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Diphosphine bifunctional chelators for low-valent metal ions. Crystal structures of the copper(I) complexes $[\mathrm{CuClL^1_2}]$ and $[\mathrm{CuL^1_2}][\mathrm{PF_6}]$ $[\mathrm{L^1}$ = 2,3-bis(diphenylphosphino)maleic anhydride]

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The chelating diphosphine 2,3-bis(diphenylphosphino)maleic anhydride ($\mathrm{L^1}$) reacted with CuCl to give $[\mathrm{CuClL^1_2}]$ **1a** in which the copper is bound to three phosphorus atoms and one chlorine in a pseudo-tetrahedral structure, as demonstrated by X-ray crystallography. Compound $\mathrm{L^1}$ reacted with $[\mathrm{Cu(MeCN)_4}][\mathrm{PF_6}]$ to give the red salt $[\mathrm{CuL^1_2}][\mathrm{PF_6}]$ **1b** in which the copper is bound by four phosphorus atoms of two chelating bidentate ligands, as demonstrated by X-ray crystallography. Addition of chloride ions to **1b** quantitatively affords **1a**. Complex **1a** can be converted quantitatively into $[\mathrm{CuL^1_2}][\mathrm{NO_3}]$ **1c** by treatment with $\mathrm{AgNO_3}$. These complexes reacted quantitatively with water, benzylamine and methanol to give the corresponding $[\mathrm{CuL^2_2}]^+$ **2**, $[\mathrm{CuL^3_2}]^+$ **3** and $[\mathrm{CuL^4_2}]^+$ **4** where $\mathrm{L^2}$ = 2,3-bis(diphenylphosphino)maleic acid and $\mathrm{L^3}$ and $\mathrm{L^4}$ are the monobenzylamide and monomethyl ester derivatives, respectively, of $\mathrm{L^2}$. Uncomplexed $\mathrm{L^1}$ can also be hydrolysed to $\mathrm{L^2}$ or derivatised with benzylamine or methanol to give $\mathrm{L^3}$ and $\mathrm{L^4}$ respectively. Compounds $\mathrm{L^2}$, $\mathrm{L^3}$ and $\mathrm{L^4}$ reacted with copper-(I) or -(II) salts to yield salts of **2**, **3** and **4**. This chemistry provides versatile routes to the synthesis of stable bioconjugates containing copper or radiocopper and of derivatised solids containing pendant diphosphine ligands.

Tertiary phosphines, and particularly chelating (bis)tertiary phosphines, are versatile ligands that, as well as contributing fundamentally to our understanding of the co-ordination chemistry of the transition metals, have found commercial application in fields such as homogeneous catalysis, asymmetric synthesis and medical imaging. These applications could be taken further through the development of simple methods of derivatising the compounds to allow covalent coupling to substrates such as biomolecules and solid supports. Phosphines in the past have not lent themselves readily to this type of modification because the synthetic difficulties are formidable. 2,3-Bis(diphenylphosphino)maleic anhydride ($\mathrm{L^1}$, Scheme 1) is a possible candidate by virtue of both its straightforward synthesis[1,2] from commercially available starting materials and the reactivity of its anhydride group. However, its chemistry and co-ordination chemistry have not yet been explored to a significant extent, despite the well established and widespread use of carboxylic anhydrides in covalent modification of proteins. Its complexes with Group 6 and 10 metals, as well as Mn, Fe and Co, have been reported but the potential reactivity of the anhydride group was not exploited.[1,3–5] A report on the use of $\mathrm{L^1}$ in the preparation of silica-bound chelating phosphines for chelating chromium, molybdenum and tungsten has appeared.[6] More recently the investigation of $\mathrm{L^1}$ has led to the production of a number of stable 17- and 19-electron complexes in which the odd electron appears to be ligand-centred.[2,7–13] The hydrolysis product $\mathrm{L^2}$ (Scheme 1),[14] and its complexes with Mo and W, have also been reported.

We have previously shown that copper(I) bis(diphosphine) complexes can serve as a basis for radiopharmaceuticals containing copper radionuclides,[15] while others have demonstrated potential applications of these complexes as anticancer agents.[16,17] In view of these applications, and the possibility that diphosphine-derivatised polymers and solids might have environmental applications in the extractions and detection of toxic metals, we have begun an investigation of the utility of $\mathrm{L^1}$ in the synthesis of conjugates and solid supports containing diphosphine ligands. In this report we describe the synthesis of copper complexes of $\mathrm{L^1}$ and $\mathrm{L^2}$ and their elaboration into conjugates with amines, alcohols and amine-derivatised silica gel.

Results and Discussion

The reactions discussed are shown in Scheme 1. In the numbering scheme adopted the boldface numeral assigned to a complex is the same as the number of the ligand it contains, and the letter further distinguishes structural types or the counter ion. Analytical and physical data for the compounds are presented in Table 1. The literature synthesis of $\mathrm{L^1}$ is very straightforward and lends itself to functionalised diphosphine synthesis on a reasonably large scale. Copper(I) chloride reacts with $\mathrm{L^1}$ in anhydrous acetonitrile to afford the brown copper complex $[\mathrm{CuClL^1_2}]$ **1a**. The solubility and conductivity properties of this complex show it to be a non-electrolyte in acetonitrile and the FAB mass spectral results suggest it is monomeric. Despite the intense colour, the elemental composition suggests that the metal is in oxidation state I. These observations were confirmed by a single-crystal structure determination. A view of the structure appears in Fig. 1. Pertinent bond angles and distances are listed in Table 2. The copper(I) ion is co-ordinated by a chloride ligand and three phosphine donors, from one chelating diphosphine and one monodentate diphosphine. The second phosphine group of the latter is not within bonding distance of the metal. The geometry is approximately tetrahedral, with distortions imposed by the small bite angle of the chelating phosphine ligand. An additional distortion is seen in the small bond angle between the chloride ligand and the monodentate phosphine donor atom. There is no obvious cause for this unexpected compression, but a high degree of plasticity has been noted previously in the co-ordination geometry of the $\mathrm{d^{10}}$ copper(I) ion, and a similarly unexpected distortion is

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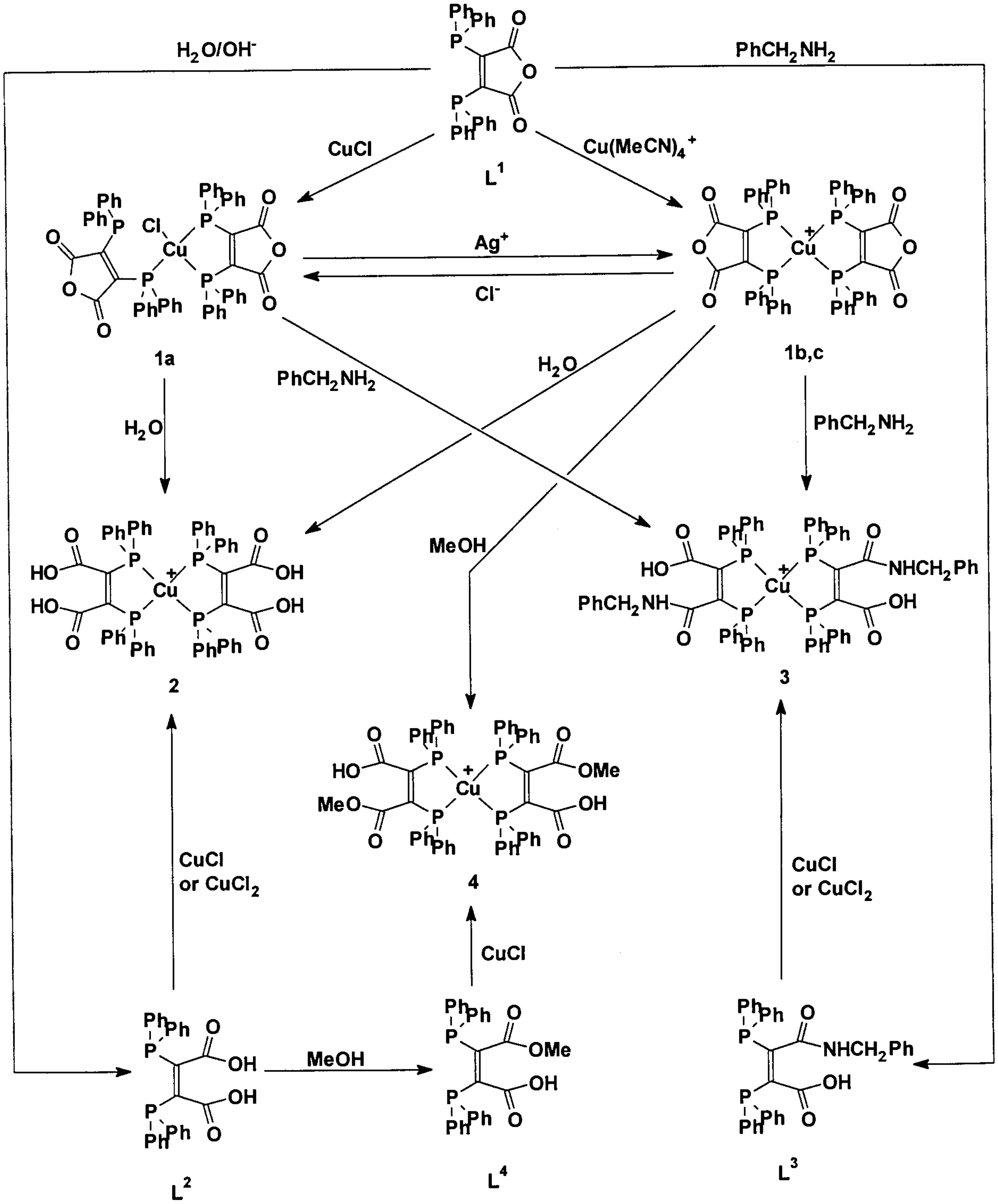

Scheme 1

observed in the complex [CuCl([9]aneS$_3$)] ([9]aneS$_3$ = 1,4,7-trithiacyclononane).[18]

If the complex [Cu(MeCN)$_4$]PF$_6$, which is free of strongly co-ordinating anions (*e.g.* chloride) is used in place of CuCl in the reaction with L^1 the product is [CuL$^1_2$]PF$_6$ **1b**. This complex is brick red both in solution and in the solid state. Again, the elemental composition suggests a copper(I) complex despite the intense colour. Conductivity measurements indicate that it is a 1:1 electrolyte in acetonitrile and FAB mass spectrometry confirms the presence of the complex cation [CuL$^1_2$]$^+$. These observations suggest a simple pseudo-tetrahedral copper(I) bis(diphosphine) core. These conclusions were confirmed by a single-crystal structure determination. A view of the structure appears in Fig. 2. Pertinent bond angles and distances are listed in Table 2. The complex cation has a roughly tetrahedral geometry, with the copper co-ordinated by four phosphorus atoms from two chelating diphosphine ligands. Distortions from the idealised tetrahedral structure are the result of the small chelate bite angles of the diphosphines (*ca.* 91°) and a twist of the two chelate planes away from mutually perpendicular. Thus, for example, P(1) of the first diphosphine ligand is closer to one phosphorus donor [P(4)] of the second diphosphine than to the other [P(3)].

The uncharged and cationic copper complexes described above are readily interconverted, with the corresponding instantaneous colour changes, by the addition of chloride ions (in the form of tetrabutylammonium chloride) and their removal (by addition of silver nitrate with resulting formation of AgCl). Complex **1a** was isolated by addition of tetrabutylammonium chloride to **1b**. Addition of an excess of silver

Table 1 Analytical, physical and spectroscopic properties of the compounds

Compound	Colour	Yield (%)	Elemental analysis (%)^a	Principal IR bands/cm^{-1}	NMR, δ^b		Conductivity^c/Ω^{-1} cm^2 mol^{-1}	FAB mass spectrum, m/z^d
					^{1}H	^{31}P		
L^3	Yellow	72	C, 73.1 (73.3); H, 4.9 (5.1); N, 2.3 (2.4)	3400w [ν(NH)], 2800–2400w [ν(carboxylic OH)], 1750–1600m [ν(C=O)]	3.9 (d, 2 H, CH_2), 6.9–7.5 (m, 25 H, Ph), 7.5 (s, 1 H, NH)	−12.14 (s)		M^+, 573 (100)
L^4	Yellow	86	C, 69.5 (69.8); H, 4.5 (4.8)	2800–2400w [ν(carboxylic OH)], 1750–1600m [ν(C=O)]	2.6 (s, 3 H, CH_3), 6.9–7.5 (m, 25 H, Ph)	−12.16 (s)		M^+, 498 (100)
1a [$CuClL^1{}_2$]	Brown	84	C, 65.0 (65.2); H, 3.8 (3.9); Cl, 3.4 (3.3)	1840, 1820m [ν(C–O–C)], 1760, 1700s [ν(C=O)]	7.2–7.6 (m, Ph)	−1.9 (s br)	43.5	M^+, 995 (95); $M^+ - L^1$, 529 (100)
1b [$CuL^1{}_2$]PF_6	Red	94	C, 58.7 (58.9); H, 3.5 (3.5)	1820s [ν(C–O–C)], 1780s [ν(C=O)]	7.2–7.5 (m, Ph)	−1.7 (s br)	140.52	M^+, 995 (100); $M^+ - L^1$, 529 (45)
2 [$CuL^2{}_2$]Cl	Yellow	89	C, 63.0 (62.9); H, 3.8 (4.1); Cl, 3.2 (3.3)	2800–2400w [ν(carboxylic OH)], 1750–1600s (br) [ν(C=O)]	7.1–7.3 (m, Ph)	13.0 (s br)		M^+, 1031 (100); $M^+ -$ L^2, 547 (48)
3a [$CuL^3{}_2$]Cl	Yellow	74	C, 67.1 (67.4); H, 4.7 (4.6); Cl, 2.6 (2.8); N, 2.1 (2.2)	3400w [ν(NH)], 2800–2400w [ν(carboxylic OH)], 1700, 1650s (br) [ν(C=O)]	4.0 (d, 4 H, CH_2), 6.9–7.4 (m, 50 H, Ph), 7.5 (s, 2 H, NH)	15.5 (s br)	136.2	M^+, 1209 (100)
3b [$CuL^3{}_2$]PF_6	Yellow	76	C, 62.1 (62.0); H, 4.7 (4.3); N, 2.4 (2.1)	3400w [ν(NH)], 2800–2400w [ν(carboxylic OH)], 1700, 1650s (br) [ν(C=O)]	4.0 (d, 4 H, CH_2), 6.9–7.4 (m, 50 H, Ph), 7.4 (s, 2 H, NH)		137.2	M^+, 1209 (100)
4 [$CuL^4{}_2$]PF_6	Yellow	67	C, 57.6 (57.8); H, 4.0 (3.9)	2800–2400w [ν(carboxylic OH)], 1750–1600m [ν(C=O)]	2.6 (s, 6 H, CH_3), 6.9–7.5 (m, 50 H, Ph)		94.1	M^+, 1059 (100)

^{a} Calculated values in parentheses. ^{b} Solvents: compound **1b** in CD_3CN; L^3 and **1a** in $CDCl_3$; **2**, **3a**, **3b**, L^4 and **4** in CD_3OD. ^{c} Measurements of complexes **1a**, **1b** and **3** performed in MeCN ([NBu_4]Cl = 142.1 Ω^{-1} cm^2 mol^{-1}) and of **4** in MeOH ([NBu_4]Cl = 96.2 Ω^{-1} cm^2 mol^{-1}). ^{d} Relative abundance (%) in parentheses. The spectra of complexes **1a** and **1b** also show a peak at *m/z* 1148, which corresponds to esterification of the anhydride group by the matrix.

nitrate to **1a** in acetonitrile caused precipitation of silver chloride and a change from brown to red. Addition of diethyl ether to the filtered solution gave a solid that contained both the nitrate salt **1c** and the analogous silver complex, as evidenced by the appearance in the FAB mass spectrum of a molecular ion [$AgL^1{}_2$]$^+$ and its fragments as well as peaks characteristic of [$CuL^1{}_2$]$^+$.

The strong coloration of complexes **1a**–**1c** contrasts with other bis(diphosphine) complexes of copper(I) which are colourless [*e.g.* those of *cis*-1,2-bis(diphenylphosphino)ethene[19]] or yellow [*e.g.* 2,3-bis(diphenylphosphino)maleic acid, see below]. Thus, it is peculiar to the unsaturated and relatively electron-withdrawing anhydride group.

The relatively electron-withdrawing nature of L^1 presumably accounts for the ease with which chloride ion displaces one of the phosphorus donor atoms from the copper co-ordination sphere of [$CuL^1{}_2$]$^+$. This displacement is also observed with 1,2-bis(diphenylphosphino)ethane.[17,20] It is not observed, at least in organic solvents, with 1,2-bis(diethylphosphino)ethane,[17] 2,3-bis(diphenylphosphino)maleic acid (see below) or *cis*-1,2-bis(diphenylphosphino)ethene,[17] all of which are more powerful ligands by virtue of either the relatively favourable entropy associated with chelation of the more rigid *cis*-ethene ligand backbone, or the greater electron-donor properties of the alkyl substituents compared to the phenyl groups. These compounds all give complexes which are 1:1 electrolytes even in the presence of chloride ions. Comparison of various structural parameters of complexes **1a** and **1b** with the structure of the analogous bis(diphenylphosphino)ethene complex[19] and a structurally related bis(diphenylphosphino)ethane complex[20] (Fig. 3 and Table 3) suggests that there are no additional chelate or ring-strain effects that would account for the weaker co-ordination of L^1. The Cu–P bond distances in **1a** and **1b** are significantly longer than their counterparts in [$Cu_2Cl_2(dppe)_3$] and [$Cu(dppey)_2$]$^+$, possibly as a result of the electron-withdrawing nature of the anhydride group. The bite angles of the chelating ligands do not differ significantly in the four complexes; in the unsaturated ligand systems the intrachelate angles at the phosphorus atoms vary within a range of less than 4°, and those at the intrachelate carbon atoms by about 2°. Thus, these complexes represent an example of a fine balance between co-ordinational preferences dictated by the electronic nature of the donor atoms (the presence or absence of the electron-withdrawing anhydride group), the chelate effect (rigid *versus* non-rigid chelating phosphine) and the charge-neutralisation requirements of the metal (neutral phosphine *versus* chloride anion).

Having established the utility of L^1 as a ligand for copper, we examined the reactivity of both free L^1 and the complexes **1a** and **1b** with nucleophiles. The reactions are shown in Scheme 1. Both L^1 and its complexes react cleanly with water (at pH 7.4), benzylamine (in MeCN) or methanol to give compounds L^2, L^3 and L^4 and corresponding complexes **2**, **3a**, **3b** and **4**, the structures of which were confirmed by FAB mass spectroscopy, elemental microanalysis, IR and ^{1}H NMR spectroscopy. The identity of the complexes was further confirmed by separate synthesis starting from CuCl and the already synthesized L^2 and L^3. Compound L^4 likewise gives a material similar in appearance to **3a**, **3b** and **4** upon reaction with CuCl, and $CuCl_2 \cdot 2H_2O$ was shown to give identical products in some

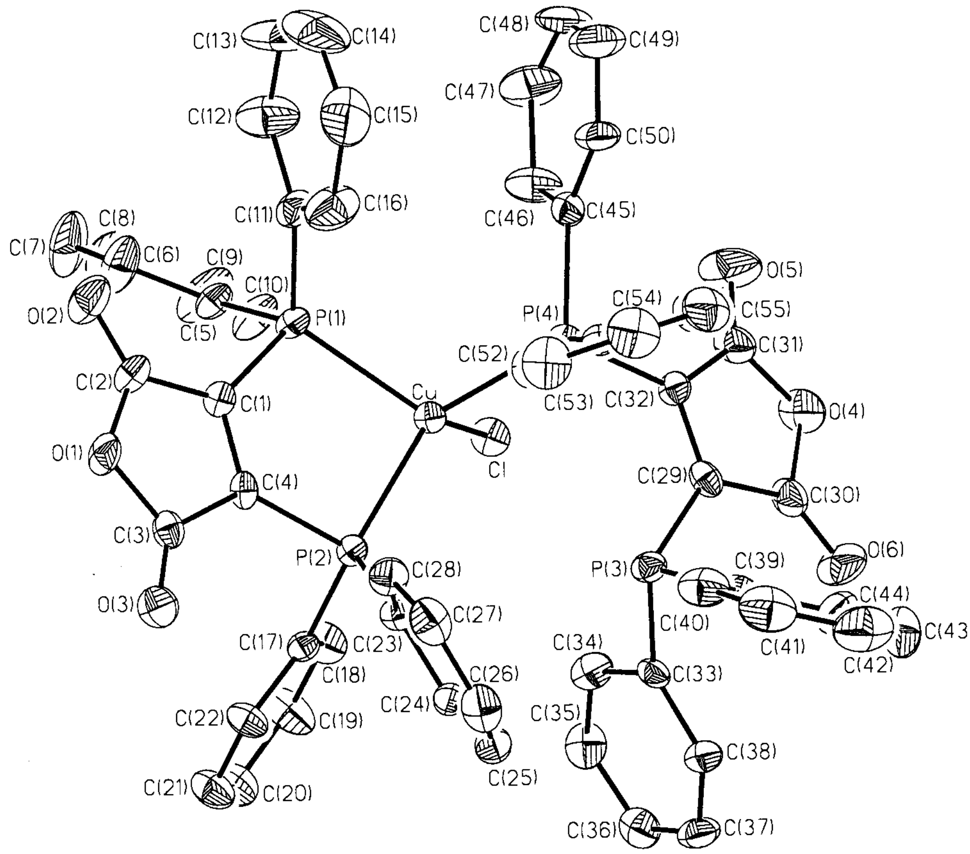

Fig. 1 Structure of complex **1a** and the atom labelling scheme

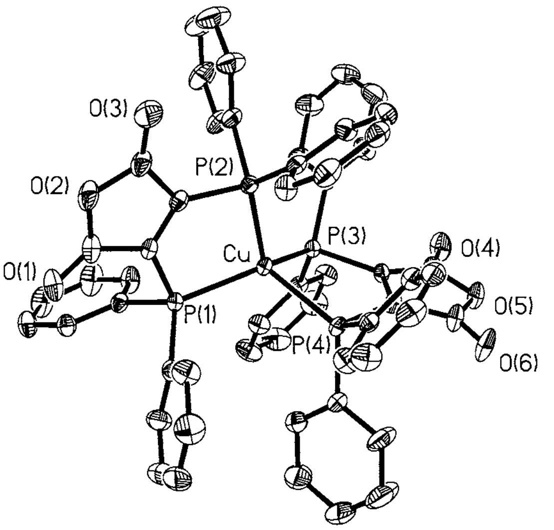

Fig. 2 Structure of complex **1b** and the atom labelling scheme

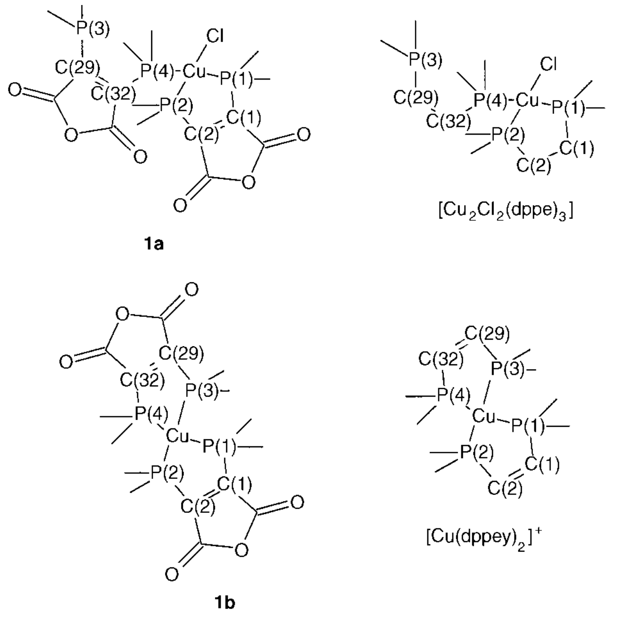

Fig. 3 Schematic structures and atom numbering schemes (adopted in Table 3) for a series of related 1,2-bis(diphosphine) complexes

cases. Exchange of the hexafluorophosphate counter ion in **1b** to the chloride counter ion in **2** was effected by addition of hydrochloric acid to the aqueous solution of hydrolysed **1b**. Although **1a** is insoluble in water, **2** is soluble at pH > 7. When copper(II) salts were used as starting materials, the phosphine presumably acted as both ligand and reducing agent. In all cases the isolated yields were good, the reactions proceeded without observable side-products and the products obtained were identical whether complexation was carried out before or after derivatisation of the ligand.

Owing to the lack of side reactions, the rapidity of the reactions and the clear distinction between ligand- and metal-centred reactivity in the above processes, this chemistry was expected to be readily amenable to exploitation for the synthesis of metalloconjugates of proteins and peptides and for derivatisation of solid supports for metal extraction, detection and catalysis. Such a derivatised surface would have amphiphilic properties compatible with both aqueous and non-aqueous solvents due to the presence of both hydrophobic phenyl groups and hydrophilic carboxylate groups. The bioconjugation applications will be described elsewhere. A simple demonstration of the compatibility with solid-supported chemistry was provided by the use of commercially available amine-derivatised silica sample-preparation columns. These

Table 2 Pertinent bond lengths (Å) and angles (°) for complexes **1a** and **1b**

$[CuClL^1_2]$ **1a**			
Cu–P(1)	2.321(3)	P(1)–Cu–P(2)	91.8(1)
Cu–P(2)	2.327(2)	P(1)–Cu–P(4)	111.4(1)
Cu–P(4)	2.315(3)	P(2)–Cu–P(4)	126.7(1)
Cu–Cl	2.299(3)	P(1)–Cu–Cl	116.1(1)
P(1)–C(1)	1.834(9)	P(2)–C(4)–C(1)	122.5(6)
P(1)–C(5)	1.819(11)	P(2)–Cu–Cl	117.1(1)
P(1)–C(11)	1.830(12)	P(4)–Cu–Cl	95.3(1)
P(2)–C(4)	1.835(9)	Cu–P(1)–C(1)	100.1(3)
P(2)–C(17)	1.848(9)	Cu–P(2)–C(4)	100.2(3)
P(2)–C(23)	1.814(10)	P(1)–C(1)–C(4)	123.2(7)
P(3)–C(29)	1.821(9)	Cu–P(4)–C(32)	109.1(3)
P(3)–C(33)	1.819(10)	P(4)–C(32)–C(29)	124.3(7)
P(3)–C(39)	1.810(11)	P(3)–C(29)–C(32)	124.4(7)
P(4)–C(32)	1.831(9)		
P(4)–C(45)	1.836(10)		
P(4)–C(51)	1.800(10)		
$[CuL^1_2]PF_6$ **1b**			
Cu–P(1)	2.3048(12)	P(1)–Cu–P(2)	91.68(4)
Cu–P(2)	2.3237(12)	P(1)–Cu–P(3)	135.63(5)
Cu–P(3)	2.3218(12)	P(1)–Cu–P(4)	112.00(5)
Cu–P(4)	2.3195(11)	P(2)–Cu–P(3)	113.25(4)
P(1)–C(1)	1.826(5)	P(2)–Cu–P(4)	114.16(4)
P(1)–C(5)	1.822(5)	P(3)–Cu–P(4)	91.26(4)
P(1)–C(11)	1.811(5)	Cu–P(1)–C(1)	100.7(2)
P(2)–C(4)	1.818(5)	Cu–P(2)–C(4)	100.8(2)
P(2)–C(17)	1.812(5)	P(1)–C(1)–C(4)	123.5(4)
P(2)–C(23)	1.821(5)	P(2)–C(4)–C(1)	122.8(4)
P(3)–C(29)	1.827(4)	Cu–P(4)–C(32)	99.6(2)
P(3)–C(33)	1.821(5)	P(4)–C(32)–C(29)	122.0(3)
P(3)–C(39)	1.808(5)	P(3)–C(29)–C(32)	122.8(3)
P(4)–C(32)	1.815(5)		
P(4)–C(45)	1.805(5)		
P(4)–C(51)	1.829(5)		
C–O	1.376–1.397		
C=O	1.173–1.188		

Table 3 Comparison of chelate structural parameters for complexes **1**, **2a** and related complexes. Bond lengths in Å, angles in °. See Fig. 4 for schematic structure and numbering scheme

	1a	$[Cu_2Cl_2(dppe)_3]^a$	**1b**	$[Cu(dppey)_2]^{+b}$
Cu–P(1)	2.321(3)	2.291(5)	2.3048(12)	2.276(2)
Cu–P(2)	2.327(2)	2.311(4)	2.3237(12)	2.288(2)
Cu–P(3)	—	—	2.3218(12)	2.289(2)
Cu–P(4)	2.315(3)	2.284(6)	2.3195(11)	2.287(2)
Cu–Cl	2.299(3)	2.312(4)	—	—
P(1)–Cu–P(2)	91.8(1)	89.5(2)	91.68(4)	89.69(7)
Cu–P(1)–C(1)	100.1(3)	100.9(5)	100.7(2)	103.7(3)
Cu–P(2)–C(4)	100.2(3)	102.8(5)	100.8(2)	103.7(3)
P(1)–C(1)–C(4)	123.2(7)	109.7(10)	123.5(4)	122.2(6)
P(2)–C(4)–C(1)	122.5(6)	109.3(14)	122.8(4)	120.6(6)
Cu–P(4)–C(32)	109.1(3)	114.1(4)	99.6(2)	103.5(2)
P(4)–C(32)–C(29)	124.3(7)	112.3(13)	122.0(3)	121.8(6)
P(3)–C(29)–C(32)	124.4(7)	112.3(13)	122.8(3)	121.4(6)

[a] dppe = 1,2-Bis(diphenylphosphino)ethane.[20] [b] dppey = *cis*-1,2-Bis(diphenylphosphino)ethene.[19]

disposable cartridges, containing 100 mg of the derivatised silica, were readily derivatised further with the diphosphine by passing an acetonitrile solution of L^1 through the column. The diphosphine bound firmly to the solid support, as evidenced by the appearance of a yellow band at the top of the column. Further washing of the column with solvents and water failed to remove this band. When solutions containing copper(II) ions were passed through the column the copper was extracted selectively into the yellow band causing a darkening of the yellow colour. Similarly, passage of an acetonitrile solution of **1a** led to irreversible binding of the complex, observed by the change from brown to a yellow band which remained at the top of the column. In contrast, passage of an acetonitrile solution of **2** through the non-phosphine-derivatised column did not result in binding of the complex, confirming the covalent nature of the ligand–column interaction. Thus, the reactions observed in the solution chemistry described above are fully compatible with solid-support chemistry. The applications of this approach are unlikely to be limited to those involving copper but should encompass other metals too.[6]

Experimental

All reactions were undertaken in air with anhydrous solvents. Elemental analyses (C, H, N) were performed by the Chemical Laboratory, University of Kent. The NMR (^1H and ^{31}P) measurements were made using a JEOL 270 MHz spectrometer. Chemical shifts were quoted relative to internal $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Chloride analysis was by Medac Ltd., Brunel University, UK. Fast atom bombardment mass spectra were recorded using 3-nitrobenzyl alcohol as the matrix material at the EPSRC Mass Spectrometry Centre, Swansea, UK and infrared spectra in the range 400–4000 cm^{-1} as Nujol mulls on KBr plates using a Perkin-Elmer spectrophotometer. Conductivities were measured using a Bibby MC1 conductivity meter on 1 mmol dm^{-3} solutions in anhydrous acetonitrile, with $[NBu_4]Cl$ as a calibrating standard. The compounds $[Cu(MeCN)_4]PF_6$,[21] 2,3-bis(diphenylphosphino)maleic anhydride[1] and the corresponding acid[14] were synthesized by literature methods. All other chemicals were from Aldrich, UK. Solid-support reactions were carried out using 100 mg Analytichem International BondElut NH_2 (Jones Chromatography, UK) columns pre-washed with acetonitrile.

Preparations

***cis*-1-Carboxy-2-(*N*-benzylcarbamoyl)-1,2-bis(diphenylphosphino)ethene (L^3).** Compound L^1 (0.19 g, 0.4 mmol) was dissolved in acetonitrile (8 cm^3). Benzylamine (0.043 g, 0.4 mmol) was added to the orange-red solution. After stirring at room temperature for 2 h a yellow precipitate had formed. The yellow solid was isolated by filtering in air.

***cis*-1-Carboxy-2-methoxycarbonyl-1,2-bis(diphenylphosphino)ethene (L^4).** Compound L^2 (0.2 g, 0.42 mmol) was taken up in methanol (15 cm^3) and warmed slightly. The mixture was stirred overnight. The methanol was removed *in vacuo* to produce a pale yellow, air-stable solid.

Chlorobis[2,3-bis(diphenylphosphino)maleic anhydride]copper(I) 1a. Compound L^1 (0.13 g, 0.28 mmol) was dissolved in acetonitrile (4 cm^3). Copper(I) chloride (0.014 g, 0.14 mmol) was added and the solution immediately turned brown. After 15 min of stirring at room temperature a brown solid precipitated which was isolated in air and washed with cold acetonitrile. The complex was recrystallised from dichloromethane–diethyl ether yielding dark brown crystals.

Compound **1a** could also be prepared by dissolving **1b** in acetonitrile, adding an excess of $[NBu_4]Cl$ and stirring at room temperature for a few minutes. The analytical and spectroscopic properties of the product were identical to those of the sample obtained above.

Bis[2,3-bis(diphenylphosphino)maleic anhydride]copper(I) hexafluorophosphate 1b. Compound L^1 (0.22 g, 0.47 mmol) was dissolved in acetonitrile (6 cm^3). The complex $[Cu(MeCN)_4]PF_6$ (0.088 g, 0.24 mmol) was added and a dark red solution immediately formed. After 15 min of stirring at room temperature the volume of acetonitrile was reduced *in vacuo* to *ca.* 2 cm^3. Diethyl ether was added to induce precipitation of a bright red microcrystalline solid. This solid was filtered off in air and washed with diethyl ether. The complex was

Table 4 Crystal data and experimental details[a] of the crystal structure determinations

	$[CuClL^1_2]$ **1a**[b]	$[CuL^1_2]PF_6\cdot MeCN$ **1b**
Empirical formula	$C_{56}H_{40}ClCuO_6P_4$	$C_{58}H_{43}CuF_6NO_6P_5$
M	1031.82	1182.32
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$
a/Å	13.678(3)	12.528(3)
b/Å	17.722(4)	17.197(4)
c/Å	11.256(2)	12.6709(9)
α/°	95.84(2)	
β/°	98.45(2)	90.166(11)
γ/°	93.46(2)	
U/Å^3	2676.8(10)	2729.8(7)
D_c/g cm^{-3}	1.286	1.438
Crystal size/mm	0.20 × 0.20 × 0.50	0.30 × 0.20 × 0.10
Crystal shape and colour	Brown block crystal	Red block crystal
μ/mm^{-1}	0.620	0.619
2θ Range/°	2–50	3–50
hkl Ranges	0–16, −21 to 21, −13 to 13	0–14, 0–20, −15 to 15
Reflections collected	9864	5017
Independent reflections	9431	5008
Reflections observed	5149 [$F > 3\sigma(F)$]	4643 [$F > 4\sigma(F)$]
Maximum, minimum transmission factors	0.942, 1.000	0.681, 0.941
Program used	SHELXTL PLUS[22]	SHELXS 86 (solution),[23] SHELXL 93 (refinement)[24]
Parameters refined	633	679
Goodness of fit	1.47	1.075
wR	0.0794 (on *F*)	0.1360 (on F^2 for all data)
R′	0.0833	0.368 [on *F* for $F > 4\sigma(F)$]
Residual electron density/e Å^{-3}	+1.629, −0.54	+0.43, −0.69

[a] Details in common: $Z = 2$; Rigaku AFC 7R diffractometer; Mo-Kα radiation (λ 0.71073 Å); 293 K; semiempirical ψ-scan absorption correction; direct methods. [b] The disordered solvent, probably MeCN, was modelled as four partial-occupancy carbon atoms. It was not possible to locate any individual molecules of solvent.

recrystallised from acetonitrile–diethyl ether yielding dark red crystals.

Bis[2,3-bis(diphenylphosphino)maleic anhydride]copper(I) nitrate 1c. Compound **1a** (0.20 g, 0.19 mmol) was suspended in acetonitrile (5 cm^3). Silver nitrate (0.065 g, 0.39 mmol) was added and the mixture turned immediately to red. After stirring at room temperature for 30 min and removal of the insoluble AgCl by filtration, the complex was isolated by the addition of diethyl ether. The lilac solid precipitated was isolated in air. The FAB mass spectrum of the solid showed evidence of the presence of both metal complexes of L^1; $[CuL^1_2]^+$, *m/z* = 995 (M^+, 32) and 529 ($M^+ - L^1$, 45); $[AgL^1_2]^+$, *m/z* = 1039, 1041 (M^+, 66), 573, 575 ($M^+ - L^1$, 100%).

Bis[2,3-bis(diphenylphosphino)maleic acid]copper(I) chloride 2. Compound L^2 (0.1 g, 0.21 mmol) was dissolved in acetonitrile (5 cm^3). Copper(I) chloride (0.01 g, 0.1 mmol) was added and a clear yellow solution formed. After stirring at room temperature for 20 min a microcrystalline yellow compound was filtered off in air and washed with cold acetonitrile. Yellow crystals were produced by recrystallisation from methanol–diethyl ether. This complex was also formed in 83% yield by the substitution of $CuCl_2\cdot 2H_2O$ (0.018 g, 0.1 mmol) for CuCl and employing the same methodology (Found: C, 62.0; H, 4.0. $C_{56}H_{44}ClCuO_8P_4\cdot H_2O$ requires C, 61.9; H, 4.1%). All spectroscopic data were identical to those in Table 1 for samples made by the first method.

Compounds **1a** and **1b** can be readily converted into **2** by addition to basic water. Typically, **1a** (0.05 g, 0.4 mmol) was added to NaOH (0.006 g, 1.5 mmol) dissolved in water (2 cm^3). The mixture was gently heated (*ca.* 60° C) until a yellow solution formed and stirred for 1 h at room temperature. 5% Hydrochloric acid was slowly added until a yellow solid was formed which was isolated in air (yield 97%). All spectroscopic data were identical to those detailed above (Found: C, 61.8; H, 4.2%).

Bis[1-carboxy-2-(*N*-benzylcarbamoyl)-1,2-bis(diphenylphosphino)ethene]copper(I) chloride 3a. Complex **1a** (0.10 g, 0.1 mmol) was dissolved in acetonitrile (5 cm^3). Benzylamine (0.02 g, 0.2 mmol) was added and the initially red solution turned pale yellow. It was stirred at room temperature for 30 min and the solvent then removed *in vacuo*. The remaining yellow oil was triturated in cold diethyl ether to yield a bright yellow solid, analytical and spectroscopic details of which are given in Table 1. This compound is also produced by the direct complexation of L^3 with CuCl in acetonitrile stirring at room temperature. The complex was isolated as above (Found: C, 67.4; H, 5.0; N, 3.2. $C_{70}H_{58}ClCuN_2O_6P_4\cdot MeCN$ requires C, 67.2; H, 4.8; N, 3.3%).

The corresponding hexafluorophosphate salt **3b** was produced by reaction of complex **1b** with benzylamine following the same experimental methodology.

Bis[1-carboxy-2-methoxycarbonyl-1,2-bis(diphenylphosphino)ethene]copper(I) hexafluorophosphate 4. This compound was produced by the direct reaction of **1b** with methanol. The complex was taken up in methanol, stirred for 2 h and isolated by removal of the solvent *in vacuo*. A material of similar appearance, presumed to be the corresponding chloride salt, was prepared by reaction of L^4 with CuCl using a similar procedure to that described for **3a**.

Solid-support experiments

These were performed on BondElut NH_2 columns. The columns were initially washed with anhydrous acetonitrile (5 cm^3), then a solution of L^1 or complex **1a** or **1b** in acetonitrile was passed whereupon, in the case of L^1 and **1a**, a yellow band appeared at the top of the column. A solution of $CuCl_2$ was then passed.

Crystallography

Details of the crystal structure determinations are summarised in Table 4.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/375.

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