Selective solvent extraction of tetrahedrally-coordinating transition metal ions from acidic aqueous media using benzimidazole–phosphinate ligands: specificity for zinc(II) over copper(II)

Christopher D. Edlin,[a] David Parker,*[a] Justin J. B. Perry,[a] Christine Chartroux[b] and Karsten Gloe[b]

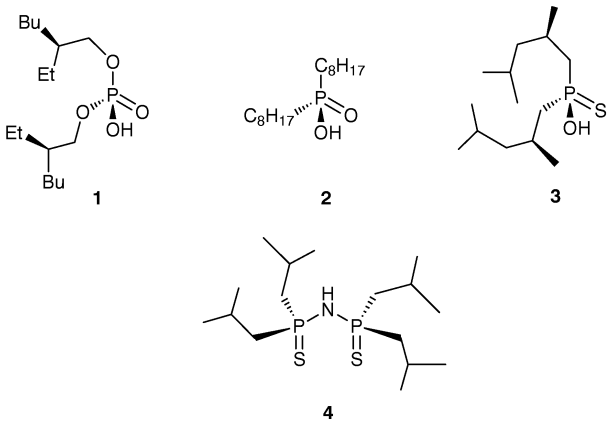
[a] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE*
[b] *Institut für Anorganische Chemie, Technische Universität Dresden, Mommsenstrasse 13, Dresden, D-01062, Germany*

Received 26th April 1999, Accepted 29th May 1999

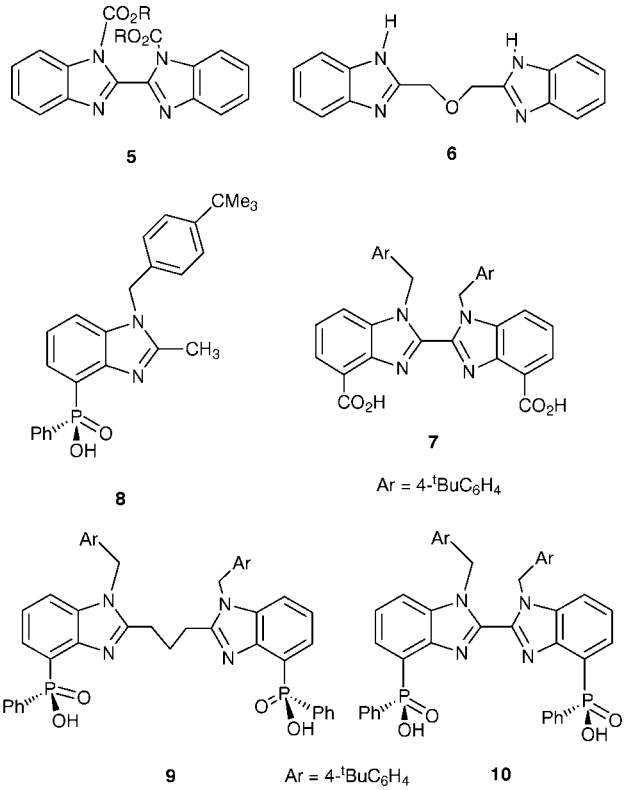
The synthesis, solution complexation behaviour and solvent extraction ability of related chelating mono-and bis-(benzimidazole)phosphinate ligands **8** and **9** has been assessed. ^{31}P NMR, fluorescence and absorption spectroscopy and electrospray mass spectrometry revealed preferential formation of 1 : 1 complexes with the divalent ions Zn, Co and Ni, and ML_2 complex formation with the bidentate ligand. Extraction studies showed that **9** extracted Zn > Co ≫ Ni with *no* extraction of copper(II), but avid extraction of copper(I), generated *in situ*, consistent with the ligand's preference for the binding of tetrahedrally-coordinating metal ions.

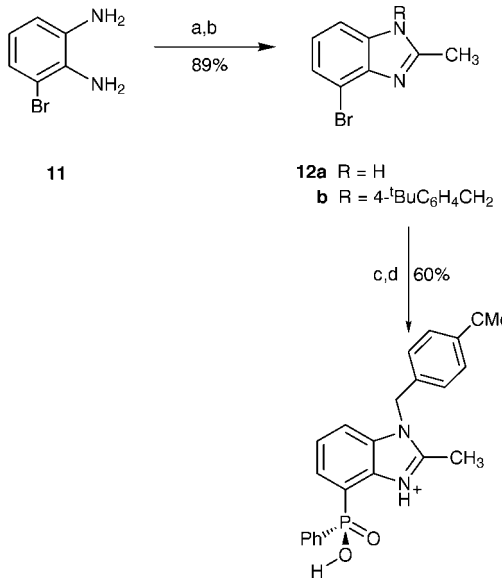
The selective solvent extraction of transition metal ions from 0.01 M acidic aqueous solutions, requires the use of a lipophilic ligand with sufficient avidity for the target metal ion that the derived complex partitions selectively into the organic phase. Such hydrometallurgical processes are therefore of commercial use for the recovery of metal ions,[1] as they may avoid some of the high costs associated with pyrometallurgical methods, involving elevated temperatures.[2] For the recovery of zinc, a mixture of hydrochloric acid and ferric chloride is often used as the leach solution, and during solvent extraction the pH is held below 2.5 to inhibit precipitation of ferric hydroxide. The organic phase may then be extracted with 0.1 M sulfuric acid to generate a zinc sulfate solution which is subsequently electrolysed to give the pure metal. The electrolyte solution must be free of other metal ion impurities to prevent formation of metals which possess a lower reduction potential than Zn^{II}. It is particularly important to achieve high selectivity over Fe^{III} and Cu^{II}, as they are common contaminants which are readily reduced.

The properties of the ligand that will allow the selective extraction of zinc are well-defined: it must bind zinc rapidly at pH 2 and release it quickly below pH 1; it must be readily synthesised and be sufficiently robust to withstand many cycles of complexation and decomplexation in a continuous recovery process; it must be sufficiently lipophilic to avoid ligand loss to the aqueous phase and the metal complex must be soluble in the organic solvent; the zinc complex must be charge-neutral to prevent co-transport of chloride ions to the pure zinc sulfate stream, otherwise chlorine evolution may occur at the anode. The solvent extraction of zinc is now used in a limited number of operating plants, using extractants such as di(2-ethylhexyl)phosphoric acid **1**,[3] di(n-octyl)phosphinic acid **2**,[4] and 'Cyanex 302' **3**[5] which is a thiophosphinic acid proposed to enhance extraction at lower pH. A particular problem with these three ligands is co-extraction of Fe^{III}, and to a lesser extent Cu(II). Some of these problems may be addressed by the thiophosphoramide ligands *e.g.* **4**,[6] being developed by Zeneca (UK), although **4** is sensitive to oxidation, especially in the presence of one-electron redox couples.



The issue of the selectivity of a ligand for zinc(II) over Fe(III) and Cu(II) may be discussed in terms of respective donor atom, coordination number and geometric preferences. Thus zinc is the only one which may prefer a tetrahedral geometry with hard donors and different types of tetrahedrally-coordinating ligands have been examined recently.[7–9] The phosphinic acid group is strongly acidic and sufficiently favours binding of zinc(II) over copper(II) that the Irving–Williams stability series may be inverted.[10] N-Substituted benzimidazole ligands have been studied for the purpose of zinc extraction for some time[11–14] but selectivity for zinc only occurs in aqueous media containing ⩾3 M Cl^-, consistent with the formation of overall neutral $L_2M_2Cl_4$ or $LMCl_2$ complexes observed by crystallography with **5** and **6**, respectively.[11,15] Following earlier work with **7**[8] which forms a charge neutral Zn_2L_2 complex, we set out to examine the behaviour of the benzimidazole–phosphinates **8**, **9** and **10**.[16] It was envisaged that these may form neutral ML_2, ML and M_2L_2 complexes[17] respectively with 'tetrahedral' ions. Solubility problems limited the study of complex formation with **10**,[18] so that details are presented here only for the complexation behaviour of **8** and **9**.





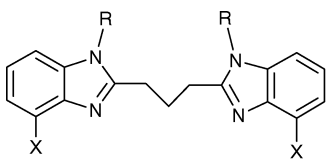
Scheme 1 (a) Ac_2O, 110 °C; H_3O^+; (b) 4-^{t}BuC$_6$H$_4$CH$_2$Br, DMF, Cs_2CO_3, 25 °C; (c) PhPH(O)(OEt), $Pd(PPh_3)_4$, Et_3N, 110 °C, PhMe; (d) 6 M HCl, 110 °C, 16 h.

Results and discussion

Ligand synthesis

Practicable syntheses of **8** and **9** were devised starting from 1,2-diamino-3-bromobenzene, **11**, using a palladium-catalysed activation of the aryl halide to promote carbon–phosphorus bond formation, (Scheme 1). The precursor amine **11** was prepared by a modification of the literature route[19] wherein nitration of *N*-acetyl-2-bromoaniline used a 4 : 3 v/v mixture of fuming nitric acid and trifluoroacetic with 1% added water; the reaction took place over 10 h to generate a roughly 1 : 1 mixture of *ortho* and *para*-nitration products which were separated by crystallisation from $CHCl_3$ at 0 °C. Formation of the benzimidazole **12a** involved a modified Phillips procedure[20] and regioselective N-alkylation occurred at the least-hindered nitrogen to give **12b**, confirmed by a ^{1}H NOE enhancement (3%) between the benzylic CH_2 and H-7 of the benzimidazole ring. Cross-coupling of the *N*-alkyl-bromobenzimidazole with ethyl phenylphosphinate, in the presence of $Pd(PPh_3)_4$–Et_3N in boiling toluene, followed a procedure reported by Xu and Huang[21] and yielded the desired phosphinate ester in 62% yield, following flash chromatography.

Condensation of the diamine **11** with dimethyl glutarate in polyphosphoric acid[22] at 180 °C for 18 h afforded the bis(benzimidazole) **13a**. Alkylation at N-1 with *tert*-butylbenzyl bromide in DMF followed by a palladium-catalysed coupling with ethyl phenylphosphinate yielded the diester **13c** from which ligand **9** was obtained by acid hydrolysis, in 42% overall yield from **11**.



13a X = Br, R = H
b X = Br, R = 4-^{t}BuC$_6$H$_4$CH$_2$
c X = PhP(O)OEt, R = 4-^{t}BuC$_6$H$_4$CH$_2$

Solution complexation behaviour

The behaviour of the ligands **8** and **9**, in the presence of Zn^{2+} and related metal ions, was studied by ^{31}P NMR, fluorescence, absorption spectroscopy and electrospray mass spectrometry, prior to an examination of their extraction ability. Anhydrous metal triflates were used as the salts and the solvent used was methanol or methanol–chloroform mixtures. Incremental addition of zinc trifluoromethanesulfonate to a solution of **8** and **9** was monitored by ^{31}P NMR (293 K, 75% $CDCl_3$–25% CD_3OD), and the variation of the ^{31}P shift plotted as a function of M : L ratio. With **9**, the phosphorus signal shifted to higher frequency with increasing M : L ratios, and a single peak was observed indicating that free and bound ligands were in fast-exchange on the NMR timescale (293 K, 101 MHz). The variation of $\Delta\delta_p$ with Zn : L ratio (Fig. 1), is consistent with formation of a 1 : 1 complex with $K_{ML} \geqslant 10^4$. With the monobenzimidazole, **8**, a similar overall binding curve was obtained but with a positive deviation from linearity over the M : L range 0 to 1 : 1. Such behaviour suggested that an ML_2 complex may be formed at lower zinc concentrations. Accordingly a Job plot[23] was obtained to allow the determination of the predominant complex stoichiometry in solution. The turning point was observed at a ligand percentage of *ca.* 66% (Fig. 2), and is consistent with formation of an ML_2 complex.

While ^{31}P NMR is very useful for monitoring phosphinate binding to the metal ion, coordination of the benzimidazole

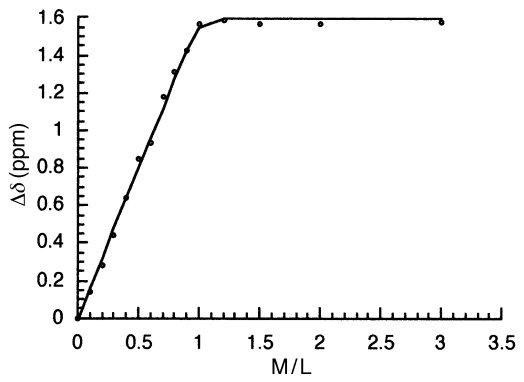


Fig. 1 ^{31}P NMR titration of **9** with $Zn(CF_3SO_3)_2$ (293 K; 75% $CDCl_3$–25% CD_3OD), showing behaviour consistent with formation of an ML complex.

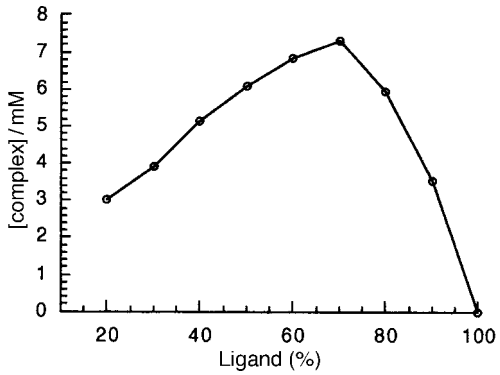


Fig. 2 Variation of complex concentration with the percentage of ligand **8** (Job plot; 293 K; 75% $CDCl_3$–25% CD_3OD).

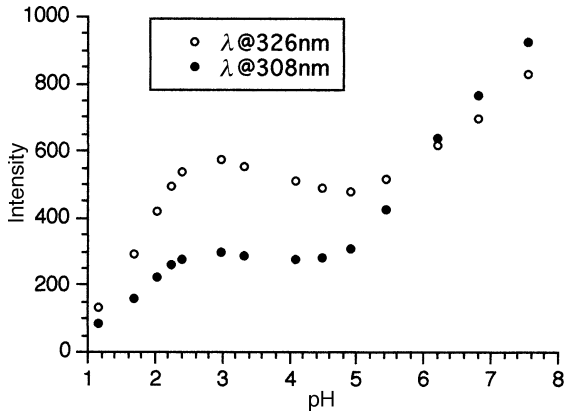


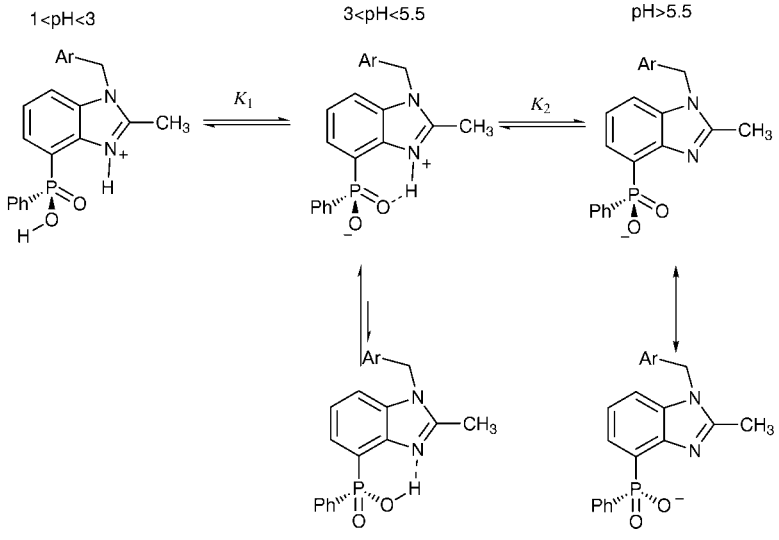
Fig. 3 Variation in emission intensity for ligand **8** as a function of pH (λ_{exc} 290 nm, λ_{em} 308 or 326 nm, 90% MeOH–10% H_2O, 293 K).

nitrogen may be probed by changes in the ligand fluorescence emission. Variations in the fluorescence emission spectrum of **8** were recorded as a function of pH over the range 1.2 to 8 (293 K; 10% H_2O–90% MeOH). Under acidic conditions (pH < 5), the emission spectrum gave a peak with maximum intensity around 326 nm, which increased in intensity and shifted by *ca.* 15 cm^{-1} to shorter wavelength at pH > 6. N-Protonation changes the relative energies of the HOMO and LUMO† and the energy gap is less for the protonated species. Protonation will also affect the internal charge transfer (ICT) excited state that is present in such benzimidazoles. Evidence for the occurrence of an ICT state was provided by an examination of the fluorescence emission spectrum of **8** in solvents of increasing polarity. In the series THF, CH_2Cl_2, CH_3CN, MeOH and H_2O (with polarities of 0.21, 0.31, 0.46, 0.76 and 1.0 on the E_T[30] scale),[25] the emission maximum shifted to the red in direct proportion to solvent polarity.

The variation of emission intensity from **8** as a function of pH (293 K, 10% H_2O–90% MeOH) revealed a pattern of behaviour that may be interpreted in terms of the changing proportions in solution of the appropriate differently protonated species, (Scheme 2 and Fig. 3). Over the pH range 1 to 3, the emission intensity at 326 and 308 nm increased, reached an approximately stable value over the range 3 to 5, before rising again beyond pH 5. Given that diphenylphosphinic acids typically have a pK_a of *ca.* 2.9 [26,10] and that the ground-state pK_a in the polar medium used is not likely to be very different from the pK_a of the first singlet (π,π^*) excited state, the inflection observed at a pH of between 2.6 and 3.0 may be associated with the maximal concentration of the zwitterionic structure, formed at this pH value. This species may be stabilised by an intramolecular hydrogen bond providing extra rigidity which may be associated with the emission intensity enhancement. At higher pH, deprotonation of the benzimidazole nitrogen occurs, and in the anion the phosphorus oxygen double bond is less likely to be conjugated with the benzimidazole ring, as lone-pair conjugation requires that the PO_2^- moiety at the tetrahedral P centre is coplanar. The inflection in emission intensity around pH 5 is consistent with the ground-state pK_a values of *ca.* 5.5 observed for related benzimidazoles.[27] A similar pattern of behaviour with varying pH was shown by **9**.

Incremental addition of $Zn(CF_3SO_3)_2$ to a methanolic solution of **8** (10 μM, 293 K, 90% MeOH–10% H_2O, effective pH 4.4), was monitored by fluorescence (Fig. 4). An increase in the intensity of emission at 309 nm was observed, with the emission maximum at 326 nm shifting to this lower value. Complexation of zinc by **8** under these conditions leads to a displacement of the bound proton on the benzimidazole nitrogen and the Zn–N bond length is likely to be about 1 Å longer than the N–H distance, so that there is much less perturbation of the π system in the zinc chelate structure. By assuming a 1 : 1 limiting binding stoichiometry (most likely *via* an intermediate ML_2 complex at higher L : M ratios), non-linear least-squares analysis of this binding isotherm indicated that $K_{ZnL} = 1.3(\pm 0.15) \times 10^4\ M^{-1}$, in agreement with the estimate

† Gas phase energies of the HOMO for the parent benzimidazole and benzimidazolium cation (−8.87 and −13.51 eV) and LUMO energies of −0.09 and −5.20 eV were calculated using semi-empirical orbital calculations using MOPAC 6.0[24] and the AM force-field operating in commercial software packages (CaChe, 1996, Oxford Molecular).



Scheme 2

Table 1 Major species observed by electrospray mass spectrometry[a] in the complexation of **8** and **9** by metal perchlorate salts

Complex	Observed species	Observed mass	Calculated mass	Relative intensity (%)
Zn/**9**	$[LZn]^-$	911.14	911.28	100
	$[LZnCl]^-$	945.09	945.36	77
	$[LZnClO_4]^-$	1012.63	1012.84	33
	$\frac{1}{2}[LZn]^-$	456.26	456.15	56
Cu/**9**	$[LCuCl]^-$	943.95	943.24	73
	$[LCuClO_4]^-$	1008.60	1008.77	41
Ni/**9**	$[LNiCl]^-$	938.76	938.74	5
	$[LNiClO_4]^-$	1004.63	1004.32	3
Zn/**8**	$[LH]^+$	419.65	419.88	73
	$[L_2ZnH]^+$	899.19	899.28	100
	$[L_2ZnNa]^+$	922.83	922.27	89
Cu/**8**	$[LH]^+$	419.65	419.88	100
	$[L_2CuH]^+$	898.10	898.43	33
	$[L_2CuNa]^+$	920.28	920.63	67
Ni/**8**	$[LH]^+$	419.65	419.88	100
	$[L_2NiH]^+$	893.24	893.37	9
	$[L_2NiNa]^+$	915.23	915.65	7

[a] 30 V cone voltage, 60 °C source temperature, 5×10^{-5} M solutions of metal salt and ligand in MeOH. Only the most intense peak in the isotope cluster is shown: in all cases good agreement was obtained between observed and calculated isotope distribution patterns.

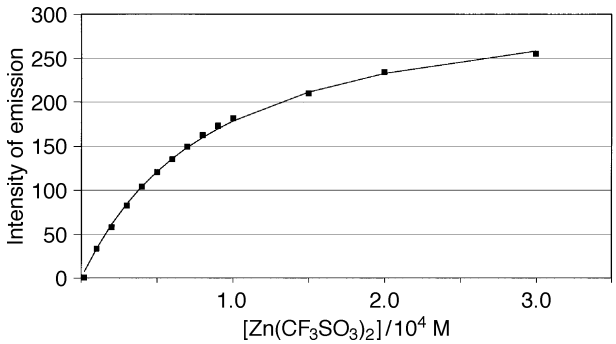


Fig. 4 Variation in emission intensity for **8** (293 K, 10 μM, 90% MeOH–10% H_2O; λ_{exc} 270 nm, λ_{em} = 309 nm) as a function of added zinc trifluoromethanesulfonate, showing the fit (line) to the observed data for $K_{ML} = 1.3(\pm 0.15) \times 10^4\ M^{-1}$.

provided by ^{31}P NMR analysis.‡ That relatively little change occurs to the energy of the frontier (π) orbitals in the benzimidazole ring system on binding to zinc(II) was confirmed by examination of the absorption spectrum. In the presence of a five-fold excess of $M(ClO_4)_2$ (M = Zn, Co, Cu and Ni) in 90% MeOH, the absorption spectrum in the region 250–290 nm underwent no significant shifts in absorption maxima, compared to the free ligand spectrum. A 70 → 90% enhancement in the intensity of the higher energy transition at 210 nm was observed in each case, with a reduction in intensity in each band, in the region 250 → 280 nm. No time-dependence was observed over a period of 24 h and similar behaviour was shown by ligand **9**.

Electrospray mass spectrometry

Speciation in methanolic solution was studied using ESMS,[28] recording spectra at 1 : 1 M : L ratios over a range of sample concentrations from 10^{-4} to 10^{-5} M using metal perchlorate salts. With **9**, more consistent results were obtained by examination of the negative ion spectrum, and ML complexes were observed as perchlorate or chloride adducts (Cl^- arose from the hydrochloride salt of **9** used in these studies), with peak intensity falling in the series Zn > Cu > Ni (Table 1). No peaks were observed for complexes of Fe(III), under these conditions. For the monobenzimidazole ligand, **8**, positive ion mass spectra were most informative and ML_2 complexes were identified as their proton or sodium adducts. The observed intensity of the $[ML_2H]^+$ species followed the order Zn > Cu > Ni and again no complex species were observed in the presence of ferric ions.

‡ Under identical conditions the variation of emission intensity of the tetradentate bis(benzimidazole) **9** with added zinc showed a rather different dependence on added metal concentration. The fluorescence intensity reached a maximum at an M : L ratio of 0.5 : 1 and then remained constant. In this case, intermediate formation of an ML_2 complex may also occur in which the zinc must be bound preferentially by 4 nitrogen donors: at higher added metal concentrations the ML complex will form but with no observable change in the fluorescence as the N-5 nitrogen remains bound. Such an interpretation is consistent with the ^{31}P NMR study and the result of extraction experiments (see below).

Liquid–liquid extraction studies

In order to assess the ability of ligands **8** and **9** to transport metal ions across an aqueous–chloroform interface, radiolabelled metal salts were used and the distribution of metal ions in each phase measured at equilibrium by counting the solution activity (Table 2). Studies were carried out in microreaction vials with equal volumes of $CHCl_3$ and a buffered aqueous medium at pH 2 (298 K, NaOAc–HCl buffer 0.1 M). The initial metal salt concentration in the aqueous phase was 10^{-4} M and the ligand concentration was varied from 0.25 to 5.0 mM. Equilibrium values were obtained within 30 min for $^{64}CuCl_2$, $^{65}ZnCl_2$, $^{60}Co(NO_3)_2$ and $^{203}HgCl_2$, whereas a 2 h incubation was used for experiments with $^{59}FeCl_3$ and $^{63}Ni(NO_3)_2$. Even under these conditions, equilibrium was not deemed to have been obtained for **8** with $^{59}FeCl_3$ and in the extraction of $^{63}Ni(NO_3)_2$ by **9**. Experiments with $^{64}CuCl_2$ were also carried out in the presence of a fifty-fold excess of the reducing agent hydroxylammonium sulfate, in order to generate the copper(I) complex *in situ*.

Table 2 Estimated extraction constants using ligand **9** (298 K, pH 2, $CHCl_3$, $[M^{n+}] = 0.1$ mM)[a]

Metal ion	log K_{ML}^{ex}	log $K_{ML_2}^{ex}$
Zn	4.1	6.3
Hg	3.0	6.1
Co	3.4	4.8
Fe(III)	2.7	6.9
Cu(I)[b]	n.d.	11

[a] Ligand **8** was insufficiently soluble at higher ligand concentrations to allow reliable measurements of extraction constants, but with copper(I) and copper(II) complex formation occurred readily at sufficiently low ligand concentrations to allow estimates of extraction constants: **8**/Cu(I): log $K_{ML_2}^{ex} = 8.7$; **8**/Cu(II): log $K_{ML}^{ex} = 3.9$, log $K_{ML_2}^{ex} = 8.6$. [b] For Cu(II), no extraction was observed *i.e.* log $K_{ML} < 0.1$.

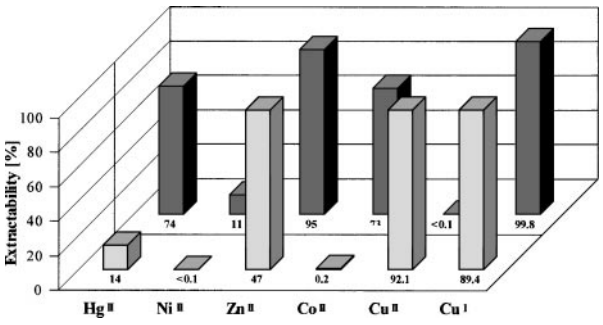


Fig. 5 Percentage extractability of metal ions from an aqueous acidic phase (pH 2) to chloroform [298 K, 10^{-3} M ligand, 10^{-4} metal salt: front **8**; rear **9.** N.b. Cu(II) extraction by **9** is $<0.1\%$].

The relative efficiency of ligands **8** and **9** to extract the different metal ion shows some striking differences in behaviour (Fig. 5). Thus, the mono(benzimidazole), **8**, extracted copper-(I) and -(II) and zinc(II) in preference to Hg(II) and virtually no extraction of nickel(II) and cobalt(II) occurred. With **9** , zinc(II) and copper(I) [and to a lesser extent Hg(II) and Co(II)] were extracted efficiently, but *no* measurable ($< 0.1\%$) extraction of copper(II) was found. Evidently the preference for a tetrahedral geometry in the 1 : 1 complex of **9** (when it acts as a tetradentate ligand) is being dramatically demonstrated by the failure to extract the copper(II) ion, which although adopting a range of coordination geometries in coordination numbers 4 to 6, tends to favour square planar or square pyramidal coordination geometries. On the other hand, copper(I), zinc(II) and cobalt(II) are known to form tetrahedral complexes in aqueous media, and even the kinetically sluggish Ni(II) ion is extracted to some extent (11%). Time dependent extraction was also noted for $^{59}FeCl_3$ with **8**, although **9** extracted it efficiently (99.5%).

Information regarding the overall stoichiometry of complexation was obtained by measuring the ratio of cation concentrations (D_M) in the organic–aqueous phase, as a function of total ligand concentration. From the variation of log D_M with the logarithm of the ligand concentration, information on the stoichiometry (from the slope) and extraction affinity may be obtained (Fig. 6). In all cases at higher concentrations of **9** there was some evidence for the formation of ML_2 complexes. In the case of copper(I), only an ML_2 complex was observed with **9**. The sequence of extraction constants for the 1 : 1 complexes of **9** follows the order Zn(II) > Co(II) > Ni(II) ≫ Cu(II), consistent with the ligand's preference to act as a tetradentate N_2O_2 ligand, rigidly imposing a tetrahedral coordination geometry at the metal. Competitive ML_2 formation with copper(I) and the observed affinity for the ferric ion, suggest that the ligand can also act as a bidentate (N_2) donor, presumably *via* coordination of the N-7 nitrogen. Further work is therefore warranted using either acid-stable, lipophilic carbamate, arylsulfonyl, or amide derivatives (protecting the N-7 nitrogen site), or exploring the behaviour of the related series of indole ligands, which lack this alternative binding site.

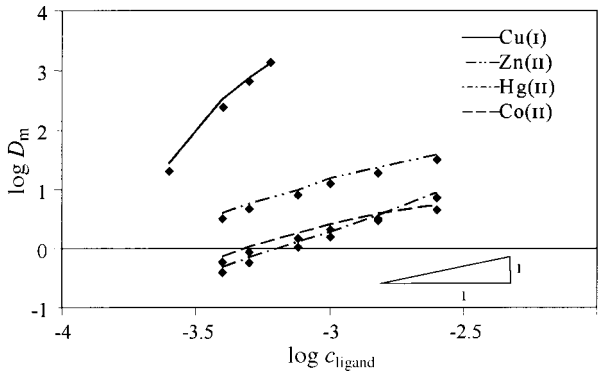


Fig. 6 Variation of log D_M with log[**9**] for the extraction of Hg^{2+}, Zn^{2+}, Co^{2+} and Cu^+ (298 K; pH 2, $CHCl_3$; [metal salt] = 0.1 mM).

Conclusions

The study of the solution complexation behaviour of ligands **8** and **9** has been aided by the complementarity of information deduced from ^{31}P NMR, fluorescence and absorption spectroscopy, electrospray mass spectrometry and liquid–liquid extraction studies. The bidentate, monobasic ligand **8** forms ML_2 complexes (^{31}P NMR, ESMS, extraction data) with an affinity that follows the sequence Cu > Zn > Hg ≫ Co > Ni. For the tetradentate ligand **9**, 1 : 1 complex formation was consistent with all data obtained, and the complexes with Zn, Co and Ni probably involve N_2O_2 ligation. No extraction of copper(II) was observed with ligand **9**. With copper(I), binding also involved an ML_2 species but in this case the ligand may act as a bidentate N_2 donor, possibly *via* N-7 coordination. Such a binding mode may also occur in the presence of excess ligand with other metal ions (*e.g.* Fe^{III}) and in seeking to eliminate this competitive coordination, future work should perhaps target the behaviour of derivatives of **9** in which N-7 coordination may not occur.

Experimental

All reactions were carried out under argon in apparatus which had been oven dried.

Basic alumina refers to Merck Alumina activity II-III, alumina refers to Merck alumina pre-soaked in ethyl acetate for at least 24 h prior to use and silica refers to Merck Kieselgel 230–400 mesh.

^1H, ^{13}C and ^{31}P NMR spectra were obtained with a Bruker AC 250 operating at 250.13, 62.9 and 101.26 MHz respectively, a Varian Mercury 200 operating at 200, 63 and 81 MHz respectively; proton and carbon spectra were also obtained using a Varian Unity 300 operating at 300 and 75 MHz or a Varian VXR 400s operating at 399.96 and 100.58 MHz respectively. Spectra are described in ppm to higher frequency of Sime4 with coupling constants, *J* in Hz. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer as KBr discs, neat films or using a Golden Gate accessory. Ultraviolet spectra were recorded using a Unicam 2 spectrometer and fluorescence emission spectra were recorded with a Perkin-Elmer LS50B spectrofluorimeter using FLwinlab as the data collection program. Mass spectra were recorded on a VG 7070E, operating in FAB, EI^+ or DCI ionisation modes as stated. Electrospray ionisation mass spectra were obtained on a VG platform II (Fisons Instruments), where major fragments are quoted as a percentage of the base peak intensity. Accurate mass spectroscopy was performed by the EPSRC Mass Spectroscopy service using FAB, EI^+ or DCI ionisation modes.

Combustion analysis was performed using an Exeter Analytical Inc CE440 elemental analyser and metal concentration was determined by atomic absorption spectroscopy using a Perkin Elmer 5000 atomic absorption spectrophotometer. Melting points were determined on a Köfler block melting point apparatus and are uncorrected.

All solvents were dried by distillation from the appropriate drying agent and water was purified by the PURITE system.

NMR titrations

NMR titrations were carried out in a 5 mm oven dried tube. A solution of the ligand was prepared (typically 0.04 M) in the deuteriated solvent (25% CD_3OD–75% $CDCl_3$) and 0.75 ml of the solution transferred to the tube by Gilson pipette. A solution of the metal trifluoromethanesulfonate salt was also

prepared in the deuteriated solvent (typically 0.4 M). The metal solution was then added in increments of known volume to the ligand solution and the shift of a given proton or phosphorus resonance monitored as a function of the M : L ratio. Typically the M : L ratios examined were 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 : 1. The change in shift of the given resonance was then plotted against the M/L ratio and the binding isotherm analysed using standard least-squares fitting procedures to give an approximate value for the 1 : 1 formation constant, *K*.

Fluorescence titrations

Fluorescence titrations were carried out in a quartz cell; stock solutions of the ligand (typically 1 mM) and metal perchlorate (10 mM) were prepared. For the pH titrations, 25 ml of a 0.01 mmol solution of the ligand was prepared in a 9 : 1 mixture of methanol and water. The pH was adjusted to approximately 1 with trifluoracetic acid and sodium hydroxide solution (50 mM) was added to raise the pH. The pH of the solution was measured with a standard pH electrode.

For the zinc titrations a 25 ml solution of the ligand (0.01 mM) was prepared in methanol. To this was added incremental amounts of zinc perchlorate solution (1 mM) so that the total volume change was less than 5%; typically M : L ratios of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 : 1 were examined. Data were analysed by a least-squares fitting procedure operating in Microsoft Excel.

Speciation analysis by electrospray mass spectrometry

Stock solutions of the ligand and metal salts (triflate or perchlorate) were prepared (typically 1 mmol) in freshly distilled methanol (Aristar, MeOH). To a sample of the ligand solution (1 ml) and methanol (1 ml) was added the appropriate volume of metal triflate solution to make a 1 : 1 or 1 : 2 metal to ligand ratio. The resultant sample was diluted to give a final concentration of 1 to 10 μM. Mass spectra were obtained on a VG Platform (II) electrospray mass spectrometer, in positive or negative ionisation mode using a typical source temperature of 60 °C , a capillary voltage of 4 kV and a cone voltage of 30 V. A 10 ml sample was introduced into the flowing solvent using an injection valve with a 10 ml steel loop and transported to the electrospray capillary through a silica tube.

Liquid–Liquid extraction

Liquid–liquid extraction studies were carried out at the Technical University of Dresden. The extraction studies were performed at 25 ± 1 °C in 2 ml micro-centrifuge tubes with mechanical shaking. Unless stated the shaking time was 30 min and the phase ratio $V_{(org)} : V_{(aq)}$ was 1 : 1 (0.5 ml each). All samples were centrifuged after extraction. The determination of metal concentrations in both phases was carried out radiometrically using γ-radiation measurement of $^{65}ZnCl_2$, $^{64}CuCl_2$, $^{59}FeCl_3$, $^{60}Co(NO_3)_2$ and $^{203}HgCl_2$ in a NaI(Tl) scintillation counter (Cobra II; Canberra-Packard), and β-radiation of $^{63}NiCl_2$ in a liquid scintillation counter (Tricarb 2500, Canberra-Packard). Aqueous 0.1 mM solutions of metal salts were prepared and the pH adjusted to 2.0 (±0.1) with NaOAc–HCl buffer. Chloroform solutions of the ligands were prepared with a concentration of between 5 mM and 0.25 mM. For the extraction of copper(I), the procedure was carried out in the presence of a 50-fold excess of hydroxylammonium sulfate (0.05 M)

Ligand synthesis

***N*-Acetyl-2-bromo-6-nitroaniline.** This was prepared by a modification of the literature method:[28] to a mixture of fuming nitric acid (6 ml), trifluoroacetic acid (4.5 ml) and water (2 drops) was added *N*-acetyl-2-bromoaniline (4 g, 18.69 mmol) with gentle heating over a period of 30 min. The mixture was stirred at room temperature for 10 h and the reaction followed by TLC (silica, 1% methanol–99% dichloromethane, R_f product = 0.2). The mixture was poured onto crushed ice (10 ml) and the brown solid collected by filtration and washed with water (60 ml). Recrystallisation from chloroform gave the required isomer as white needle-shaped crystals (2.17 g, 45%), mp 193–194 °C (lit.,[29] 193 °C). $\delta_H(CDCl_3)$ 2.24 (3H, s, CH_3), 7.26 (1H, dd, $^3J_{H4H3} = 8.7$, $^3J_{H4H5} = 7.6$, H4), 7.71 (1H, br s, NH), 7.86 (1H, dd, $^3J_{H3H4} = 8.7$, $^4J_{H3H5} = 1.4$, H3), 7.91 (1H, dd, $^3J_{H5H4} = 7.6$, $^4J_{H5H3} = 1.4$, H5)

2-Bromo-6-nitroaniline. A 33% ethanol–hydrochloric acid mixture (50 ml; 6 M HCl) was added to *N*-acetyl-2-bromo-6-nitroaniline (4 g, 15.4 mmol) and the mixture heated under reflux for 3.5 h. The mixture was poured onto a basic ice solution (10 ml) and the pH adjusted to 14 by addition of NaOH pellets. The resultant solid was collected by filtration, washed with water and dried under vacuum to give a bright yellow crystalline solid which was used without further purification (3.35 g, 100%), mp 74–75 °C (lit.,[30] 73–74 °C). δ_H ($CDCl_3$) 5.72 (1H, br s, NH), 6.62 (1H, br s, NH), 6.61 (1H, dd, $^3J_{H4H3} = 8.8$, $^3J_{H4H5} = 12.1$, H4), 7.69 (1H, dd, $^3J_{H4H5} = 12.1$, $^4J_{H5H3} = 1.1$, H5), 8.14 (1H, dd, $^3J_{H3H4} = 8.8$, $^4J_{H3H5} = 1.1$, H3)

1,2-Diamino-3-bromobenzene 11. To a solution of tin(II) chloride dihydrate (8.36 g) in concentrated hydrochloric acid (43 ml) was added 2-bromo-6-nitroaniline (2.19 g, 8.45 mmol) and the mixture stirred at room temperature for 5 min. The mixture was heated under reflux for 30 min, poured onto crushed ice and the solution made basic (pH 14, NaOH pellets) and the aqueous layer extracted exhaustively with diethyl ether (5 × 100 ml). The organic fractions were combined, dried (K_2CO_3) and the solvent removed under reduced pressure to give a pale yellow crystalline product (1.85 g, 96%), mp 52–53 °C (lit.,[19] 52–54 °C). δ_H (CD_3OD) 6.38 (1H, dd, $^3J_{H5H4} = 9.2$, $^3J_{H5H6} = 7.9$, H5), 6.57 (1H, d, $^3J_{H6H5} = 7.9$, H6), 6.76 (1H, d, $^3J_{H4H5} = 9.2$, H4).

4-Bromo-2-methylbenzimidazole[31] 12a. To 1,2-diamino-3-bromobenzene (2.5 g, 13.37 mmol) was added acetic anhydride (15 ml) and the solution heated at 110 °C for 2 h. The mixture was left to cool to room temperature and water (20 ml) was added and the solution heated at 60 °C for 1 h. Hydrochloric acid (3M, 20ml) was added and the mixture heated at 100 °C for a further 2 h. Activated carbon (500 mg) was added, and the solution filtered through a Celite plug. The aqueous filtrate was made basic (ammonia 0.880 solution) and extracted with dichloromethane (4 × 100 ml), dried (K_2CO_3) and the volatile organics removed under reduced pressure to give an off-white solid (2.82 g, 89%), mp 136–138 °C (lit.,[31] 137 °C). δ_H ($CDCl_3$) 2.65 (3H, s, CH_3), 7.08 (1H, dd, $^3J_{H6H5} = 7.6$, $^3J_{H6H7} = 7.9$, H6), 7.38 (1H, d, $^3J_{H7H6} = 7.6$, H7), 7.46 (1H, d, $^3J_{H5H6} = 7.9$, H5).

4-Bromo-1-(4-*tert*-butylbenzyl)-2-methylbenzimidazole 12b. Dimethylformamide (15 ml) was added to a mixture of 4-bromo-2-methylbenzimidazole (2.5 g, 11.84 mmol) and caesium carbonate (4.24 g, 13.03 mmol) and the mixture stirred under argon for 2 h. 4-(*tert*-Butyl)benzyl bromide (2.93 ml, *d* = 1.236, 13.03 mmol) was added and the mixture heated at 40 °C for 12 h. After cooling, the DMF was removed by vacuum distillation, and the residue taken up in dichloromethane (15 ml), washed with water (3 × 20 ml), dried (K_2CO_3) and the dichloromethane reduced to minimal volume (1 ml) followed by precipitation of the product with

diethyl ether (10 ml). This precipitate was filtered off and dried to yield an off-white solid (4.01 g, 95%), mp 134–135 °C. δ_H ($CDCl_3$) 1.25 (9H, s, ^tBu), 2.57 (3H, s, CH_3), 6.91 (2H, d, $^3J_{H10H11} = 2.6$, H10), 7.01 (1H, dd, $^3J_{H6H7} = 8.1$, $^3J_{H6H5} = 7.6$, H6), 7.14 (1H, d, $^3J_{H7H6} = 8.1$, H7), 7.28 (2H, d, $^3J_{H11H10} = 2.6$, H11, 7.38 (2H, d, $^3J_{H5H6} = 7.6$, H5). δ_C ($CDCl_3$) 16.2 (CH_3), 33.3 (^tBu), 36.56 (C2), 49.3 (CH_2), 110.8, 114.5, 125.2, 127.0, 127.9, 128.0, 134.3, 137.9, 153.2, 154.8; *m/z* (EI), 356 (51%, M^+), 358 (49%, M^+); Found: M^+ 356.0888. $C_{19}H_{21}N_2Br$ requires M^+ 356.0888. Found: C, 63.62: H, 5.98: N, 7.58. $C_{19}H_{21}N_2Br$ requires C, 63.87: H, 5.92: N, 7.58%.

Ethyl 1-(4-*tert*-butylbenzyl)-2-methylbenzimidazol-4-yl-(phenyl)phosphinate. Using a procedure adapted from Huang,[21] 4-bromo-1-(4-*tert*-butylbenzyl)-2-methylbenzimidazole (300 mg, 0.84 mmol), ethyl phenylphosphinate (0.14 ml, 0.924 mmol) and triethylamine (0.39 ml, 2.77 mmol) were mixed in dry degassed toluene (5 ml). Tetrakis(triphenylphosphine)palladium(0) (46 mg, 0.04 mmol) was added and the mixture degassed three times (freeze–thaw cycle), then heated at 100 °C for 96 h. The solution was diluted with dichloromethane (10 ml), washed with 5% aqueous hydrochloric acid (2 × 10 ml) and water (3 × 20 ml), dried (K_2CO_3) and the solvent removed under reduced pressure to give an off-white solid. Purification by column chromatography [alumina, eluant 2% MeOH–98% dichloromethane increasing to 8% MeOH–92% dichloromethane, R_f product = 0.38 (8% MeOH–92% dichloromethane)] gave a white solid (233 mg, 62%), mp 56–57 °C. δ_H ($CDCl_3$) 1.19 [9H, s, $C(CH_3)_3$], 1.32 (3H, t, $^3J = 7.2$, OCH_2CH_3), 2.52 (3H, s, 2-CH_3), 4.09 (2H, qd, $^3J = 7.2$, $^2J_{HP} = 2.2$, OCH_2CH_3), 5.18 (2H, s, NCH_2Ar), 6.91 (2H, d, $^3J_{H11H10} = 8.4$, H11), 7.01 (2H, ddd, $^3J_{HmPhHoPh} = 7.4$, $^3J_{HmPhHpPh} = 6.9$, $^4J_{HmPhP} = 3.6$, H*m*Ph), 7.12 (2H, d, $^3J_{H10H11} = 8.4$, H10), 7.25 (1H, dd, $^3J_{HpPhHmPh} = 6.9$, $^5J_{HpPhP} = 7.4$, H*p*Ph), 7.31 (1H, ddd, $^3J_{H6H7} = 8.2$, $^3J_{H6H5} = 7.4$, $^4J_{H6P} = 2$, H6), 7.47 (1H, d, $^3J_{H7H6} = 8.2$, H7), 7.79 (2H, dd, $^3J_{HoPhHmPh} = 7.4$, $^3J_{HoPhP} = 13.1$, H*o*Ph), 7.99 (1H, dd, $^3J_{H5H6} = 7.4$, $^3J_{H5P} = 12.9$, H5), δ_C ($CDCl_3$) 14.1 [$C(CH_3)_3$], 16.5 (d, $^3J_{CP} = 7.6$, OCH_2CH_3), 31.1 [$C(CH_3)_3$], 34.4 (NCH_2Ar), 46.7 (2-CH_3), 61.3 (d, $^2J_{CP} = 7.1$, OCH_2CH_3), 113.7 (d, $^3J_{CP} = 3.5$, C6), 120.6 (d, $^1J_{CP} = 160$, C*i*Ph), 121.4 (d, $^2J_{CP} = 15.5$, C5), 125.8 (C11), 125.9 (C12), 127. 4 (d, $^4J_{CP} = 9.7$, C7), 127.9 (d, $^3J_{CP} = 16$, C*m*Ph), 131.6 (d, $^3J_{CP} = 3.4$, C8), 131.86 (d, $^2J_{CP} = 13$, C*o*Ph), 132.2 (d, $^3J_{CP} = 168$, C4), 135.6 (d, $^4J_{CP} = 15$, C*p*Ph), 143.2 (d, $^2J_{CP} = 12$, C9), 150.9, 153.1 (C2). δ_p ($CDCl_3$) 31.3. *m/z* (ES) 447.15 (100%, LH^+). υ_{max} (KBr) 3439, 2961, 1602, 1438, 1419, 1209, 1035 cm^{-1}. Found: M^+ 446.2123. $C_{27}H_{31}N_2PO_2$ requires M^+ 446.2123. Found: C, 72.83: H, 7.16: N, 6.35. $C_{27}H_{31}N_2PO_2$ requires C, 72.62: H, 6.99: N, 6.27%.

1-(4-*tert*-Butylbenzyl)-2-methylbenzimidazol-4-yl(phenyl)-phosphinic acid hydrochloride 8. To ethyl 1-(4-*tert*-butylbenzyl)-2-methylbenzimidazole-4-yl(phenyl)phosphinate (200 mg, 0.45 mmol) was added hydrochloric acid (6 M, 10 ml) and the mixture heated at 110 °C for 16 h. After cooling, the acid was removed under reduced pressure to give a white solid (202 mg, 99%), mp 172–174 °C. δ_H (CD_3OD) 1.25 (9H, s, ^tBu), 3.10 (3H, s, 2-CH_3), 5.67 (2H, s, NCH_2Ar), 7.02 (1H, dd, $^3J_{H6H7} = 8.4$, $^3J_{H6H5} = 8.4$, H6), 7.09 (2H, d, $^3J_{H10H11} = 8.3$, H10), 7.30 (1H, dd, $^3J_{HmPhHpPh} = 7.9$, $^4J_{HpPhP} = 7.8$, H*p*Ph), 7.32 (2H, d, $^3J_{H11H10} = 8.3$, H11), 7.50 (2H, ddd, $^3J_{HmPhHoPh} = 7.2$, $^3J_{HmPhHpPh} = 7.9$, $^4J_{HmPhP} = 3.2$, H*m*Ph), 7.59 (1H, d, $^3J_{H5H6} = 8.4$, H5), 7.17 (1H, d, $^3J_{H7H6} = 8.4$, H7), 8.07 (2H, dd, $^3J_{HpPhHmPh} = 7.2$, $^5J_{HpPhP} = 12.4$, H*p*Ph). δ_C (CD_3OD) 22.6 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$], 34.6 (2-CH_3), 48.5 (NCH_2Ar), 114.6 (C2), 124.1 (C8′), 125.3 (d, $^2J_{CP} = 12.6$, C*o*Ph), 126.3 (C10), 126.6 (C11), 128.5 (d, $J_{CP} = 13.3$, C*m*Ph), 129.1, 129.8. 129.8 (d, $^1J_{CP} = 143$, C*i*Ph), 132.2, 132.3, 132.3 (d, $^1J_{CP} = 132$, C4), 152.1, 152.5. δ_p (CD_3OD) 28.0. *m/z* (ES) 419.29 (100%, LH^+). υ_{max} (KBr) 3418, 2958, 2864, 1678, 1546, 1544, 1424, 1218, 1132 cm^{-1}. Found: MH^+ 419.1888, $C_{25}H_{28}N_2PO_2$ requires MH^+ 419.1888.

4,4′-Dibromo-2,2′-propane-1,3-diyldi(1*H*-benzimidazole) 13a. To a mixture of 1,2-diamino-3-bromobenzene (730 mg, 3.90 mmol) and dimethyl glutarate (313 mg, 1.95 mmol) was added polyphosphoric acid (10 ml) and the mixture heated at 180 °C for 18 h. The black solution was allowed to cool to 100 °C and poured in a thin stream into well stirred water (100 ml), and stirring continued for 1 h. The mixture was filtered, the pH adjusted to 8 by addition of NaOH solution (3 M) and the resultant dark solid was collected by filtration and washed with water (2 × 10 ml). The solid was dissolved in methanol (50 ml) and treated with activated charcoal at 80 °C for 30 min, filtered through Celite and solvent removed under reduced pressure to give an orange solid (500 mg, 59%), mp 85–87 °C. δ_H ($CDCl_3$) 2.34 (2H, t, $^3J = 6.7$, 3-propyl CH_2), 3.05 (4H, t, $^3J = 6.7$, 2-propyl CH_2), 7.13 (2H, dd, $^3J_{H6H7} = 8.0$, $^3J_{H6H5} = 7.9$, H6), 7.44 (2H, d, $^3J_{H7H6} = 8.0$, H7), 7.53 (2H, d, $^3J_{H5H6} = 7.9$, H5). δ_C ($CDCl_3$) 18.4 (CH_2), 36.2 (CH_2), 107.8 (C-Br), 115.0, 131.1, 133.5, 134.5, 141.6 (C2). *m/z* (ES) 434.32 (45%, LH^+), 435.54 (100%, LH^+), 436.71 (51%, LH^+). υ_{max} (KBr) 3134, 2928, 2760, 1652, 1536, 1422, 1215, 1190, 1048, 932 cm^{-1}. Found: C, 47.36; H, 3.62; N, 12.45. $C_{17}H_{14}N_4Br_2$ requires C, 47.03; H, 3.25; N, 12.90%.

4,4′-Dibromo-1,1′-di(*tert*-butylbenzyl)-2,2′-propane-1,3-diyldi(1*H*-benzimidazole) 13b. Dimethylformamide (15 ml) was added to a mixture of 4,4′-dibromo-2,2′-propane-1,3-diyldi(1*H*-benzimidazole) (920 mg, 2.12 mmol) and caesium carbonate (1520 mg, 4.66 mmol, 2.2 equiv.) and the mixture stirred under argon for 2 h. 4-(*tert*-Butyl)benzyl bromide (0.86 ml, $d = 1.236$, 4.66 mmol, 2.2 equiv.) was added and the mixture heated at 80 °C for 16 h. The DMF was removed by vacuum distillation, and the residue taken up into dichloromethane (40 ml), washed with water (3 40 ml), dried (K_2CO_3) and the dichloromethane reduced to a minimal volume (1 ml) followed by precipitation of the product with diethyl ether (5 ml). This yielded a pale orange solid (1477 mg, 96%), mp 79–80 °C. δ_H ($CDCl_3$) 1.23 (18H, s, ^tBu), 2.44 (2H, t, $^3J = 6.6$, 2-propyl CH_2), 2.95 (4H, t, $^3J = 6.6$, 1- and 3-propyl CH_2), 5.38 (4H, s, CH_2), 7.21 (4H, d, $^3J_{H10H11} = 2.9$, H10), 7.33 (2H, dd, $^3J_{H6H7} = 8.1$, $^3J_{H6H5} = 7.6$, H6), 7.45 (2H, d, $^3J_{H7H6} = 8.1$, H7), 7.61 (2H, d, $^3J_{H11H10} = 2.9$, H11), 7.69 (4H, d, $^3J_{H5H6} = 7.6$, H5). δ_C ($CDCl_3$) 16.1 (CH_3), 18.0, 33.2 (^tBu), 36.5, 49.2 (CH_2), 110.8, 114.5, 125.1, 126.9, 127.9, 127.9, 134.3, 137.9, 153.1, 154.8. *m/z* (ES) 724.51 (55%, LH^+), 726.33 (100%, LH^+), 727.27 (60%, LH^+). υ_{max} (KBr) 3388, 2954, 1894, 1732, 1628, 1532, 1426, 1274, 1182, 1064, 924, 738 cm^{-1}. Found: C, 64.2; H, 5.95; N, 7.79. $C_{39}H_{42}N_4Br_2$ requires C, 64.5; H, 5.79; N, 7.71%.

1,1′-Di(*tert*-butylbenzyl)-4,4′-di[ethoxy(phenyl)phosphonyl]-2,2′-propane-1,3-diyldi(1*H*-benzimidazole) 13c. Using a procedure adapted from Huang,[21] 4,4′-dibromo-1,1′-di(*tert*-butylbenzyl)-2,2′-propane-1,3-diyldi(1*H*-benzimidazole) (300 mg, 0.41 mmol), ethyl phenylphosphinate (0.14 ml, 0.87 mmol, 2.1 equiv.) and triethylamine (1 ml) were mixed in dry degassed toluene (3 ml). Tetrakis(triphenylphosphine)palladium(0) (10 mg) was added and the mixture degassed three times (freeze–thaw cycle), then heated at 125 °C for 48 h. The solution was diluted with dichloromethane (20 ml), washed with hydrochloric acid (1 M, 2 × 20 ml) and water (3 × 20 ml), dried (K_2CO_3) and the solvent removed under reduced pressure to give an off-white solid. Purification by column chromatography [silica gel, eluant 100% dichloromethane increasing to

8% MeOH–92% dichloromethane, R_f product = 0.2 (8% MeOH–92% dichloromethane)] gave a light orange solid (230 mg, 62%), mp 64–66 °C. δ_H ($CDCl_3$) 1.13 [18H, s, C(CH_3)$_3$], 1.29 (6H, t, ^3J = 7.2, OCH_2CH_3), 2.41 (2H, t, ^3J = 6.6, 2-propyl CH_2), 2.94 (4H, t, ^3J = 6.6, 3-propyl CH_2), 4.09 (4H, qd, ^3J = 7.2, $^2J_{HP}$ = 2.0, OCH_2CH$_3$), 4.97 (4H, s, NCH_2Ar), 6.61 (4H, d, ^3J = 8.0, H10), 6.90 (4H, d, ^3J = 8.0, H11), 7.22 (2H, ddd, $^3J_{H6H7}$ = 7.8, $^3J_{H6H5}$ = 7.9, $^4J_{H6P}$ = 2, H6), 7.46 (4H, ddd, $^3J_{HmPhHoPh}$ = 8.0, $^3J_{HmPhHpPh}$ = 7.5, $^4J_{HmPhP}$ = 3.6, H*m*Ph), 7.62 (2H, dd, $^3J_{HpPhHmPh}$ = 7.5, $^5J_{HpPhP}$ = 8.0, H*p*Ph), 7.56 (2H, d, $^3J_{H7H6}$ = 7.8, H7), 7.83 (4H, dd, $^3J_{HoPhHmPh}$ = 8.0, $^3J_{HoPhP}$ = 13.5, H*o*Ph), 8.16 (2H, dd, $^3J_{H5H6}$ = 7.9, $^3J_{H5P}$ = 13.6, H5). δ_C ($CDCl_3$) 14.3 [*C*(CH_3)$_3$], 16.7 (d, $^3J_{CP}$ = 7.6, OCH_2*C*H$_3$), 29.0, 31.2 [C(*C*H$_3$)$_3$], 34.6 (N*C*H$_2$Ar), 46.7, 61.2 (d, $^2J_{CP}$ = 7.0, O*C*H$_2$CH$_3$), 114.0 (d, $^3J_{CP}$ = 3.1, C6), 120.9 (d, $^1J_{CP}$ = 162.5, C*i*Ph), 121.7 (d, $^2J_{CP}$ = 16.0, C5), 126.1 (C11), 126.1 (C12), 127. 7 (d, $^4J_{CP}$ = 9.8, C7), 128.2 (d, $^3J_{CP}$ = 16.5, C*m*Ph), 131.9 (d, $^3J_{CP}$ = 3.8, C8), 132.3 (d, $^2J_{CP}$ = 13.3, C*o*Ph), 132.4 (d, $^3J_{CP}$=169, C4), 135.8 (d, $^4J_{CP}$ = 15.5, C*p*Ph), 143.5 (d, $^2J_{CP}$ = 12.8, C9), 151.2, 153.3 (C2). δ_P ($CDCl_3$) 29.2. *m*/*z* (ES) 905.31 (100%, LH$^+$). υ_{max} (KBr) 3420, 2962, 2868, 1725, 1709, 1690, 1483, 1270, 1112, 1044, 1012, 830, 746, 666 cm^{-1}. Found: MH$^+$ 905.4325. $C_{55}H_{63}N_4P_2O_4$ requires MH$^+$ 905.4324.

1,1′-Di(*tert*-butylbenzyl)-4,4′-di[hydroxy(phenyl)phosphoryl]-2,2′-propane-1,3-diyldi(1*H*-benzimidazole) dihydrochloride 9. To a solution of 1,1′-di(*tert*-butylbenzyl)-4,4′-di[ethoxy-(phenyl)phosphonyl]-2,2′-propane-1,3-diyldi(1*H*-benzimidazole) (100 mg, 0.11 mmol) in 1,4-dioxane (6 ml) was added concentrated hydrochloric acid (10 M, 4 ml). The solution was heated at 110 °C and the reaction followed by ^{31}P NMR [δ_P (starting material) = 29.22, δ_P (product) = 16.44] until the reaction was complete (*ca.* 20 h). The solvent was removed under reduced pressure to give a pale orange solid (92 mg, 99%), mp 173–175 °C. δ_H (CD_3OD) 1.23 (18H, s, ^{t}Bu), 2.01 (2H, t, ^3J = 6.8, 2-propyl CH_2), 2.65 (4H, t, ^3J = 6.8, 1- and 3-propyl CH_2), 5.52 (4H, s, NCH_2), 7.35 (1H, dd, $^3J_{H6H7}$ = 8.5, $^3J_{H6H5}$ = 8.3, H6), 7.09 (2H, d, $^3J_{H10H11}$ = 8.3, H10), 7.30 (1H, dd, $^3J_{HpPhHmPh}$ = 7.7, $^5J_{HpPhP}$ = 7.2, H*p*Ph), 7.32 (2H, d, $^3J_{H11H10}$ = 8.3, H11), 7.62 (2H, ddd, $^3J_{HmPhHoPh}$ = 7.1, $^3J_{HmPhHpPh}$ = 7.7, $^4J_{HmPhP}$ = 3.2, H*m*Ph), 7.72 (1H, d, $^3J_{H5H6}$ = 8.3, H5), 7.89 (1H, d, $^3J_{H7H6}$ = 8.5, H7), 8.23 (2H, dd, $^3J_{HpPhHmPh}$ = 7.7, $^5J_{HpPhP}$ = 12.0, H*p*Ph). δ_C (CD_3OD) 22.6 [*C*(CH_3)$_3$], 28.0, 31.1 [C(*C*H$_3$)$_3$], 34.6, 48.8 (N*C*H$_2$Ar), 114.9 (C2), 124.3 (C8′), 125.5 (d, $^2J_{CP}$ = 12.2, C3′), 126.5 (C10), 126.9 (C11), 128.7 (d, J_{CP} = 13.8), 129.3, 130.0. 130.1 (d, $^1J_{CP}$ = 153.6), 132.5, 132.6, (d, $^1J_{CP}$ = 130.8), 152.3, 152.8; δ_P (CD_3OD) 16.4. *m*/*z* (ES) 847.23 (100%, M$^-$). υ_{max} (KBr) 3316, 2966, 2924, 2860, 1852, 1725, 1709, 1690, 1648, 1512, 1258, 1140, 1090, 830, 794 cm^{-1}. Found: MH$^+$ 848.3621. $C_{51}H_{55}N_4P_2O_4$ requires MH$^+$ 848.3620. Found: C, 71.8; H, 6.54; N, 5.68. $C_{51}H_{55}N_4P_2O_4 \cdot 2HCl \cdot 2H_2O$ requires C, 72.1; H, 6.37; N, 5.85%.

Acknowledgements

We thank EPSRC for support under the CASE scheme, the Royal Society for a Leverhulme Trust Senior Research Fellowship (DP), and Professor Peter Tasker, Dr Domenico Cupertino and Dr Troy Leese (Zeneca Specialties, Blackley, UK) for support under the CASE scheme.

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Paper 9/03534F