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Synthesis and solution complexation behaviour of tetradentate diamines with hard phosphinate donors

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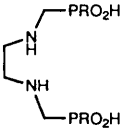
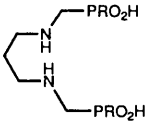
Seven acyclic tetradentate compounds of varying lipophilicity incorporating two nitrogen and two alkyl or aryl phosphinate donors have been prepared and their complexation of divalent ions has been studied in aqueous solution by pH-metric, NMR and electrospray mass spectrometric methods of analysis. The hard phosphinate oxygen donor favours binding to the charge-dense Mg^{2+} ion but binds copper(II) only very weakly in solution. Nickel and zinc ions do form 1 : 1 complexes involving significant phosphinate ligation and this donor-atom preference leads to an inversion of the Irving–Williams stability sequence.

There are some well defined differences in the complexation chemistry of proligands that incorporate α-aminoalkylphosphinic acids when compared to the more common α-aminocarboxylic acid. First, the phosphinate oxygen is more difficult to protonate both in the acid and in its metal complexes.[1–4] A consequence of this is that certain azaphosphinate metal complexes are remarkably resistant to proton-catalysed dissociation pathways. This has been studied in some detail in relation to the *in vivo* applications of radiolabelled complexes for imaging and therapy and with respect to paramagnetic contrast agents in magnetic resonance imaging.[5–9] Secondly, the lower basicity of the nitrogen and oxygen donor atoms in azaphosphinate ligands results in lower formation constants with respect to their azacarboxylate analogues.[1–4] Thirdly the pentavalency of phosphorus either allows control of complex lipophilicity[5] or affords a means of conjugation[9,10] through variation of the phosphorus alkyl or aryl substituent. Finally, when one of the phosphinate oxygens is bound to a metal centre a stereogenic centre is created at phosphorus.[3,7] In macrocyclic systems incorporating such phosphinate donors one major diastereoisomer is generally observed in solution which is configurationally stable with respect to racemisation.[11,12]

In seeking to define the complexation behaviour and coordination preferences of acyclic azaphosphinate ligands, we have prepared a set of tetradentate compounds with two nitrogen and two phosphinate oxygen donors L^1–L^7. The synthesis, based on an ethane-1,2-diamine or propane-1,3-diamine moiety, L^1–L^4, allows the effect of chelate-ring size to be assessed, whilst the compounds L^5–L^7 are of varying lipophilicity (PMe *vs.* PPh *vs.* PCH_2Ph) and are based on 1,10-phenanthroline. Attention has been focused on the complexation of dipositive ions and where possible a comparison is made with the behaviour of the corresponding carboxylates.



L^1 R = Me
L^2 R = Ph



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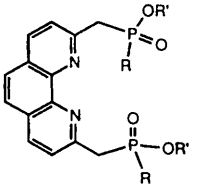
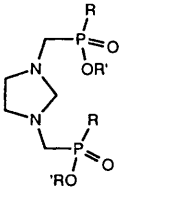
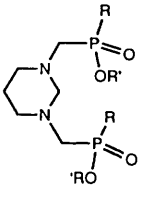


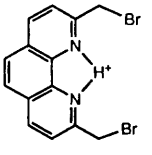
L^{5a} R = Me, R' = Et
L^{5b} R = Me, R' = H
L^{6a} R = Ph, R' = Et
L^{6b} R = Ph, R' = H
L^{7a} R = CH_2Ph, R' = Et
L^{7b} R = CH_2Ph, R' = H



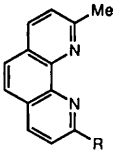
L^8 R = Me, R' = Et
L^9 R = Ph, R' = Me



L^{10} R = Me, R' = Et
L^{11} R = Ph, R' = Me



L^{12}



L^{13} R = CH_2PMeO_2Et
L^{14} R = Me

Results and Discussion

Synthesis

Reaction of ethane-1,2-diamine with freshly sublimed paraformaldehyde and $MeP(OEt)_2$ in dry tetrahydrofuran (thf) yielded the corresponding tetrahydroimidazole, L^8, in 54% yield after purification by chromatography on neutral alumina.[10] Acid hydrolysis (6 mol dm^{-3} HCl, 110 °C, 18 h) yielded the compound L^1 in quantitative yield. The corresponding phenylphosphinate L^2 was made by an analogous two-step sequence, but the desired reaction proceeded only when dimethoxyphenylphosphine was used: attempted reaction of $PhP(OEt)_2$ with ethane-1,2-diamine and $(CH_2O)_n$ surprisingly gave very little of the desired diester and the major product of the reaction was $PhP(CH_2OH)O_2Et$. Using propane-1,3-diamine in place of ethane-1,2-diamine, the corresponding diacids L^3 and L^4 were prepared *via* the intermediacy of the appropriate diesters L^{10} and L^{11}. The precursor for the synthesis of the 1,10-phenanthroline-based compounds L^5–L^7 was 2,9-bis(bromomethyl)phenanthroline L^{12}.[13] An Arbuzov reaction between L^{12} and $MeP(OEt)_2$, $PhCH_2P(OEt)_2$ or $PhP(OEt)_2$ in boiling, anhydrous MeCN yielded the phosphinate esters L^{5a}, L^{6a} and L^{7a}. This reaction was particularly sensitive to the presence of adventitious water in the case of L^{5a} and unless anhydrous conditions were maintained the

methylphenanthroline derivatives L^{13} and L^{14} were formed. Competitive halophilic attack of $MeP(OEt)_2$ may occur to generate the azomethine ylide which readily protonates to give a methyl group (Scheme 1). A similar sort of halophilic reaction has been reported when triphenylphosphine reacts with an α-halogenoketone.[14] In this case protonation of the enolate yields a methyl ketone, although addition of triethylamine allows phosphonium salt formation to predominate.[15]

Different hydrolysis conditions for the esters L^{5a}–L^{7a} were required according to the nature of the phosphorus substituent in order to prepare the desired compounds. For the methyl and the benzyl derivatives L^5 and L^7 acidic hydrolysis afforded the product (6 mol dm^{-3} HCl, 110 °C). Proton NMR analysis of the acid L^{7b} in CD_3OD revealed that the phenanthroline methylene protons readily underwent H/D exchange. This effect was also observed with L^{5b} and L^{6b}, and the rate of H/D exchange (as monitored by ^1H NMR spectroscopy) was $L^{6b} > L^{7b} \approx L^{5b}$ in accord with the effect of increasing conjugative stabilisation of the phosphoenolate intermediate. For the phenyl derivative, base hydrolysis (pH 13, aqueous NaOH) at room temperature afforded the desired salt from which the desired acid L^{6b} was isolated.

Protonation and metal complex equilibria

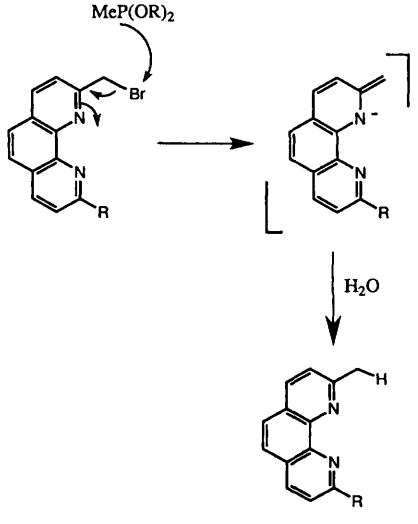
Protonation constants for the pro-ligands in aqueous solution were measured using standard pH-metric techniques Table 1, and show some expected trends. Compounds L^1–L^3 are less basic than the parent diamines, and the more strongly electron-withdrawing phenylphosphinate group exerts its influence most noticeably in the reduced second pK_a (L^2 *vs.* L^1 *vs.* ethane-1,2-diamine). With the phenanthroline-based compounds, the first pK_a was the same as that found for 2,9-dimethylphenanthroline.[16] In all cases but one, protonation at oxygen could not be determined accurately in the pH range studied. With L^{6b} a second protonation constant of 2.7 was measured, although there was a significant error associated with this value.

Stepwise formation constants for complex formation with the divalent metal ions Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were measured in aqueous solution. In the case of complexes of L^{6b} the relatively poor aqueous solubility of the neutral complexes necessitated the use of an aqueous methanol solvent (30% v/v MeOH). It has previously been noted that anionic phosphinates are good σ donors for charge-dense ions.[2,3] This effect is also established in polyazaphosphonates where some further pronounced examples of Mg/Ca selectivity have been reported.[17,18] The slightly higher values for the 1:1 ML formation constants for Mg^{2+} with L^1–L^3 (compared to Ca^{2+}) are therefore not unexpected. With L^3, engendering a six-ring chelate on binding to Mg^{2+} a small metal ion which should intrinsically favour six-membered ring chelate formation,[19] the reported formation constant log $\beta_{MgL(OH)} = 12.8$ relates to the sum of the ML and ML + OH formation constants. Assuming that the ML(OH) constant is of the order of 7, then this compound may exhibit quite good Mg^{2+}/Ca^{2+} selectivity (ratio of log β_{ML} values is *ca.* 2.4). That the phosphinate donor is an effective binding moiety for Mg^{2+} can also be seen by examining the 1:1 formation constant for Mg^{2+} with H_2edda (ethylenediiminodiacetic acid) (Table 2, 3.95). Notwithstanding the lower amine basicity, the overall values for complexation of Mg^{2+} with L^1–L^3 are comparable.

Values for complexation of Ni^{2+}, Cu^{2+} and Zn^{2+} with L^1–L^3, when compared to those reported for ethane-1,2-diamine, propane-1,3-diamine and H_2edda, reveal some significant donor-atom preferences. Binding of the copper(II) ion seems only to be occurring to the two nitrogen donors: the range of values (6.56–8.03) for ML formation when compared to H_2edda (16.2) and ethane-1,2-diamine (10.54), for example, suggest strongly that the phosphinate oxygens are not contributing significantly to the overall formation constant notwithstanding the reduced basicity of the amino groups. This effect is also seen with L^{5b}. In contrast, it is evident that complexation of zinc(II) by all of the azaphosphinates studied does involve phosphinate ligation. The 1:1 formation constants are all higher than those for ethane-1,2-diamine (or 2,9-dimethylphenanthroline). This donor preference results in an inversion of the classical Irving–Williams stability[20] order sequence with L^2 and L^{5b}.

The speciation of the zinc–L^{5b} system was studied in more detail and analysis of the titration data revealed formation of an ML(OH) species, in addition to an ML_2 complex. When zinc trifluoromethanesulfonate (triflate) was added incrementally to L^{5b} in D_2O (pD 8 initially) ^{31}P NMR spectroscopy revealed the presence of resonances ascribed to free and bound phosphinate species. After addition of 0.5 equivalent of $Zn(O_3SCF_3)_2$ (*ca.* 10^{-3} mol dm^{-3} solution) two singlets were observed (L, δ 40.7; ML, δ 42.5) of roughly equal intensity. Beyond a 1:1 M:L stoichiometry only the higher-frequency resonance was evident ($\omega_{\frac{1}{2}} = 20$ Hz, 298 K, 101.3 MHz), consistent with formation of a 1:1 complex in which free and bound phosphinate are in slow exchange on the NMR timescale. This behaviour sets a lower limit on ML formation (*i.e.* log $\beta_{ML} > 5.5$), which compares well with the measured value (log $\beta_{ZnL^{5b}} = 6.01$).

With the phenylphosphinate L^{6b}, inspection of the ML_2 formation constants (Table 2), reveals that binding must involve four nitrogens (*cf.* values for 2,9-dimethylphenanthroline). Given that the N_4-bound copper(II) species is likely to involve the four nitrogens binding in the same plane, then it is evident that the 2,9-dialkyl substituents are not sufficiently sterically bulky to inhibit this binding mode. Inhibition of a



Scheme 1

Table 1 Protonation constants for compounds L^1, L^2, L^3, L^{5b} and L^{6b} (298 K, I = 0.1 mol dm^{-3} NMe_4NO_3)[a]

Compound	log β_{HL}	log β_{H_2L}
L^1	8.35	13.68
L^2	8.63	12.97
L^3	8.91	15.91
Ethane-1,2-diamine[b]	9.89	16.97
N,*N*′-Dimethylethane-1,2-diamine[b]	10.05	17.06
Propane-1,3-diamine[b]	10.52	19.26
L^{5b}	5.96(2)	—
L^{6b}	5.93(2)	8.63(10)

[a] Error (unless stated) is ± 0.03 units. 2,9-Dimethyl-1,10-phenanthroline has a first pK_a of 5.95 under these conditions.[16] [b] Data from ref. 16.

Table 2 Stability constants for complex formation with L^1, L^2, L^3, L^{5b} and L^{6b} (298 K, I = 0.1 mol dm^{-3} NMe_4NO_3)

	log β_{ML}				
Compound	MgL	CaL	NiL	CuL	ZnL
L^1	3.96	3.85	8.35	8.03	7.64
L^2	3.14	2.92	8.14	6.56	7.03 (12.13, log β_{ZnL_2})
L^3	(12.8) log $\beta_{ML(OH)}$	3.40	7.85	7.43	7.35
L^{5b}	—	—	5.39	5.04	6.01 (8.80, log $\beta_{ML(OH)}$ 10.68, log β_{ZnL_2})
L^{6b}[a]	—	—	6.24 (10.14; log β_{NiL_2})	6.95 (12.75, log β_{CuL_2})	6.64 (10.24, log β_{ZnL_2})
Ethane-1,2-diamine[b]	0.37	—	7.35[c]	10.54[d]	5.7
Propane-1,3-diamine[b]	—	—	6.31	9.66	—
H_2edda[b]	3.95	—	13.5	16.2	11.2
2,9-Dimethyl-1,10-phenanthroline[b]	—	—	5.0 (8.5, log β_{NiL_2})	5.2 (11.0, log β_{CuL_2})	4.1 (7.7, log β_{ZnL_2})

[a] Values measured in 30% v/v MeOH–water. Protonation constants were the same (0.02) as those measured in water alone. [b] Data from ref. 16. [c] This value is 6.89 for *N*,*N*′-dimethylethane-1,2-diamine. [d] log β_{CuL} is 10.02 for *N*,*N*′-dimethylethane-1,2-diamine.

planar N_4 array with co-operative 1,10-phenanthroline ligation does occur with more bulky 2,9-substituents, such as aryl groups.[21,22]

Complex formation in 95% methanol–water with L^{5b}, L^{6b} and L^{7b} was examined by positive-ion electrospray mass spectrometry (ESMS). With each of these compounds, binding of Cu^{II}, Zn^{II} and Ni^{II}, as the triflate salt, gave rise to a major $[MLNa]^+$ species (Na^+ ions are present in the solvent). No evidence for formation of ML_2 complexes was seen even at M : L ratios of 1 : 5, which is not surprising given the low sample concentrations used in the ESMS experiment. Attempts were made to isolate the 1 : 1 complexes following admixture of equimolar amounts of metal perchlorates (or triflates) to aqueous or methanolic solutions of L^{5b}, L^{6b} and L^{7b}. With L^{7b}, addition of zinc or copper salts led to rapid precipitation of colourless solids. Combustion analysis of samples prepared from different zinc salts (Cl^-, $MeCO_2^-$, $CF_3SO_3^-$, ClO_4^-) indicated clearly that no anion was incorporated in the isolated solid, but the insolubility of the product (presumably oligomeric) precluded further detailed characterisation. With L^{6b}, solid complexes slowly precipitated from aqueous solution and microanalysis revealed that they were partially hydrated 1 : 1 neutral complexes (Table 3). The presence of water of crystallisation was evident in the Fourier-transform IR spectra of the isolated solids [ν_{OH} = 3420 (br) cm^{-1}]. With the more hydrophilic methylphosphinate ligand L^{5b} no solid complexes could be isolated from aqueous or aqueous methanolic solutions.

In summary, tetradentate diazaphosphinate ligands form neutral 1 : 1 complexes with divalent ions in solution. The hard phosphinate donor in these tetradentate N_2O_2 compounds does not appear to bind the copper(II) ion significantly in aqueous solution, but does bind to nickel(II) and zinc(II) ions enhancing the stability of their complexes.* The phosphinate oxygen binds effectively to particularly charge dense ions such as Mg^{2+} and this can lead to modest selectivity in binding over Ca^{2+}.

Experimental

All reactions were carried out in apparatus which had been oven-dried and cooled under argon. Solvents were dried from an appropriate drying agent and water was purified using the PURITE system. Alumina refers to Merck alumina activity II–III which was soaked in ethyl acetate for at least 24 h prior to use. Silica refers to Merck silica gel F60 (230–400 mesh). Preparative TLC was carried out using either Merck 5726 Alumina plc 150 F_{254} (type T) pre-coated 1.55 mm plates or Merck silica plc 60 F_{254} precoated 2 mm plates. Analytical and preparative HPLC were performed on a Varian Vista 5500 or Star 5065 instrument fitted with a reversed phase column ('Dynamax' P60).

Proton and ^{13}C NMR spectra were obtained with a Bruker AC 250 spectrometer operating at 250.13 and 62.90 MHz respectively, a Varian Gemini 200 operating at 200 and 50 MHz respectively, a Varian XL 200 operating at 200 MHz, and a Varian VXR 400S operating at 400 MHz. All chemical shifts are given in ppm relative to the residual solvent resonance. The ^{31}P NMR spectra were obtained with a Bruker AC 250 spectrometer operating at 101.3 MHz. Mass spectra were recorded on a VG 7070E instrument operating in FAB, positive-ion electron inpact (EI) or desorption chemical ionisation (DCI) modes as stated, electrospray mass spectra using a VG Platform II (Fisons instruments) operating in positive-ion mode or were performed by the EPSRC Mass Spectroscopy service at Swansea. Accurate mass spectroscopy was performed by the latter service. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier-transform spectrometer as a thin film or KBr disc as stated, UV spectra on a Uvikon 930 spectrometer. Combustion analysis was performed using an Exeter Analytical Inc CE440 elemental analyser. Metal concentration was determined by atomic absorption spectroscopy using a Perkin-Elmer 5000 atomic absorption spectrophotometer. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

Table 3 Microanalysis data for formation of hemihydrated 1 : 1 complexes of L^{6b} with metal ions*

	$ZnL{\cdot}0.5H_2O$		$CdL{\cdot}0.5H_2O$		$NiL{\cdot}0.5H_2O$	
Atom	Calc.	Found	Calc.	Found	Calc.	Found
C	55.3	55.5	51.4	51.1	56.3	56.1
H	3.95	3.75	3.50	3.50	3.80	3.90
N	4.85	5.00	4.60	4.60	5.05	4.90
M	11.6	11.8	18.5	18.4	10.6	10.3

* With copper a non-stoichiometric hydrated 1 : 1 complex was formed.

Electrospray mass spectrometry complexation analysis

Stock solutions of the pro-ligand (10 cm^3, 0.3 mol dm^{-3}) in methanol containing about 1–5% water and the metal triflates

* It has previously been established that the copper-binding affinity of a phosphinate group in α-aminophosphinates is less than that of the corresponding α-aminophosphonates and α-aminocarboxylates.[23]

(10 cm^3, 1.5 mmol dm^{-3}) in methanol were prepared. To a sample of the pro-ligand solution (1 cm^3) was added the appropriate amount of metal triflate solution (in the order of 0.2 cm^3) to make a 1:1 metal–ligand ratio. Using 10 μl of the test solution, mass spectra were obtained on a VG Platform II electrospray mass spectrometer (cone voltage 30 V, sample temperature 60 °C) with positive ionisation. Samples were diluted with methanol where appropriate.

Potentiometric titrations

The titration cell was a double-walled glass vessel of approximately 5 cm^3 capacity (internal dimensions, 1.2 cm in diameter by 5 cm in depth). The contents were kept at a constant temperature by passing water between the glass walls using a Grant thermostatically controlled water-bath and pump. The solutions in the vessel were mixed with a cross-shaped magnetic stirrer bar using an IKA-mini-MR magnetic stirrer. An IBM-PC program (MOLSPIN version 1.44, Academic Software) was used to collect and store the measured pH readings during the titration (using a Corning semimicro pH combination electrode) and operated the autotitrator (1 cm^3 capacity) (Molspin, Newcastle-upon-Tyne, UK). The titrant was delivered to the titration cell through a rigid plastic tube (internal bore 0.05 mm). The end of the tube was held so that it was always above the surface of the solution in the titration cell and met the glass wall at an angle of 30°. The volume increments, the time between additions (governed by the pH stability over the 'time delay') and final volume added were all controlled by the program and were set before each titration. The pH electrode was calibrated using two National Bureau of Standards buffer solutions (Philips Scientific) of pH 4.008 (phthalate) and 6.865 (phosphate) at 25 °C. The collected data (volume of titrant added and pH) were transferred to a UNIX mainframe and analysed by two non-linear least-squares programs SCOGS 2 and SUPERQUAD.

All solutions were prepared from 'Purite' water that had been boiled for 30 min, with nitrogen gas bubbling through it to remove carbon dioxide. Pro-ligand solutions (25 or 10 cm^3, 0.001 mol dm^{-3}) were prepared in a constant ionic strength background solution of tetramethylammonium nitrate (0.1 mol dm^{-3}). Two or three equivalents of inorganic acid (HCl) were added to obtain an initial pH of between 2 and 2.5. Metal nitrate solutions (10 cm^3, 0.01 mol dm^{-3}) in a background of 0.1 mol dm^{-3} NMe_4NO_3 were prepared and the exact metal concentration determined by atomic absorption spectroscopy prior to use. The exact molarity of the titrant base solution, tetramethylammonium hydroxide (about 0.05 mol dm^{-3}) in a background of 0.1 mol dm^{-3} NMe_4NO_3 was determined by titrating against a standard hydrochloric acid solution (3 cm^3, 0.01 mol dm^{-3}) at 25 °C. From the titration curve a 'GRAMS' plot was obtained (using the MOLSPIN program) which allowed the end-point to be determined and hence the exact concentration. This was repeated three times until consistent results were obtained.

Measurement of pK_a and metal stability constants

The pro-ligand solution (3 cm^3, 0.001 mol dm^{-3}) was added to the titration cell and the calibrated pH electrode placed into the solution so that its frit was below the liquid surface. With the solution temperature maintained at 25 °C and with efficient stirring the base solution (NMe_4OH, 0.05 mol dm^{-3}) was titrated in (increments of 0.002 cm^3, time delay 5 s). The pH curve was analysed as mentioned above to determine the pK_a values. The total number of data points was >150, and each determination was repeated twice to give three consistent measurements.

For metal stability constants the appropriate volume of metal nitrate solution (about 0.3 cm^3, 0.01 mol dm^{-3}) was added to the pro-ligand solution (3 cm^3, 0.001 mol dm^{-3}) to obtain a metal:ligand ratio of 1:1. The titration was performed as above (increments of 0.0025 cm^3, time delay between 10 and 450 s depending on the kinetics of complexation over 150 data points, three replicate measurements). Knowing the pK_a values of the pro-ligand, the metal stability constants were determined by using the analysis programs and the change in the pH profile.

Titration of 1,10-phenanthroline-2,9-diyldimethylenebis(phenylphosphinic acid) in a mixed solvent

As the zinc complex of 1,10-phenanthroline-2,9-diyldimethylenebis(phenylphosphinic acid) had poor solubility in water a mixed solvent methanol–water (3:7) was used. The pro-ligand, metal and base solutions were prepared as before, in this solvent composition. The electrode was calibrated in aqueous buffer solutions of pH 4.008 and 6.865 at 25 °C. The base was titrated against standard hydrochloric acid [0.01 mol dm^{-3} in methanol–water (3:7)] and the end-point determined by a GRAMS plot using the MOLSPIN software. A correction factor δ [24] (subtraction of 0.0314) was applied to all the measured pH values to take into account the different solvent conditions between the electrode calibration and pH titration. In the analysis the autoprotolysis constant [24] was set at 14.055, the pro-ligand pK_a constant and the zinc complex stability constants were determined as before.

Syntheses

2,9-Bis(bromomethyl)-1,10-phenanthroline. A modification to the method of Chandler *et al.*[13] was made. A solution of HBr in acetic acid (48% v/v, 130 cm^3) was added to 2,9-bis(hydroxymethyl)-1,10-phenanthroline (3.71 g, 15.6 mmol) and the mixture stirred at 45 °C for 15 h. After cooling, the solution was poured into diethyl ether (1 l), and the yellow precipitate filtered off and dried under vacuum, 8.0 g. After neutralising the solid with aqueous potassium carbonate solution (200 cm^3) the product was extracted with chloroform (3 × 150 cm^3), dried (K_2CO_3), filtered and concentrated to give a yellow solid, 3.93 g (69%), m.p. 110 °C (lit.,[13] 110–111 °C); $\delta_H(CDCl_3)$ 4.97 (4 H, s, CH_2), 7.80 (2 H, s, H^5 and H^6), 7.91 (2 H, d, H^3 and H^8) and 8.30 (2 H, d, H^4 and H^7); *m/z* (CI) 365, 367 and 369 ($M^+ + 1$).

Diethyl 1,10-phenanthroline-2,9-diyldimethylenebis(benzylphosphinate), L[7a]. To a slurry of 2,9-bis(bromomethyl)-1,10-phenanthroline (0.5 g, 1.37 mmol) in dry acetonitrile (10 cm^3) was added diethyl benzylphosphonite (1 cm^3). The mixture was stirred at room temperature for 15 min and then heated at 60 °C for 4 h. The reaction was followed by ^{31}P NMR spectroscopy (starting material, δ_P 175). Concentration gave a light brown oil. Purification by column chromatography on neutral alumina [100% CH_2Cl_2 to 99.5% CH_2Cl_2–0.5% MeOH, R_f(product) = 0.2] gave a clear glass, 0.28 g (36%); $\delta_P(CDCl_3)$ 47.62; $\delta_H(CDCl_3)$ 1.12 (6 H, t, CH_3), 3.30 (4 H, d, PhCH_2, ^2J = 8.5), 3.71 (4 H, d, phen CH_2, ^2J = 8.5), 3.95 (4 H, qnt, OCH_2), 7.24 (6 H, m, phenyl *o*- and *p*-H), 7.47 (4 H, d, phenyl *m*-H), 7.73 (2 H, dd, H^3 and H^8), 7.77 (2 H, s, H^5 and H^6) and 8.21 (2 H, d, H^4 and H^7); $\delta_C(CDCl_3)$ 16.36 (d, ^3J = 5.8, CH_3), 35.84 (d, ^1J = 88, PhCH_2), 39.54 (d, ^1J = 88, phen–CH_2), 61.00 (d, ^2J = 7.0, OCH_2), 124.2 (d, ^3J = 3.4, C^3 and C^8), 125.9 (s, C^5 and C^6), 126.6 (d, ^5J = 3.4 Hz, Ph *p*-C), 127.2 (s, C^{4a}), 128.4 (d, ^4J = 2.8, Ph *m*-C), 130.1 (d, ^3J = 5.78, Ph *o*-C), 131.5 (d, ^2J = 8.3, aryl CCH_2), 136.5 (s, C^4 and C^7), 145.5 (s, C^{10b}) and 153.5 (d, ^2J = 6.8 Hz, C^2 and C^9); *m/z* (DCI, NH_3) 573 ($M^+ + 1$), 482 ($M^+ - CH_2Ph$), 454 ($M^+ - CH_2Ph - Et + 1$), 391 [$M^+ - EtP(O)CH_2Ph$], 271 ($M^+ - 2CH_2Ph - 2Et + 2$) and 208 [$M^+ - 2EtP(O)CH_2Ph$]; $\tilde{\nu}_{max}/cm^{-1}$ (thin film) 1496, 1227, 1033 and 726.

1,10-Phenanthroline-2,9-diyldimethylenebis(benzylphosphinic acid), L[7b]. To diethyl 1,10-phenanthroline-2,9-diyldimethylenebis(benzylphosphinate) (0.165 g, 0.288 mmol) was added hydrochloric acid (6 mol dm^{-3}, 10 cm^3) and the solution heated at 105 °C for 18 h. The reaction was followed by ^{31}P NMR spectroscopy (product, δ_P 45.07). Concentration and vacuum drying gave a light yellow glass. Recrystallisation from methanol gave a colourless solid, m.p. 145–146 °C; $\delta_P(CD_3OD)$ 43.2; $\delta_H(CD_3OD)$ 3.44 (4 H, d, ^1J = 19.6, CH_2Ph), 4.04 (4 H, d, ^1J = 16.4, phen-CH_2), 7.08 (6 H, m, Ph *o*- and *p*-H), 7.30 (4 H, d, Ph *m*-H), 7.98 (2 H, d, H^3 and H^8), 8.08 (2 H, s, H^5 and H^6) and 8.75 (2 H, d, H^4 and H^7); $\delta_C(CD_3OD)$ 38.0 (br, phen-CH_2), 38.29 (d, ^1J = 90, CH_2Ph), 127.9 (d, ^3J = 3.4, C^3), 128.1 (s, C^5), 128.4 (d, ^5J = 3.9, Ph *p*-C), 129.6 (d, ^4J = 2.5, Ph *m*-C), 131.1 (d, ^3J = 6.0, Ph *o*-C), 132.2 (d, ^2J = 8.3, aryl CCH_2-CH_2), 138.0 (d, ^4J = 1.4, phen NC), 142.8 (s, C^4) and 154.7 (d, ^2J = 8.6 Hz, C^2); *m/z* (DCI, NH_3) 518 (M^+ + 2), 363 [M^+ − PhCH$_2$P(O)OH] and 209 [M^+ − 2PhCH$_2$P(O)OH]; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2710, 1603, 1216, 1185, 934 and 698 (Found: C, 58.40; H, 5.30; N, 4.55. $C_{28}H_{26}N_2O_4P_2$·HCl·1.5H$_2$O requires C, 58.00; H, 5.20; N, 4.85%).

Dimethyl 1,10-phenanthroline-2,9-diyldimethylenebis(phenylphosphinate), L[6a]. To a stirred slurry of 2,9-dibromo-1,10-phenanthroline (2.0 g, 5.46 mmol) in dry acetonitrile at room temperature, was added dimethyl phenylphosphonite (3.25 g, 16.4 mmol). Under a nitrogen atmosphere the mixture was allowed to stir for 30 min and then heated at 60 °C for 3 h. Concentration gave an orange-brown viscous oil. Purification by column chromatography on neutral alumina (100% CH_2Cl_2 to 99.5% CH_2Cl_2–0.5% MeOH), then TLC on alumina [99% CH_2Cl_2–1% MeOH, R_f(product) = 0.15] gave a light yellow glass, 0.93 g (31%); $\delta_P(CDCl_3)$ 38.73; $\delta_H(CDCl_3)$ 1.24 (6 H, t, CH_3), 3.96 (1 H, qd, OCH_2), 3.98 (4 H, d, ^2J = 17, CH_2P), 4.15 (1 H, qd, OCH_2), 7.46 (6 H, m, phenyl *o*- and *p*-H), 7.62–7.89 (8 H, m, phenyl *m*-H, H^5, H^6, H^3 and H^8) and 8.10 (2 H, d, H^4 and H^7); $\delta_C(CDCl_3)$ 16.38 (d, ^3J = 6.4, CH_3), 41.44 (d, ^1J = 92, CH_2P), 61.24 (d, ^2J = 6.4, OCH_2), 124.0 (d, ^3J = 2.9, C^3), 125.9 (s, C^5), 127.3 (d, ^5J = 1.9, phen NC*C*), 128.4 (d, ^2J = 13, Ph *o*-C), 130.6 (d, ^1J = 126, Ph*C*P), 131.7 (d, ^3J = 10.0, Ph *m*-C), 132.3 (d, ^4J = 2.8, Ph *p*-C), 136.2 (s, C^4), 145.4 (s, phen NC) and 153.1 (d, ^2J = 6.6, C^2); *m/z* (DCI, NH_3) 544 (M^+ + 1), 376 [M^+ − PhP(O)OEt], and 208 [M^+ − 2PhP(O)OEt]; $\tilde{\nu}_{max}$/cm^{-1} (neat) 1591, 1224, 1122 and 954.

1,10-Phenanthroline-2,9-diyldimethylenebis(phenylphosphinic acid), L[6b]. To the ester diethyl 1,10-phenanthroline-2,9-diyldimethylenebis(phenylphosphinate) (52.3 mg, 0.096 mmol) was added potassium hydroxide solution (1 cm^3, 50% v/v MeOH–water) and the solution stirred at room temperature. The reaction was followed by ^{31}P NMR spectroscopy, monitoring the disappearance of starting material (δ_P 43.3). After 48 h the solution was neutralised with hydrochloric acid to pH 6.5 and pumped dry. The product was extracted with ethanol (3 × 10 cm^3) and concentrated to give a white solid; $\delta_P(CD_3OD)$ 25.3; $\delta_H(CD_3OD)$ 3.61 (4 H, d, ^2J = 16.8, CH_2), 7.21 (2 H, dd, phenyl *p*-H), 7.37 (6 H, m, aryl), 7.72 (6 H, m, aryl) and 8.09 (2 H, d, H^4 and H^7); $\delta_C(CD_3OD)$ 45.0 (br d, CH_2), 126.1 (d, ^3J = 3.3, C^3), 126.8 (s, C^5), 128.5 (d, ^5J = 2.0, phen NC*C*), 128.9 (d, ^2J = 12.1, Ph *o*-C), 131.5 (d, ^4J = 2.5, Ph *p*-C), 132.5 (d, ^3J = 9.1, Ph *m*-C), 137.7 (s, C^4), 139.3 (d, ^1J = 128, Ph*C*P), 146.1 (d, ^4J = 2.2, phen NC) and 158.3 (d, ^2J = 8 Hz, C^2); *m/z* (ESMS) 554.9, 555.9 (MNa_3^+); $\tilde{\nu}_{max}$/cm^{-1} (KBr disc) 3385, 1589, 1174, 1129 and 1043.

Diethyl 1,10-phenanthroline-2,9-diyldimethylenebis(methylphosphinate), L[5a]. 2,9-Bis(bromomethyl)-1,10-phenanthroline (0.6 g, 2 mmol), diethoxymethylphosphine (1 g, 7 mmol) and acetonitrile (10 cm^3) were mixed under an inert atmosphere at room temperature for 90 min, until the initially red solution had developed an orange precipitate. After heating at 70 °C under reflux for 6 h the solvent was evaporated under reduced pressure to leave a clear light brown oil which was purified by column chromatography on alumina using dichloromethane with an increasing gradient (0–10%) of added methanol to give a pale yellow oil (0.42 g, 47%), R_f = 0.45 (Al_2O_3, 10% MeOH–CH_2Cl_2); $\delta_P(CDCl_3)$ 51.59; $\delta_H(CDCl_3)$ 1.21 (3 H, t, $POCH_2CH_3$), 1.55 (3 H, d, PCH_3, ^2J = 9.0), 3.69 (2 H, d, NCH_2P, ^2J = 8.2), 4.05 (2 H, m, $POCH_2CH_3$), 7.6 and 7.7 (4 H, m, H^3, H$^{5/6}$, H^8, aromatic) and 8.16 (2 H, d, H^4, H^7); $\delta_C(CDCl_3)$ 13.7 (d, PCH_3, ^1J = 96), 16.4 (t, $POCH_2CH_3$), 41.1 (d, NCH_2P, ^1J = 84 Hz), 60.41 ($POCH_2CH_3$), 124.0 (s, C^3), 125.89 (s, C^5), 127.2 (s, phen NC*C*), 136.68 (s, C^4), 145.22 (s, phen NC) and 153.51 (s, C^2); *m/z* (DCI): 421.1446 (M^+ + 1); $C_{20}H_{27}N_2O_4P_2$ requires 421.1446 (M^+ + 1).

1,10-Phenanthroline-2,9-diyldimethylenebis(methylphosphinic acid), L[5b]. The diester L[5b] (0.35 g, 7.8 mmol) was heated to reflux for 16 h in 6 mol dm^{-3} HCl. The solvent was then removed under reduced pressure, leaving a pale brown powder (0.23 g, 91%), decomposition point 150 °C; $\delta_P(D_2O$, pD 0.5) 45.32; $\delta_H(D_2O$, pD 0.5) 1.58 (3 H, d, PCH_3, ^2J = 14); 3.82 (2 H, d, aryl-CH_2P, ^2J = 17), 7.64 (1 H, s, C^5), 7.84 (1 H, d, C^4, ^3J = 4) and 8.43 (1 H, d, C^3, ^3J = 4); $\delta_C(D_2O$, pD 0.5) 13.7 (d, PCH_3, ^1J = 96), 41.1 (d, aryl-CH_2P, ^1J = 84 Hz), 124.0 (s, C^3), 125.89 (s, C^5), 127.2 (s, phen NC*C*), 136.68 (s, C^4), 145.22 (s, phen NC) and 153.51 (s, C^2) (Found: C, 43.50, H, 6.05, N, 5.65; P, 8.45. $C_{16}H_{18}N_2O_4P_2$·HCl·2H$_2$O requires: C, 43.55; H, 5.90; N, 5.65, P, 8.75%).

Diethyl tetrahydroimidazole-1,3-diyldimethylenebis(methylphosphinate), L[8]. A mixture of ethane-1,2-diamine (0.24 g, 4 mmol) and diethoxymethylphosphine (2.0 g, 16 mmol) in dry thf (30 cm^3) was heated under argon. While still hot, freshly resublimed paraformaldehyde (0.6 g, 10 mmol) was added and the mixture heated under reflux for 18 h. After removal of solvent under reduced pressure, the residue was purified by chromatography on neutral alumina, eluting with an increasing gradient of MeOH in dichloromethane (0–5%). A colourless oil was separated (R_f = 0.58, 10% MeOH–CH_2Cl_2), 0.67 g, (54%); $\delta_P(CDCl_3)$ 51.1; $\delta_H(CDCl_3)$ 1.23 (6 H, t, OCH_2CH_3), 1.45 (6 H, d, PMe, ^2J = 14), 2.84 (8 H, d, NCH_2P, ^2J = 10), 2.89 (4 H, m, CH_2N), 3.53 (2 H, br s, NCH_2N), and 4.02 (4 H, dq, $POCH_2$); $\delta_C(CDCl_3)$ 12.05 (d, PMe, ^1J = 94), 15.9, 16.0 (d, OCH_2CH_3, ^3J = 6), 53.35 (d, PCH_2N, ^1J = 115), 53.55 (d, $POCH_2$, ^2J = 9), 59.55 (d, CH_2N, ^3J = 8) and 78.65 (d, CH_2N, ^3J = 5 Hz); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 2950 (C–H), 1300 (PC), 1220 (PO) and 1050 (P–O); *m/z* (DCI): 313.1447 (M^+ + 1); $C_{11}H_{27}N_2O_4P_2$ requires 313.1446.

Dimethyl tetrahydroimidazole-1,3-diyldimethylenebis(phenylphosphinate), L[9]. This was prepared and purified as described for L[8] (52% yield) using dimethoxyphenylphosphine to yield a colourless oil (R_f = 0.68, 10% MeOH–CH_2Cl_2, Al_2O_3); $\delta_P(CDCl_3)$ 40.8; $\delta_H(CDCl_3)$ 2.83 (4 H, s, CH_2N), 3.05 (4 H, d, PCH_2N, ^2J = 9), 3.46 (2 H, d, NCH_2N, ^4J = 3), 3.62 (6 H, dd, OMe, J = 2.5 and 11), 7.50 (6 H, m, aryl H) and 7.77 (4 H, m, *o*-H); $\delta_C(CDCl_3)$ 51.37 (d, OMe, ^2J = 6), 53.87 (d, NCH_2P, ^1J = 120), 53.99 (d, CH_2N, J = 7), 79.2 (t, NCH_2N, ^3J = 10), 128.5 (d, *o*-C, ^3J = 12), 129.7 (d, ^1J = 124), 132.0 (d, *m*-C, ^3J = 9), and 132.6 (d, *p*-C, J = 4 Hz); *m/z* (DCI) 409.1446; $C_{19}H_{27}N_2O_4P_2$ requires 409.1446 (M^+ + 1).

Dimethyl hexahydropyrimidine-1,3-diyldimethylenebis(phenylphosphinate), L[11]. This reaction was carried out in the same way as for L[8] using 1,3-diaminopropane (0.29 g, 4 mmol), dimethoxyphenylphosphine (2.7 g, 16 mmol) and paraformaldehyde (0.4 g, excess). Purification was by column chromatography on alumina to give a clear colourless oil (0.68 g, 48%), R_f = 0.62 (Al_2O_3, 10% methanol); $\delta_P(CDCl_3)$ 40.72; $\delta_H(CDCl_3)$ 1.3 (2 H, t, NCH_2CH_2), 2.5 (4 H, m, NCH_2CH_2) 2.68 (4 H, d,

NCH_2P, ^2J = 9), 3.17 (2 H, d, NCH_2N, ^4J = 5), 3.40 (6 H, d, $POCH_3$, ^3J = 7), 7.3 (6 H, m, aryl) and 7.6 (4 H, m, *o*-H); $\delta_C(CDCl_3)$ 19.67 (s, NCH_2CH_2), 50.24 (d, $POCH_3$, ^2J = 13), 51.45 (d, NCH_2P, ^1J = 122), 52.35 (d, NCH_2CH_2, ^4J = 6), 77.2 (NCH_2N), 127.4 (d, ^3J = 12), 128.6 (d, ^1J = 123), 130.1 (d, ^2J = 10) and 131.35 (d, ^4J = 3 Hz); $\tilde{\nu}_{max}/cm^{-1}$ 2800–3100m (C–H aromatic and aliphatic), 1600 and 1490w (P–Ph), 1440m (POMe), 1170–1300br s (tertiary amine and P=O), 1120m (POMe) and 700–800s cm^{-1} (POMe); *m/z* (DCI) 423.1606 (M^+ + 1); $C_{20}H_{29}N_2O_4P_2$ requires 423.1605.

Diethyl hexahydropyrimidine-1,3-diyldimethylenebis(methylphosphinate) L[10]. This was prepared as described for L[8] using 1,3-diaminopropane (0.29 g, 4 mmol) and diethoxymethylphosphine (2 g, 16 mmol). A clear colourless oil (0.55 g 50.5%) was obtained after purification by column chromatography, R_f = 0.83 (Al_2O_3, 10% MeOH–CH_2Cl_2); $\delta_P(CDCl_3)$ 52.23; $\delta_H(CDCl_3)$ 1.3 (3 H, t, OCH_2CH_3), 1.46 (3 H, d, PCH_3, ^2J = 14), 1.50 (1 H, t, NCH_2CH_2), 2.63 (2 H, m, NCH_2CH_2), 2.61 (2 H, d, NCH_2P, ^2J = 10), 3.35 (1 H, br, NCH_2N) and 4.02 (2 H, qnt, OCH_2CH_3); $\delta_C(CDCl_3)$ 12.48 (d, PCH_3, ^1J = 114), 16.36 (s, OCH_2CH_3), 20.70 (s, NCH_2CH_2), 52.50 (d, NCH_2P, ^1J = 115 Hz), 53.34 (s, NCH_2CH_2), 59.94 (s, OCH_2CH_3) and 77.2 (m, NCH_2N); $\tilde{\nu}_{max}/cm^{-1}$ 2950m (C–H aliphatic), 1400–1450m (POEt), 1300m (P–CH_3), 1220br s (tertiary amine and P=O), 1050s (P–OEt), 950s (P–CH_3) and 800–750s (POEt); *m/z* (DCI) 327.1605 (M^+ + 1); $C_{12}H_{29}N_2O_4P_2$ requires 327.1605.

Ethylenediiminodimethylenebis(methylphosphinic acid), L[1]. Compound L[8] (0.67 g) was heated at reflux for 18 h in 6 mol dm^{-3} hydrochloric acid. The solvent was removed to leave a colourless solid which was dried under vacuum (0.62 g, 93%), m.p. 246–248 °C; $\delta_P(D_2O$, pD 0.7) 32.13; $\delta_H(D_2O$, pD 0.7) 1.43 (6 H, d, PCH_3, ^2J = 14.2) 3.27 (4 H, d, PCH_2N, ^2J = 9.6) and 3.57 (4 H, s, amine); $\delta_C(D_2O$, pD 0.7) 15.7 (d, PCH_3, ^1J = 98), 45.55 (d, amine, ^3J = 8) and 47.0 (d, PCH_2N, ^1J = 89 Hz) (Found: C, 22.70; H, 6.55; Cl, 22.9; N, 8.45; P, 19.6. $C_6H_{18}N_2O_4P_2$·2HCl·2H_2O requires C, 22.85; H, 6.40; Cl, 23.3; N, 8.90; P, 19.8%).

Ethylenediiminodimethylenebis(phenylphosphinic acid), L[2]. Compound L[9] (0.62 g) was heated at reflux for 18 h in 6 mol dm^{-3} hydrochloric acid. The solvent was removed to leave a white solid which was dried under vacuum (0.54 g, 98%), m.p. 276–278 °C; δ_P(NaOD, pD 12.5) 24.78; δ_H(NaOD, pD 12.5) 2.50 (4 H, t, NCH_2CH_2), 2.79 (4 H, d, NCH_2P, ^2J = 11), 7.51 (3 H, m, *o*- and *p*-H), and 7.70 (2 H, m, *m*-H); δ_C(NaOD, pD 12.5), 47.36 (NCH_2CH_2), 48.10 (d, NCH_2P, ^1J = 113), 129.1 (d, ^3J = 12, aromatic), 131.43 (d, ^2J = 9, aromatic), 132.19 (br, aromatic) and 135.05 (d, ^1J = 129 Hz, aromatic) (Found: C, 47.9; H, 5.60; Cl, 8.80; N, 6.75; P, 15.50. $C_{16}H_{22}N_2O_4P_2$·HCl requires C, 47.5; H, 5.70; Cl, 8.80; N, 6.90; P, 15.35%); *m/z* (FAB) 368 (M^+ + 1).

Trimethylenediiminodimethylenebis(phenylphosphinic acid), L[4]. This was prepared as described for L[1], from the ester L[11]; $\delta_P(D_2O$, pD 0.5) 20.43; $\delta_H(D_2O$, pD 0.5) 1.6 (2 H, t, NCH_2CH_2), 2.65 (4 H, t, NCH_2CH_2), 2.89 (4 H, d, NCH_2P, ^2J = 10), 7.14 (m, aromatic) and 7.33 (m, aromatic); $\delta_C(D_2O$, pD 0.5) 20.91 (s, NCH_2CH_2), 45.5 (d, NCH_2P, ^1J = 94), 45.29 (d, NCH_2CH_2, ^4J = 6), 128.0 (d, aromatic, ^3J = 13), 129 (d, aromatic, ^1J = 130), 130.3 (d, aromatic, ^2J = 10 Hz) and 131.73; *m/z* (FAB) 383 (M^+ + 1).

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