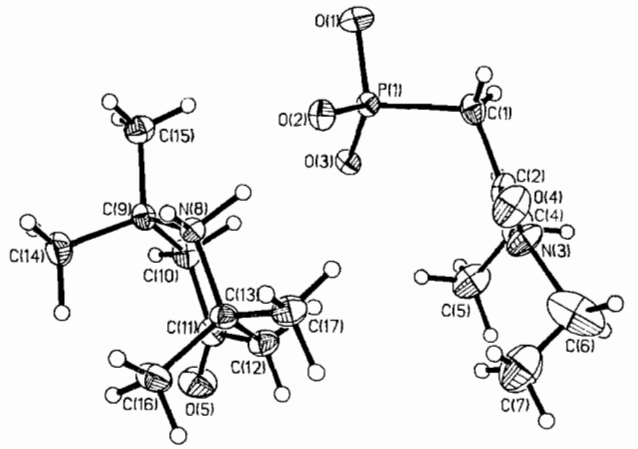



Fig. 2. Molecular structure and atom labeling scheme for **11**.

The P=O distances, 1.464(4) and 1.444(5) Å, are significantly shorter than the P–Oi-Pr distances (av. 1.562 Å), and these distances are comparable with the values found in the trifunctional ligand $[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2C(O)NEt_2$ [19]: P=O 1.459 Å (3) and av. P–Oi-Pr 1.575 Å. The C=O distances 1.231(7) and 1.220(8) Å are identical with the carbonyl distances in the trifunctional ligand: 1.228(3) and 1.223(3) Å [7]. The backbone (O)C–N distances, C(2)–N(1) 1.349(7) and C(5)–N(2) 1.335(10) Å, are shorter than C–N distances for the $N\text{–}Et_2$ groups (av. distance 1.477 Å), and a similar trend is found in the

TABLE 4. Selected bond distances (Å) and bond angles (°) for **4b** and **11**

| **4b** | | | | **11** | |
|---|---|---|---|---|---|
| Bond distances | | | | | |
| P(1)–O(1) | 1.464(4) | P(2)–O(5) | 1.444(5) | P(1)–O(1) | 1.554(3) |
| P(1)–O(2) | 1.563(5) | P(2)–O(6) | 1.580(4) | P(1)–O(2) | 1.504(2) |
| P(1)–O(3) | 1.560(4) | P(2)–O(7) | 1.545(5) | P(1)–O(3) | 1.503(2) |
| P(1)–C(1) | 1.819(6) | P(2)–C(4) | 1.811(5) | P(1)–C(1) | 1.799(4) |
| C(1)–C(3) | 1.523(7) | C(3)–C(4) | 1.549(9) | C(1)–C(2) | 1.500(7) |
| C(2)–O(4) | 1.231(7) | C(5)–O(8) | 1.220(8) | C(2)–O(4) | 1.224(6) |
| C(2)–N(1) | 1.349(7) | C(5)–N(2) | 1.335(10) | C(2)–N(3) | 1.340(6) |
| N(1)–C(6) | 1.479(8) | N(2)–C(16) | 1.484(12) | N(3)–C(4) | 1.470(7) |
| N(1)–C(8) | 1.462(10) | N(2)–C(18) | 1.483(8) | N(3)–C(6) | 1.532(10) |
| | | | | C(11)–O(5) | 1.207(5) |
| | | | | C(10)–C(11) | 1.485(6) |
| | | | | C(9)–C(10) | 1.533(5) |
| | | | | N(8)–C(9) | 1.523(5) |
| | | | | N(8)–C(13) | 1.515(5) |
| | | | | C(13)–C(12) | 1.529(5) |
| Bond angles | | | | | |
| O(1)–P(1)–O(2) | 115.7(3) | O(5)–P(2)–O(6) | 115.3(3) | O(1)–P(1)–O(2) | 108.0(2) |
| O(1)–P(1)–O(3) | 116.8(2) | O(5)–P(2)–O(7) | 116.2(3) | O(1)–P(1)–O(3) | 112.2(2) |
| O(2)–P(1)–O(3) | 99.0(2) | O(6)–P(2)–O(7) | 103.8(3) | O(2)–P(1)–O(3) | 114.0(1) |
| O(1)–P(1)–C(1) | 112.9(3) | O(5)–P(2)–C(4) | 116.0(3) | O(1)–P(1)–C(1) | 103.8(2) |
| O(3)–P(1)–C(1) | 105.6(3) | O(7)–P(2)–C(4) | 101.4(3) | O(2)–P(1)–C(1) | 109.3(2) |
| O(2)–P(1)–C(1) | 105.2(2) | O(6)–P(2)–C(4) | 102.0(2) | O(3)–P(1)–C(1) | 109.0(2) |
| C(2)–N(1)–C(6) | 125.6(6) | C(5)–N(2)–C(16) | 125.4(2) | C(2)–N(3)–C(4) | 127.4(5) |
| C(2)–N(1)–C(8) | 118.5(5) | C(5)–N(2)–C(18) | 118.1(6) | C(2)–N(3)–C(6) | 117.7(5) |
| C(6)–N(1)–C(8) | 116.0(5) | C(16)–N(2)–C(18) | 116.0(7) | C(4)–N(3)–C(6) | 113.9(4) |
| O(4)–C(2)–C(1) | 118.9(5) | O(8)–C(5)–C(4) | 120.4(6) | O(4)–C(2)–C(1) | 119.8(4) |
| O(4)–C(2)–N(1) | 121.6(6) | O(8)–C(5)–N(2) | 120.9(5) | O(4)–C(2)–N(3) | 122.3(5) |
| N(1)–C(2)–C(1) | 119.4(5) | N(2)–C(5)–C(4) | 118.7(6) | C(1)–C(2)–N(3) | 117.8(4) |
| | | | | C(10)–C(11)–C(12) | 113.1(3) |
| | | | | C(10)–C(11)–O(5) | 123.9(4) |
| | | | | C(12)–C(11)–O(5) | 122.9(4) |

trifunctional ligand: av. (O)C–N 1.353, av. N–$Et_2$ 1.462 Å.

The structure of **11** confirms that the compound consists of the 2,2,6,6-tetramethylpiperidone cation and monophosphonic acid anion. In the anion, the $PO_2(OH)$ unit is tetrahedral, and the P–OH distance, 1.554(3) Å, is distinctly longer than P(1)–O(2) and P(1)–O(3) distances, 1.504(2) and 1.503(2) Å. These distances may be compared with the corresponding distances in the di-acid $[(HO)_2P(O)][C(O)NEt_2]CHCH_2C_6H_4OH$: P=O 1.489(2), P–OH 1.537(3), and 1.545(2) Å [17]. The C(2)=O(4) bond distance, 1.224(6) Å, is comparable with the carbonyl distances in $[(HO)_2P(O)][C(O)NEt_2]CHCH_2C_6H_4OH$, 1.235(4) Å and in $[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2C(O)NEt_2$, 1.228(3) and 1.223(3) Å. The C(2)=O(4) group is nearly in-plane with the P(1)–O(2) group. The amide group, as expected, is planar at the C(2) and N(3) atoms, and the C(2)–N(3) bond distance, 1.340(6) Å, is intermediate between the related (O)C–N distances in $[(HO)_2P(O)][C(O)NEt_2]CHCH_2C_6H_4OH$, 1.314(4) Å, and in $[(i\text{-}PrO)_2P(O)][C(O)NEt_2]CHCH_2C(O)NEt_2$, 1.353 Å. As is the case with **4b** and the above two compounds, the N–$Et_2$ distances (av. 1.501 Å) are considerably longer than the backbone C(2)–N(3) distance.

The structure of the piperidone cation is relatively regular, with an approximate mirror plane passing through the N(8), C(11), and O(5) atoms. The geometry about the C(11) atom is trigonal planar with a short C(11)–O(5) distance, 1.207(5) Å.

The results of this study indicate that a series of multifunctional ligands are easily prepared from metathesis reactions employing CMP carbanions **2**. Further, new phosphonic acid derivatives have been produced from $Me_3SiBr$ attack on organyl phosphonates followed by hydrolysis of the silyl ester. The coordination chemistry of the acids **4b** and **11** should prove interesting, and studies of that chemistry are in progress.

## Supplementary material

A full description of the structure solution of **4b** and **11** is available from author R.T.P.

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