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Chiral N_2S_2 and N_4S_4 macrocycles as precursors to mixed phospha/thia macrocycles and cyclic amidinium salts

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The cyclo-condensation of 1*R*,2*R*-diaminocyclohexane with 2,2'-(ethane-1,2-diyldisulfanediyl)dibenzaldehyde gave the 1:1 addition compound chxn-$^{im}N_2S_2$ in high yield. When the same condensation reaction was performed with 1*R*,3*S*-diamino-1,7,7-trimethylcyclopentane as the diamine, the 2:2 addition compound tmcp-$^{im}N_4S_4$ was obtained selectively. Reduction of the diimines gave the saturated analogues chxn-N_2S_2 (**1**) and tmcp-N_4S_4 (**3**) the former of which could be phosphorylated with $PhP(NMe_2)_2$ to give the novel 13-membered macrocycle chxn-PS_2, **2**. Introduction of the phenylphosphine function proved stereoselective with a preference for the N(*R*)/N(*S*) configuration at the nitrogen atoms. The coordination chemistry of the novel phosphine has been explored with Cu(I) and Mo(0) through formation of the complexes Cu(**2**)I, **4**, and $Mo(CO)_3$(**2**), **5**. Extension of the phosphorylation chemistry to tmcp-N_4S_4 (**3**) proved unsuccessful but ring closure reactions of both **1** and **3** with triethylorthoformate gave cyclic amidinium salts which are potential precursors to macrocyclic N-heterocyclic carbenes.

Introduction

Mixed donor ligands are ubiquitous in coordination chemistry. They are of many types and can incorporate similar but distinct donors (hard/hard or soft/soft), or consist of mismatched combinations (hard/soft).[1] These latter systems attract interest because of a potential HSAB conflict between the one or more of the donor atoms and the metal ion which may compromise complex stability and hence induce unusual reactivity.[2] The development of so-called hemilabile ligands is a classic example of the application of hard/soft mixed donor ligands which have, on occasion, proved useful in catalysis. Examples of hard/hard ligands are multifold and include common types such as salens and the aza-crowns. Heterotopic soft/soft combinations with donors such as phosphorus and sulphur are less familiar and, in stark contrast to the extensive chemistry reported for homoleptic sulphur[3] and, to a lesser extent, phosphorus macrocycles,[4] cyclic systems of the PS_2 type are extremely rare.[5] The predominant ring-size of this exclusive class is 9-membered, although 10-,[5e] 11-,[5f] and 12-membered[5g] examples have been reported. Larger cycles and systems containing an asymmetric element are, however, notable by their absence. The non-appearance of such species, coupled with our longstanding interest in P-containing macrocycles[4a,b,d,6] and chirality in coordination compounds,[7] prompted us to investigate the fundamental coomplexation chemistry of selected PS_2 derivatives. Our initial focus was the design and synthesis of inherently chiral phosphadithiamacrocycles derived from diazadithia macrocycles. The rationale behind this choice was the perceived accessibility of N_2S_2 macrocycles with secondary amines that could be reacted with electrophilic phosphine species to generate the desired PS_2 macrocycles. This paper highlights our initial foray in the area and presents the synthesis of novel, asymmetric 14-membered N_2S_2 and 30-membered N_4S_4 macrocycles with secondary nitrogens their subsequent reaction with electrophilic phosphorus reagents. The parent macrocycles have also been used in the synthesis of amidinium salts which are potential precursors to cyclic $C^{NHC}S_2$ ligands.

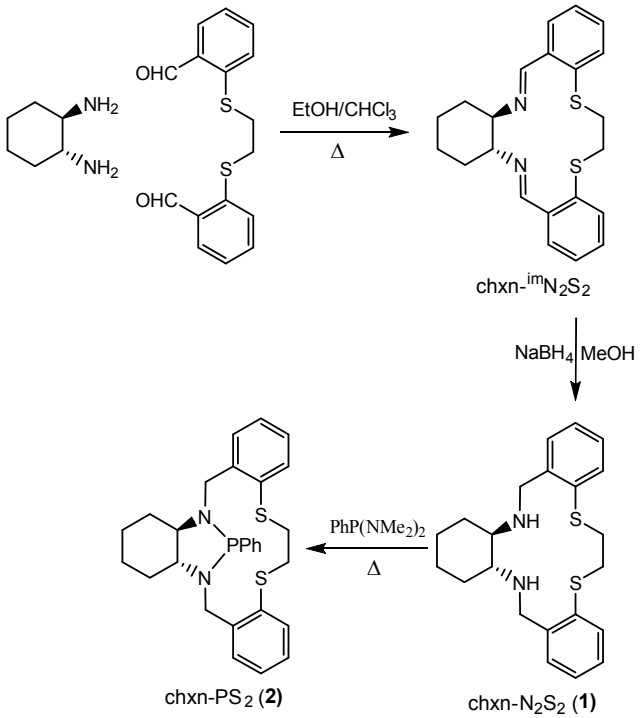
Results and Discussion

Synthesis of chxn-S_2P (2) and attempted preparation of tmcp-S_4P_2 (4)

Our strategy for the preparation of asymmetric PS_2 macrocycles required the initial synthesis of N_2S_2 macrocycles containing appropriately positioned secondary amines that could be reacted with a dichloroarylphosphine, or related phosphorus precursor, to generate the desired cyclic PS_2 ligand(s). The most obvious means for introducing the asymmetric element was through the use of a chiral diamine and, given our previous experience with both 1*R*,2*R*-diaminocyclohexane (*R*,*R*-chxn) and 1,2,2-trimethyl-1*R*,3*S*-diaminocyclopentane (tmcp), these were chosen as the N_2 units. The differing nature of the two diamines was also advantageous as it presented an opportunity to explore cyclic N_2S_2, and ultimately PS_2 macrocycles, of inherently different ring sizes.

The synthesis of the diimine precursor chxn-$^{im}N_2S_2$ was achieved through the condensation of *R*,*R*-chxn with 2,2'-(ethane-1,2-diyldisulfanediyl)dibenzaldehyde under semi-high dilution conditions in a mixed solvent of chloroform and ethanol as shown

in scheme 1. The solid isolated after work-up showed a singlet for the N=C*H* hydrogens at 8.74 ppm in the ^{1}H NMR spectrum, in addition to three signals for the aromatic protons, two for the non-equivalent geminal benzylic hydrogens and multiplets for the remaining hydrogens. The simplicity of the ^{1}H NMR spectrum indicated the formation of a single product which was confirmed by mass spectrometry to be the [1+1] cyclo-condensation compound chxn-$^{im}N_2S_2$ (scheme 1). The isolation of one product in high yield under the moderate dilution conditions employed was pleasing as the flexible CH_2CH_2 bridge of the dialdehyde might have been expected to lead to some non-cyclic and/or larger cyclic products. The subsequent reduction of the diimine proceeded cleanly and in high yield to give diamine chxn-N_2S_2, **1**, as a white solid. The compound was isolated as a single isomer as indicated by the simple ^{1}H and ^{13}C{^{1}H} NMR spectra which showed the expected equivalencies for a C_2 symmetric species. These observations were unsurprising as nitrogen inversion was expected to be facile at room temperature.



Scheme 1 Synthesis of chxn-N_2S_2 and chxnPS_2

Efforts to introduce the PPh unit through the reaction of the **1** with $PPhCl_2$ with various solvent/base combinations were unanimous failures. In all cases highly complex ^{31}P{^{1}H} NMR spectra were observed for the reaction mixtures and the residues after work-up were completely intractable. However, when the reaction of chxn-N_2S_2, **1**, with $PhP(NMe_2)_2$ in hot mesitylene was monitored by ^{31}P{^{1}H} NMR spectroscopy over 48 hrs, clean conversion of the phosphorus starting material to a single new species was observed and ultimately chxn-S_2P, **2**, was isolated as a white solid. The ^{31}P{^{1}H} NMR spectrum of **2** consists of a singlet at δ_P = 102.7 ppm, a shift that compares with reported values for related compounds.[8] The ^{1}H NMR spectrum (part of which is shown in figure 1) shows all four benzylic hydrogens α- to the nitrogens to be inequivalent as represented by the four resonances at δ_H = 5.01 (dd, $^2J_{H\text{-}H}$ = 11.6, $^3J_{H\text{-}P}$ = 2.1 Hz), 4.92 (t, $^2J_{H\text{-}H}$, $^3J_{H\text{-}P}$ = 12.2 Hz), 4.44 (dd, $^2J_{H\text{-}H}$ = 11.6, $^3J_{H\text{-}P}$ = 19.5 Hz) and 3.98 (dd, $^2J_{H\text{-}H}$ = 12.2, $^3J_{H\text{-}P}$ = 34.5 Hz) ppm. All the remaining hydrogens are also unique emphasising a lack of C_2 symmetry in the ligand. This is not too surprising as, even if the nitrogens assume a planar conformation, the configuration at the phosphorus is tetrahedral and fixed (at least at room temperature) leading to C_1 symmety. However, as noted previously for related systems,[8] it is likely that the nitrogens do not assume strictly planar geometries; the fact that the $^3J_{H\text{-}P}$ coupling constants are 2.1, 12.2, 19.5 and 34.5 Hz may also be indicative of a more distorted C_2N_2P heterocycle than one where both nitrogens are planar. This is supported by the ^{13}C{^{1}H} NMR data where two doublets with $^2J_{C\text{-}P}$ coupling constants of 2.9 and 5.9 Hz are observed for the methine carbons of the cyclohexane ring and two doublets with absolute $^2J_{C\text{-}P}$ values of 25.9 and 20.9 Hz for the N*C*H$_2$ carbons. The magnitude of these couplings implies that the phosphorus lone pair is situated close to the benzylic methylene carbons but is remote from the methine carbons.[9] The small value of the $^3J_{C\text{-}P}$ coupling constants (3.7 and 3.1 Hz) for the cyclohexane carbons supports the assignment of an axial phenyl and an equatorially disposed lone pair at the phosphorus.

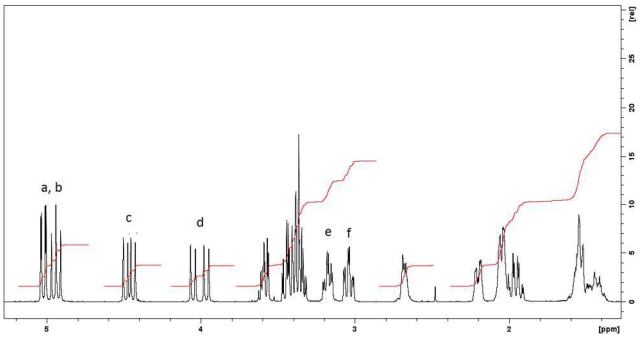
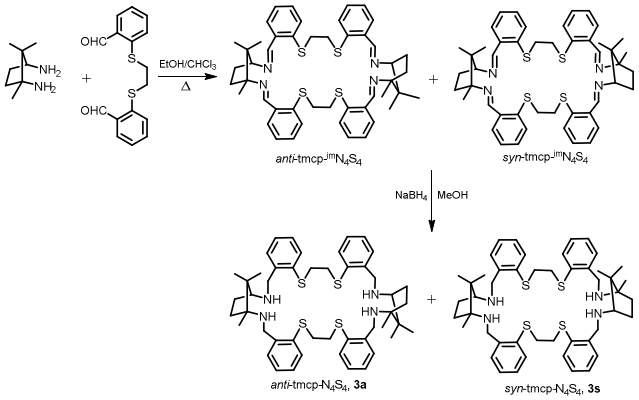


Figure 1 Section of the ^{1}H NMR spectrum of chxnPS_2. The peaks labelled a-d are those of the benzylic hydrogens alpha to the nitrogens and those labelled e,f are the methine hydrogens.

The observation of an apparent single species in solution by NMR spectroscopy invites the conclusion that the synthesis produces only one isomer and that the introduction of the phosphorus unit locks out a single conformer where the stereochemistry at the nitrogens is defined by the stereogenic carbons. In the absence of a crystal structure both the overall geometry and the absolute configuration of the nitrogens are unknown but support for this notion is provided by the structure of the Cu(I) complex discussed below.

Unlike the reaction of the dithiadialdehyde with 1*R*,2*R*-chxn, the product of the cyclo-condensation with 1*R*,3*S*-diamino-1,2,2-trimethylcyclopentane precipitated during the course of the reaction and was isolated by filtration in a yield of 70%. The ^{1}H NMR spectrum of the solid is more complex than that of chxn-N_2S_2, **1**, with four singlets of unequal intensity around 8.85 ppm assignable to N=C*H* hydrogens and six singlets for the methyl groups. This clearly indicates a product mixture that results either from a combination of [1+1] and [2+2] (and possibly higher) species or is an isomeric mixture of a [2+2] (or higher) macrocycle. The mass spectrum of the solid shows a parent ion peak at 817.34 amu that confirms the presence of the [2+2] cyclocondensation product (scheme 2). The isomeric complexity

can be explained by the presence of two isomers, *syn* and *anti* (scheme 2), both of which will have at least two inequivalent imine groups. Reasons for the [2+2] selectivity can only be speculated upon but the fact that the compound precipitates from solution during the reaction must play a part. Condensation reactions are typically equilibria and although the [1+1] product may be formed during the course of the reaction, any equilibria involving [1+1] and [2+2] compounds will be driven towards the latter by virtue of its poor solubility in the reaction medium. The precipitation of the [2+2] product also explains the high yield as a cycloaddition reaction often produces a complex mixture when all reacting species remain in solution.



Scheme 2 Synthesis of *syn*- and *anti*-tmcp-N_4S_4

No attempt was made to isolate the individual isomers of the tetraimine and the mixture was reduced without further purification to give the tetramine tmcp-S_4N_4, **3**, as a 4:1 mixture of *syn* (**3s**) and *anti* (**3a**) isomers (scheme 2). Selective solubilisation of the minor isomer through trituration in EtOH enabled isolation of the major EtOH-insoluble form which was recrystallised further from $CHCl_3$. Unfortunately the resultant crystals were not of sufficient quality for structural assignment through single-crystal X-ray techniques, however, a diamidinium derivative could be structurally characterised and confirmed the major isomer as *syn* (see below). The ^{1}H NMR spectrum of **3s** is less complex than that of the precursor imine with three (albeit broadened) singlets for the methyl groups reflecting an averaged C_2 symmetry for the compound. The peak broadening, which is not limited to the methyl resonances, may result from conformational restrictions dictated by the macrocyclic ring.

Attempts to prepare a phosphorylated ligand akin to **2** were, for the tmcp-N_4S_4 derivative, unsuccessful. When the reaction between the major isomer (or the *syn,anti*-mixture) of **3** and two equivalents of $PPh(NMe_2)_2$ in hot mesitylene was followed by $^{31}P\{^1H\}$ NMR spectroscopy, a small peak at 132 ppm was seen to appear within a few hours, however, the predominant peak was that for $PPh(NMe_2)_2$. Continued heating did not significantly improve the yield of the species resonating at δ_P 132 ppm and after eleven days the spectrum was still dominated by unreacted $PPh(NMe_2)_2$. As these conditions were not conducive to the formation of a phosphorus containing macrocycle, a second approach was attempted. This involved the direct reaction of the tetramine with two equivalents of $PPhCl_2$ in the presence of base. However this gave a mixture by $^{31}P\{^1H\}$ NMR spectroscopy from which nothing proved tractable. Although this was a source of frustration, it is not unprecedented as we have previously had difficulty adding a PPh function to derivatives of 1,2,2-trimethyl-1,3-diaminocyclopentane.

Complexes of chxn-PS_2 (2)

The impetus for the current work stems from a longstanding interest in chiral metal complexes and the factors that influence and/or control stereoselection in coordination compounds.[3] These past studies have focussed on ligands with a predefined source(s) of chirality and kinetically inert metal ions predominantly. The present work represents something of a departure as, although the current ligands do have configurationally rigid stereo-centres, other sources of (potential) asymmetry are not preordained, *i.e.* the pseudo-tetrahedral nitrogens and the pro-chiral sulphur atoms in **2**. It has already been established from the spectroscopic data for **2,** and previous observations on related diazaphosphacycles with a 1*R*,2*R*-chxn framework, that the stereogenic carbon atoms in the hinge of the bicyclic skeleton do influence the stereochemistry at the non-planar nitrogens which in turn influence the disposition of the phosphine phenyl group and lone pair. However, as noted above, the exact nature of the nitrogen geometry could not be determined for the ligand itself. In addition the pro-chiral sulphur centres become stereogenic upon coordination and it was to address these two outstanding issues that complexes of the ligand with Cu(I) and Mo(0) have been prepared and characterised.

The reaction of 1 mole equivalent of **2** with CuI in THF gave, after work-up, the complex [Cu(**2**)I], **4**, as a cream solid. $^{31}P\{^1H\}$ NMR spectroscopic analysis of the solid revealed a single broad peak (width at half-height ~ 150 Hz) at δ_P = 108.6 ppm with a small but typical coordination shift.[10] There is no broadening evident in the ^{1}H NMR spectrum of **4** which is distinguished by the presence of four individual signals for the CH_2 hydrogens alpha to the nitrogen atoms at 5.03 (1H, t, $^2J_{H\text{-}H}$, $^3J_{H\text{-}P}$ = 14.3 Hz), 4.37 (1H, t, $^2J_{H\text{-}H}$, $^3J_{H\text{-}P}$ = 15.8 Hz), 4.08 (1H, dd, $^3J_{H\text{-}P}$ = 22.6 Hz, $^2J_{H\text{-}H}$ =14.3 Hz) and 3.09 (1H, obs) respectively. This highlights a lack of C_2 symmetry already noted for the free ligand and exemplified by the observation of unique resonances for every hydrogen in the complex and a total of 10 aliphatic carbon resonances in the $^{13}C\{^1H\}$ NMR spectrum. The $|^3J_{H\text{-}P}|$ values for the three unobscured NCH_2 hydrogens are 14.3, 15.8 and 22.6 Hz respectively, and the magnitude of the $^2J_{C\text{-}P}$ coupling to the benzylic carbons is 21.9 and 13.3 Hz. As mentioned above, it is known that the magnitude of these coupling constants depends upon the angular relationship between the coupling nuclei. Although there are complications associated with the interpretation of the data for $\sigma^3\lambda^3$ phosphorus compounds, Karplus curves are more reliable for σ^4 compounds.[9] If an approximate Karplus relation for the $^3J_{H\text{-}P}$ couplings is assumed, then none of the dihedral relationships are close to orthogonal. In order to confirm this, and other aspects of the geometry of the coordinated ligand, a single-crystal x-ray determination of the molecular structure of **4** was performed and an Ortep view of the complex is shown in figure 2.

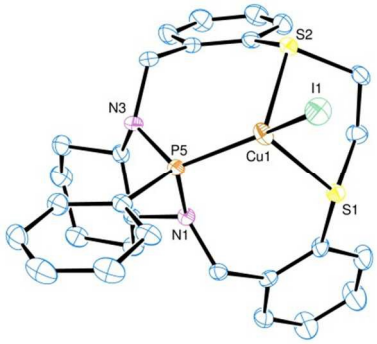


Figure 2 Ortep view of the molecular structure of [Cu(**2**)I], **4**. Hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths (Å) and angles(°): Cu1-P5 2.1729(12); Cu1-S1 2.4990(13); Cu1-S2 2.3563(12); Cu1-I1 2.5396(7); N1-P5-N3 93.20(19); P5-Cu1-S1 103.49(4); P5-Cu1-S2 109.95(5); P5-Cu1-I1 135.65(4); S1-Cu1-S2 90.81(4); S1-Cu1-I1 106.45(4); S2-Cu1-I1 101.61(4).

The compound is an extremely rare example of a structurally characterised Cu(I) complex of a PS_2 macrocycle as highlighted by the fact that only two other examples could be found on the CSD database.[5a,b] The Cu(I) adopts a distorted tetrahedral geometry with a large P-Cu-I angle of 135.65(4)° and an acute S-Cu-S bond angle of 90.79°. The latter value is largely dictated by the five-membered chelate and although expanded L-Cu-I angles are known, for example values of 128.6° and 128.2° are observed in Cu(9aneS$_3$)I[11] and a tetranuclear Cu(I) complex of a tripodal phosphine respectively,[12] the P-Cu-I angle in **4** is unusually obtuse. The two P-Cu-S bond angles are 103.49(4) and 109.95(5)° and the Cu-I and Cu-P bond lengths are unremarkable. The Cu-P and one of the Cu-S bond lengths {2.3563(12) Å} in our 13-membered PS_2 macrocyclic Cu(I) complex compare closely with those of 2.246(3), 2.354(3) and 2.366(4) Å reported by Blower, while the other Cu-S bond is somewhat longer at 2.499 Å. The disparity in the Cu-S bond lengths is partly a consequence of conformational differences in the two seven-membered chelates, with one possessing a pseudo-envelope geometry and the other an asymmetric skew conformation; the Cu-P-N-C torsion angles of 12° and 60° reflect the difference between the two. The five-membered chelate ring has an asymmetric envelope λ conformation and the sulphur atoms have the *R,S* configuration with their remaining lone pair directed away from the macrocycle and towards the iodide. The two aromatic rings and the cyclohexane ring of the macrocycle all project away from the copper so that the molecule has a calix-like appearance.

A further interesting feature of the complex is the heavily distorted nature of the phosphine donor which is partly due to the containment of the phosphorus atom within the five membered diazaphospha ring. The small number of structurally characterised metal complexes of ligands containing the octahydro-1*H*-1,3,2-benzodiazaphosphole framework are of the divalent group 10 metals[8,13] and there are no reports of Cu(I) complexes with such ligands. The acute N-P-N bond angle of 93.2° in **4** is a consequence of the nature of the octahydro-1*H*-1,3,2-benzodiazaphosphole skeleton and compares with similar values noted elsewhere.[8,14] The other intraphosphorus angles are disparate with an N-P-C average of 105.8(2)°, 117.69(15)° for C-P-Cu and values of 119.78(12) and 111.25(14)° for the two N-P-Cu angles. The two nitrogen atoms adopt geometries somewhere between planar and tetrahedral as evidenced by the sum of the angles about each which are 115.17(3)° (Σ_{N3}) and 115.45(3)° (Σ_{N1}) respectively. This distortion orientates the nominal lone pair on each of the nitrogens away from the methine hydrogen of the neighbouring carbon such that the absolute configuration of each nitrogen is *S*; this appears to be common to the few reported structures of octahydro-1*H*-1,3,2-benzodiazaphosphole ligands derived from *R,R*-chxn.[8] The intermediate geometry affects the P-N bonds which are shorter, at 1.693 and 1.696 Å, than typical single bonds reflecting some partial double bond character.[14]

These conclusions are largely in line with those deduced from the NMR analysis of **2**, which supports the notion that the ligand has a pre-arranged conformation that does not change grossly upon coordination. The crystal structure shows the four P-N-C-H dihedral angles involving the benzylic hydrogens to be 32.6, 148.8, 114.6 and 2.6° respectively, which corroborate the earlier spectroscopic deduction that these do not approximate to 90°. This provides evidence that the gross solid-state structure is maintained upon dissolution and is supported by 2D NOESY spectroscopy which shows many of the correlations expected from the contacts seen in the crystal structure of **4**. Other features of the ^{1}H NMR spectrum of Cu(**2**)I, such as the large chemical shift differences for the four unique NCH_2 hydrogens, are understandable as all these hydrogens occupy quite distinct regions of space where shielding/deshielding effects are variable.

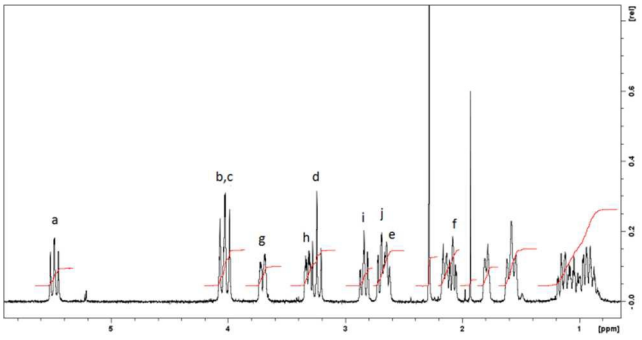
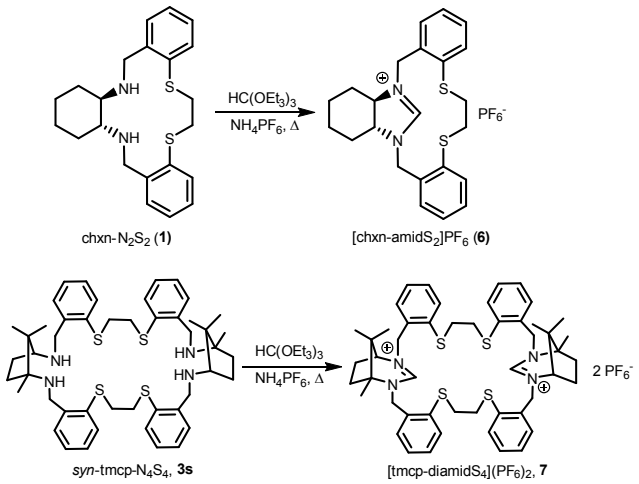


Figure 3 Section of the ^{1}H NMR spectrum of [Mo(CO)$_3$(**2**)], **5**. The peaks labelled a-d are those of the benzylic hydrogens alpha to the nitrogens and those labelled e,f are the methine hydrogens. The g-j resonances are for the hydrogens of the dimethylene bridge between the sulphur atoms.

The coordination chemistry of the few existing examples of PS_2 macrocycles has focussed on Cu(I) and Mo(0) and, for comparative purposes, it seemed appropriate to prepare and characterise the molybdenum complex [Mo(CO)$_3$(**2**)], **5**. The complex is isolated as a buff solid from the 1:1 reaction of **2** with the Mo(0) precursor [Mo(CO)$_3$(MeCN)$_3$]. The ^{31}P{^{1}H} NMR spectrum of **5** consists of a singlet at δ_P = 161 ppm with a coordination shift of 59 ppm. The ^{1}H (a section is shown in fig. 3) and ^{13}C{^{1}H} NMR spectra of **5** compare with those of **4** with separate resonances being observed for every individual hydrogen and carbon as a consequence of the lack of symmetry in the complex. The compound has three IR stretches in the carbonyl region at 1936, 1844 and 1816 cm^{-1} respectively. These are to higher energy than those reported for similar 9- and 10-membered PS_2 macrocycles[5a,e] which is not unexpected given the larger ring size of the current example and are very similar to those of the non-cyclic PS_2 systems studied by Huttner.[15]

Synthesis of [chxn-amidS$_2$]PF$_6$ (6) and [tmcp-diamidS$_4$](PF$_6$)$_2$ (7)

The inability to assign the major and minor isomers of the tmcp-N$_4$S$_4$ macrocycle was a frustration but an indirect method of achieving this was provided through the synthesis and structural analysis of a diamidinium salt derived from **3**. The major isomer of **3** was reacted with triethylorthoformate and ammonium hexafluorophosphate at elevated temperature to yield [tmcp-diamidS$_4$](PF$_6$)$_2$, **7**, as a cream solid in good yield (scheme 3). The ^{1}H NMR spectrum of the solid showed an NC*H*N singlet at 7.87 ppm, which is typical for an amidinium salt derived from this diamine.[7a,b,h] The two sets of inequivalent NC*H*$_2$- hydrogens were observed as two AB doublets at ~4.7 ppm in the ^{1}H NMR spectrum of **7** and the -SCH_2CH_2S- protons appeared as a slightly broadened singlet at 3.18 ppm reflecting coincidental equivalence. Although the isolated solid was undoubtedly a single species, NMR studies alone were not sufficient to enable unequivocal assignment of the absolute nature of the compound. This was achieved through acquisition of the solid-state structure by single-crystal X-ray techniques (Figure 4) which confirms the *syn* geometry for **7** and, by extension, for the major isomer of **3**.



Scheme 3 Synthesis of [chxn-amidS$_2$]PF$_6$, **6**, and [tmcp-diamidS$_4$](PF$_6$)$_2$, **7**.

As precursors to N-heterocyclic carbene (NHC) ligands, amidinium salts derived from both *R*,*R*-chxn and *R*,*S*-tmcp are well represented in the literature7a,b,h,[16] and, as expected, the [chxn-amidS$_2$]PF$_6$ salt, **6**, was prepared in an analogous fashion to **7**. The compound was obtained as an air- and moisture-stable white solid in high yield. This hexahydrobenzimidazolium derivative showed the resonance for the amidinium hydrogen at 9.18 ppm in its ^{1}H NMR spectrum, which accords with the 5-membered nature of the amidinium ring; upfield shifts, such as that noted for **7**, are typical for larger ring amidinium species. As anticipated for a compound with C_2 symmetry, all four NCH_2-hydrogens and the –SCH_2CH_2S- hydrogens are observed as singlets at 4.85 ppm and δ_H = 3.33 ppm, respectively, in the ^{1}H NMR spectrum of **7**. Studies on the coordination chemistry of the NHCs derived from both these amidinium salts are currently ongoing in our laboratories and will be presented in due course.

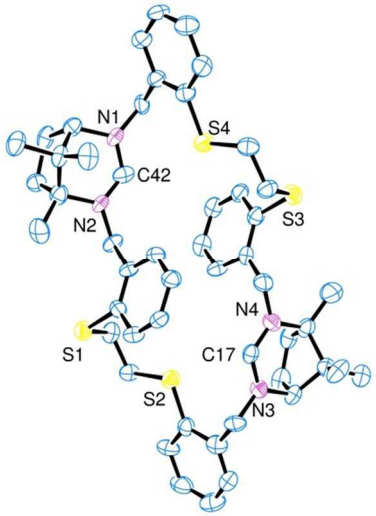


Figure 4 Ortep view of the molecular structure of the *syn*-[tmcp-diamidS$_4$] dication. Hydrogen atoms, counterions and lattice solvent are omitted for clarity. Selected bond lengths (Å) and angles(°): C17-N4 1.307(16); C17-N3 1.304(14); C42-N1 1.314(14); C42-N2 1.304(16); N1-C42-N2 123.4(12); N3-C17-N4 123.8(11).

Conclusions

The cyclocondensation of 1*R*,2*R*-diaminocyclohexane (*R*,*R*-chxn) with 2,2'-(ethane-1,2-diyldisulfanediyl)dibenzaldehyde gave the 1:1 addition product whereas the same procedure using 1*R*,3*S*-diamino-1,7,7-trimethylcyclopentane (*R*,*S*-tmcp) resulted in selective formation of the 2:2 product. The reduction of both imines gave the corresponding amino compounds. The N$_2$S$_2$ macrocycle derived from chxn was further functionalised through reaction of the secondary amines with PPh(NMe$_2$)$_2$ to give a novel 13-membered PS$_2$ macrocycle that has been coordinated to Cu(I) and Mo(0). The phenyl substituent on the phosphorus assumes an axial projection off the C$_2$N$_2$P ring which contains nitrogen centres with a flattened tetrahedral geometry where the absolute configuration (*S*,*S*) is prescribed by the chirality of the adjacent carbons. The sulphur atoms, which become stereocentres upon coordination, have the *R*,*S* configuration in the complexes. Cu(I) complexes are active catalysts for a number of important transformations including hydrosilylation and cyclopropanation. The asymmetric ligand reported here should enable these reactions to be performed stereoselectively and we are currently investigating this in our laboratories. Both cyclic amines were successfully converted into amidinium salts by ring-closure reactions using triethylorthoformate in the presence of ammonium hexafluorophosphate. These are a potential source of cyclic, donor-functionalised NHC ligands which are currently being investigated in our laboratories.

Experimental

All synthetic procedures and manipulations were performed under nitrogen using standard Schlenk line techniques. When necessary, solvents were freshly distilled from sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. All other chemicals were obtained commercially and used as received. The ^{31}P NMR spectra were recorded on a Jeol Eclipse

300 MHz spectrometer operating at 121.7 MHz, and referenced to 85% H_3PO_4 (δ = 0 ppm). ^1H and ^{13}C NMR spectra were obtained using a Bruker Avance 400 or 500 MHz spectrometers or a Jeol Eclipse 300 MHz spectrometer, operating at 100, 125.8, or 75 MHz, respectively, for the ^{13}C spectra and referenced to tetramethylsilane (δ = 0 ppm). Unless stated otherwise, infrared spectra were recorded as nu*J*ol mulls on a *J*asco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by London Metropolitan University.[17]

Syntheses

Chxn-N_2S_2, 1. A solution of 1*R*,2*R*-chxn (0.76 g, 6.62 mmol) in EtOH (50 ml) and 2,2'-(ethane-1,2-diyldisulfanediyl)dibenzaldehyde (2 g, 6.62 mmol) in $CHCl_3$ (50 ml) were added dropwise and simultaneously to EtOH (300 ml) at 50 ºC. After complete addition, which took two hours, the reaction was stirred at 50 °C for a further 12 hrs. After cooling the volatiles were removed in *vacuo* to give the diimine chxn-$^{im}N_2S_2$ as a yellow solid. Yield = quantitative. Mpt = 74-77 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.74 (2H, s), 7.60 (2H, m), 7.38 (2H, m), 7.20 (4H, m), 3.55 (2H, m), 2.77 (4H, m), 1.80 (6H, m), 1.45 (2H, m) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz) δ 161.2 (CH), 140.0 (C), 135.0 (CH), 133.8 (C), 130.2 (CH), 129.3 (CH), 128.4 (CH), 73.8 (CH), 35.0 (CH_2), 33.2 (CH_2), 24.5 (CH_2) ppm. MS (ES) *m/z* (%) ($C_{22}H_{24}N_2S_2$): 380.14 (L^+, 100%). The solid was dissolved in MeOH (300 ml) and treated portionwise with $NaBH_4$ (2.2 equivalents). After stirring overnight, the mixture was acidified with conc. HCl (1 ml), concentrated to small volume, diluted with H_2O (100 ml) and basified to pH >11 with solid NaOH. The mixture was subsequently extracted with CH_2Cl_2 (3 x 40 ml), and the organic phases combined and dried over $MgSO_4$. The $MgSO_4.xH_2O$ was removed by filtration and the volatiles removed in *vacuo* to give a tan solid. Yield = 2.30 g (91%). Mpt = 47-50 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.27 (2H, d, *J* 7.1 Hz), 7.10 (6H, m), 3.80 (2H, d, *J* 11.3 Hz), 3.72 (2H, d, *J* 11.3 Hz), 3.30 (2H, m), 3.11 (2H, m), 2.29 (2H, m), 2.18 (2H, m), 1.70 (2H, m), 1.15 (4H, m) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz) δ 140.9 (C), 133.8 (C), 131.1 (CH), 130.5 (CH), 127.9 (CH), 126.8 (CH), 61.0 (CH), 49.9 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 25.1 (CH_2) ppm. . MS (ES) *m/z* (%) ($C_{22}H_{28}N_2S_2$): 384.17 (L^+, 100%). Anal. Calcd for $C_{22}H_{28}N_2S_2$: C, 68.70; H, 7.34; N, 7.28. Found: C, 68.5; H, 7.4; N, 7.1.

Chxn-PS_2, 2. A solution of **1** (0.24 g, 6.23 x 10^{-4} mol) and $PhP(NEt_2)_2$ (1 equiv) in degassed mesitylene (8 ml) were heated at gentle reflux overnight. After cooling, the volatiles were removed in *vacuo* and the residue triturated with pentane (15 ml). The mixture was filtered and the filtrate concentrated to half volume. After leaving for several days at -25 ºC the desired compound precipitated and was isolated as a cream solid. Yield = 122 mg (40%). Mpt = 125-6 °C (dec.). ^1H NMR (CD_2Cl_2, 400 MHz) δ 7.94 (1H, d, *J* 12.8 Hz), 7.71 (1H, dd, *J* 12.5, 1.0 Hz), 7.65-7.4 (9H, m), 7.30 (1H, dt, *J* 7.5, 1.4 Hz), 7.21 (1H, dt, *J* 7.5, 1.3 Hz), 5.01 (1H, dd, *J* 11.6, 2.1 Hz), 4.92 (1H, t, *J* 12.2 Hz), 4.46 (1H, dd, *J* 19.5, 11.6 Hz), 3.98 (1H, dd, *J* 34.5, 12.2 Hz), 3.56 (1H, m), 3.39 (3H, m), 3.16 (1H, dt, *J* 10.9, 3.5 Hz), 3.03 (1H, dt, *J* 10.9, 3.4 Hz), 2.66 (1H, m), 2.18 (1H, m), 2.01 (3H, m), 1.50 (3H, m) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz) δ 145.8 (C, d, *J* 17.8 Hz), 144.1 (C, d, *J* 2.9 Hz), 141.7 (C, d, *J* 5.8 Hz), 136.1 (C, d, *J* 2.0 Hz), 134.7 (C), 133.2 (CH), 131.9 (CH), 131.7 (CH), 131.1 (CH), 130.3 (CH), 130.1 (CH), 128.2 (CH), 127.9 (CH, d, *J* 18.0 Hz), 127.7 (CH, d, *J* 5.0 Hz), 127.6 (CH), 127.0 (CH), 69.0 (CH, d, *J* 2.9 Hz), 67.4 (CH, d, *J* 5.9 Hz), 53.8 (CH_2, d, *J* 25.9 Hz), 47.1 (CH_2, d, *J* 20.8 Hz), 36.0 (CH_2, d, *J* 3.7 Hz), 34.8 (CH_2, d, *J* 3.1 Hz), 32.3 (CH_2), 29.5 (CH_2), 26.0 (CH_2), 25.4 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 Hz): 102.0 ppm. MS (ES) *m/z* (%) ($C_{28}H_{31}N_2S_2P$): 507.16 ($[L + O + H]^+$, 100%).

tmcp-N_4S_4, 3. This was prepared in a similar manner to that described for **1** except using 1*R*,3*S*-diamino-1,2,2-trimethylcyclopentane (1.90 g, 0.0134 mol) in EtOH (100 ml) and 2,2'-(ethane-1,2-diyldisulfanediyl)dibenzaldehyde (4 g, 0.0134 mol) in $CHCl_3$ (100 ml) added to EtOH (400 ml) at 50 ºC. During the addition a cream precipitate formed which proliferated overnight. After cooling, the precipitate was filtered, washed sparingly with EtOH and air-dried. Yield = 3.75g (69%). Mpt = 247-8 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.88 (s), 8.87 (s), 8.85 (s), 8.83 (s), 8.02 (m), 7.5-7.2 (m), 3.66 (t), 3.05 (m), 2.31 (m), 2.07 (m), 1.80 (m), 1.29 (s), 1.26 (s), 1.05 (s), 1.04 (s), 0.96 (s), 0.91 (s) ppm. MS (ES) *m/z* (%) ($C_{48}H_{56}N_4S_4$): 817.34 ($[L + H]^+$, 100), 409.20 ($[L + 2H]^{2+}$, 42). The solid was dissolved in MeOH/THF (1:4, 300 ml) and treated portionwise with $NaBH_4$ (2.2 equivalents). After stirring overnight, the mixture was acidified with conc. HCl (1 ml) and concentrated to small volume before diluting with H_2O (100 ml) and basifying to pH >11 with solid NaOH. The mixture was extracted with CH_2Cl_2 (3 x 40 ml), dried over $MgSO_4$, filtered and the volatiles removed in *vacuo* to give an isomeric mixture of the desired product as a cream solid. Yield = 3.50 g (93%). The solid mixture was triturated in EtOH (100 ml) for sevveral hours and filtered to obtain the major *syn* isomer which was subsequently recrystallised from $CHCl_3$. Yield = 2.10 g (56%). Mpt = 150-2 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.30 (2H, br), 7.20-7.00 (14H, m), 3.78 (8H, m), 2.85 (10H, m), 1.94 (4H, br), 1.59 (4H, br), 1.10 (6H, s br), 0.92 (6H, s br), 0.86 (6H, s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 134.6 (C), 130.0 (C), 129.5 (CH), 128.8 (CH), 127.7 (CH), 126.5 (CH), 67.4 (CH), 50.4 (C), 48.3 (CH_2), 45.2 (C), 33.0 (CH_2), 32.7 (CH_2), 27.5 (CH_2), 25.3 (CH_3), 19.7 (CH_3), 17.3 (CH_3) ppm. . MS (ES) *m/z* (%)($C_{48}H_{64}N_4S_4$): 825.41 ($[L + H]^+$, 75), 413.21 ($[L + 2H]^{2+}$, 100). Anal. Calcd for $C_{48}H_{64}N_4S_4$: C, 69.85; H, 7.82; N, 6.79. Found: C, 69.9; H, 7.9; N, 6.9.

[Cu(2)I], 4. A solution of ligand **2** (0.10 g, 2.04 x 10^{-4} mol) and CuI (39 mg, 1 equiv) was stirred overnight in THF (5 ml) and the volatiles subsequently removed in *vacuo* to give a cream solid. Air-sensitive colourless crystals were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex. Yield = 68 mg (49%). Mpt = 190-3 °C (dec.). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.74 (2H, m), 7.50 (1H, d, *J* 7.4 Hz), 7.37 (4H, m), 7.22 (1H, d, *J* 7.4 Hz), 7.13 (3H, m), 7.06 (1H, dt, *J* 8.5, 1.0 Hz), 6.96 (1H, dd, *J* 7.5, 1.1 Hz), 5.03 (1H, t, *J* 14.3), 4.37 (1H, t, *J* 15.8), 4.08 (1H, dd, *J* 22.6, 14.3 Hz), 3.72 (2H, m), 3.52 (1H, m), 3.09 (2H, m), 2.70 (1H, m), 2.23 (1H, dd, *J* 12.3, 2.2 Hz), 2.00 (1H, m), 1.81 (1H, m), 1.67 (1H, d, *J* 14.3 Hz), 1.58 (1H, d, *J* 13.4 Hz), 1.29 (2H, m), 0.87 (1H, m), 0.72 (1H, dq, *J* 12.3, 3.2 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.6 MHz) δ 142.0 (C, d, *J* 12.7 Hz),

137.8 (C, d, *J* 9.2 Hz), 135.9-126.7 (3 x C, 11 x CH), 65.1 (CH, d, *J* 4.6 Hz), 63.3 (CH), 49.8 (CH_2, d, *J* 21.9 Hz), 46.3 (CH_2, d, *J* 13.3 Hz), 38.2 (CH_2), 34.8 (CH_2), 30.7 (CH_2, d, *J* 4.6 Hz), 30.1 (CH_2), 24.3 (CH_2), 23.9 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 Hz): 108.6 br ppm. MS (ES) *m/z* (%) ($C_{28}H_{31}N_2S_2PCuI$): 594.12 ($[M - I^- + MeCN]^+$, 30). Anal. Calcd for $C_{28}H_{31}N_2S_2PCuI$: C, 49.38; H, 4.59; N, 4.11. Found: C, 49.0; H, 4.4; N, 4.1.

[Mo(CO)$_3$(2)], 5. To a stirred solution of $Mo(CO)_3(MeCN)_3$ (62 mg, 2.04 x 10^{-4} mol) in CH_2Cl_2 (5 ml) was added a solution of **2** (0.10 g, 2.04 x 10^{-4} mol) in toluene (2 ml). After stirring overnight the volatiles were removed in vacuo to give a brown solid which was successively with pentane then cold toluene to give a buff coloured solid. Yield = 45 mg (32%). A second slightly less pure crop could be obtained from the toluene washings on concentrating and cooling. Yield = 20 mg (14%). Mpt = 222-4 °C (dec.). ^1H NMR ($CDCl_3$, 250 MHz) δ 7.62 (3H, m), 7.45 (1H, d, *J* 7.4 Hz), 7.25 (8H, m), 7.08 (1H, dd, *J* 7.4, 1.7 Hz), 5.50 (1H, dd, *J* 14.8, 12.5 Hz), 4.07 (1H, dd, *J* 14.6, 7.8 Hz), 4.00 (1H, dd, *J* 14.8, 6.4 Hz), 3.69 (1H, dd, *J* 13.9, 3.4 Hz), 3.31 (1H, m obs), 3.24 (1H, t, *J* 14.6 Hz), 2.84 (1H, dt, *J* 11.6, 2.2 Hz), 2.67 (2H, m), 2.10 (2H, m), 1.79 (1H, m), 1.58 (2H, m), 1.02 (4H, m) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ 213.1 (d, *J* = 46 Hz, CO), 201.0 (CO), 143.3 (C, d, *J* 7.2 Hz), 142.3 (C, d, *J* 22.3 Hz), 137.8 (C, d, *J* 9.2 Hz), 137.0-125.2 (3 xC, 11 x CH), 66.7 (CH, d, *J* 5.0 Hz), 62.3 (CH), 48.1 (CH_2, d, *J* 17.1 Hz), 45.0 (CH_2, d, *J* 11.5 Hz), 39.7 (CH_2), 39.3 (CH_2), 30.5 (CH_2), 30.2 (CH_2, d, *J* 3.8 Hz), 24.7 (CH_2), 24.2 (CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.7 Hz): 159.0 ppm. IR (solid): 1936, 1844, 1816 cm^{-1} (C≡O). MS (ES) *m/z* (%) ($C_{31}H_{31}N_2S_2O_3PMo$): 673.07 ($[M + H]^+$, 100). Anal. Calcd for $C_{31}H_{31}N_2S_2O_3PMo$: C, 55.52; H, 4.66; N, 4.18. Found: C, 55.2; H, 4.7; N, 4.2.

[Chxn-amidS$_2$]PF$_6$, 6. A stirred mixture of **1** (1.0 g, 2.60 mmol) and NH_4PF_6 (0.47 g, 1.1 equivs) in triethylorthoformate (30 ml) was heated to 120 °C and kept at this temperature for 1 hr. After cooling, the beige solid was filtered off, washed with Et_2O (3 x 30 ml) and air-dried. Yield = 1.38 g (98%). Mpt = 228-30 °C. ^1H NMR (d6-dmso, 300 MHz) δ 9.18 (1H, s), 7.68 (2H, d, *J* 7.7 Hz), 7.51 (2H, d, *J* 6.6 Hz), 7.41 (2H, t, *J* 6.7 Hz), 7.29 (2H, t, *J* 7.3 Hz), 4.85 (4H, s), 3.33 (4H, s), 3.12 (2H, d, *J* 7.9 Hz), 2.19 (2H, d, *J* 10.8 Hz), 1.64 (2H, d, *J* 8.1 Hz), 1.13 (4H, m) ppm. $^{13}C\{^1H\}$ NMR (d_6-acetonitrile/$CDCl_3$, 125 MHz) δ 162.5 (CH), 137.2 (C), 134.5 (CH), 134.1 (C), 133.9 (CH), 132.2 (CH), 129.5 (CH), 69.1 (CH), 51.7 (CH_2), 37.5 (CH_2), 27.4 (CH_2), 25.0 (CH_2) ppm. . MS (ES) *m/z* (%) ($C_{23}H_{27}N_2S_2PF_6$): 395.16 ($[L]^+$, 100%). Anal. Calcd for $C_{23}H_{27}N_2S_2PF_6$: C, 51.11; H, 5.05; N, 5.18. Found: C, 50.9; H, 5.1; N, 5.2.

[Tmcp-diamidS$_2$](PF$_6$)$_2$, 7. The compound was isolated as a white solid by the method described for **6**. Yield = quantitative. Mpt = 250-2 °C. ^1H NMR (d_6-dmso, 300 MHz) δ 7.87 (2H, s), 7.54 (4H, t, *J* 7.3 Hz), 7.47 (4H, d, *J* 4.1 Hz), 7.45-7.36 (4H, m), 7.30 (4H, t, *J* 7.3 Hz), 4.81 (2H, d, *J* 14.8 Hz), 4.76 (2H, d, *J* 14.8 Hz), 4.70 (2H, d, *J* 14.5 Hz), 4.61 (2H, d, *J* 14.5 Hz), 3.41 (2H, d, *J* 4.6 Hz), 3.18 (8H, s), 2.36 (2H, m), 1.87 (6H, m), 1.27 (6H, s), 1.01 (6H, s), 0.91 (6H, s) ppm. $^{13}C\{^1H\}$ NMR (d_6-dmso, 75.6 MHz) δ 154.4 (CH), 136.6 – 127.1 (12 x aromatics), 71.9 (C), 65.8 (CH), 55.8 (CH_2), 51.4 (CH_2), 33.4 (CH_2), 32.9 (CH_2), 31.5 (CH_2), 21.6 (CH_3), 17.0 (CH_3), 14.5 (CH_3) ppm. . MS (ES) *m/z* (%) ($C_{50}H_{62}N_4S_4.2PF_6$): 991.41 ($[L - PF_6^-]^+$, 70%; 423.18 $[L - 2PF_6^-]^{2+}$, 100%). Anal. Calcd for $C_{50}H_{62}N_4S_4P_2F_{12}$: C, 52.81; H, 5.50; N, 4.93. Found: C, 52.9; H, 5.4; N, 4.8.

Crystallography

Data collection for **7** was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromoated Mo Kα radiation (λ(Mo-Kα) = 0.71073 Å). Data collection and cell refinement were carried out using COLLECT[18] and HKL SCALEPACK.[19] Data reduction was applied using HKL DENZO and SCALEPACK.[20] Absorption corrections were performed using SORTAV.[20] The crystal used for data collection was twinned with no simple relationship between the components. Structure determination was therefore carried out using the major component. Data for **4** were collected on an Agilent SupaNova Dual Atlas diffractometer with a mirror monochromator using Cu (λ = 1.5418 Å) radiation. Both instruments were equipped with Oxford Cryosystems cooling apparatus and data were collected at 150K.

The structures were solved using direct methods (Sir92)[21] and refined with SHELX-97.[22] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were inserted in idealised positions with Uiso set at 1.2 or 1.5 times the Ueq of the parent atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. The details of the data collection and structure solution are collected in Table 1.

Table 1 Details of x-ray crystallographic data collection for the compounds **4**· and **7**.

	4	**7**
Empirical formula	$C_{29}H_{33}Cl_2N_2S_2PCuI$	$C_{50}H_{62}F_{12}P_2N_4S_4$
Formula weight	766.00	1137.21
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	P1
a/Å	9.26190(10)	10.0461(4)
b/Å	17.2697(2)	11.1268(4)
c/Å	19.4857(3)	12.0608(4)
α °		87.564(2)
β °		82.717(2)
γ °		73.014(2)
U/Å^3	3116.74(7)	1278.93(8)
Dx, g cm-3	1.633	1.477
Z	4	1
F(000)	1536	592
θ range/°	3.420 to 73.504	2.420 to 28.691
Index ranges	-7≤h≤11, -20≤k≤21, -16≤l≤23	-13≤h≤13, -14≤k≤14, -16≤l≤16
Reflections collected	8242	9737
Independent reflections	5450	9655
R_{int}	0.0256	0.0115
Data / restraints / parameters	5450 / 105 / 371	9655 / 3 / 656
Goodness of fit on F^2	1.006	1.130
Final *R*1, *wR*2 [*I*>2σ(*I*)]	0.0290, 0.0726	0.0905, 0.2522
(all data)	0.0318, 0.0744	0.1279, 0.2723

Largest difference peak		
And hole/e Å^{-3}	0.859, -0.995	0.679, -0.588
Flack parameter	-0.008(3)	0.078(10)

Notes and references

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† Electronic Supplementary Information (ESI) available: CIF data for both structures is available. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Graphical Abstract

Chiral N_2S_2 and N_4S_4 macrocycles as precursors to mixed phospha/thia macrocycles and cyclic amidinium salts

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The cyclo-condensation of 2,2'-(ethane-1,2-diyldisulfanediyl)dibenzaldehyde with 1*R*,2*R*-diaminocyclohexane (chxn) and 1*R*,3*S*-diamino-1,7,7-trimethylcyclopentane (tmcp) gave the 1:1 and 2:2 addition compounds, respectively. The resultant macrocyclic imines were reduced to the amines and the chxn derivative converted to a novel 13-membered macrocycle, chxn-PS_2. Both macrocyclic amines were further functionalised to cyclic amidinium salts.