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Asymmetric Cationic Phosphines: Synthesis, Coordination Chemistry and Reactivity

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ABSTRACT: A single enantiomer of a cationic phosphine, [α-CgPAmHMe]BF$_4$, containing two asymmetric sub-units, an amidinium group (AmH) and a phosphacycle (CgP), has been synthesised and isolated. The ligand, which is of an extremely rare class, has been coordinated to Rh(I), Au(I), Ag(I), Cu(I) and Pt(0) to enable an empirical assessment of its donor properties. Analysis of the IR stretching frequency of the carbonyl ligand in *trans*-[Rh(α-CgPAmHMe)$_2$(CO)Cl](BF$_4$)$_2$ coupled with metric data obtained from crystal-state molecular structures of pertinent complexes confirms the strong π-accepting properties of the ligand. The integrity of the N-P bond is compromised upon addition of base to both [Cu(α-CgPAmHMe)Cl]BF$_4$ and [Ag(α-CgPAmHMe)(OTf)]BF$_4$ where, instead of isolating anticipated chelating and/or bridging forms of the neutral, deprotonated α-CgPAmMe derivative, decomposition products were obtained containing a phosphacycle fragment and/or amidine ligands. The fragility of the N-P bond is also evident in uncoordinated [α-CgPAmHMe]BF$_4$ as treatment with aqueous base releases a neutral amidine fragment and generates the P-P dimer [α,α-CgPP(O)Cg]. These fortuitous observations show [α-CgPAmHMe]BF$_4$ to be a very useful synthon for the potential production of novel asymmetric phosphines.

INTRODUCTION

The success of metal complexes in homogeneous catalysis relies critically on the nature of the attached ligand(s). Understanding the principles that dictate particular behaviour informs the design of efficient catalysts for a given application. For P-donating ligands the traditional logic is to use net donors (usually PR$_3$ where R = alkyl) when an electron-rich metal centre is necessary and net-acceptors such as phosphites when a process demands electron-deficient metals. Although successful in a number of applications, phosphites are prone to degradation, especially under aggressive reaction conditions, leading to (often catastrophic) loss of catalytic activity. This shortfall can be circumvented if more robust electron-withdrawing ligands or more reactive metal catalysts were available. Cationic phosphines containing positively-charged imidazolinium,[1-6] pyridininium[7] and cyclopropenium[8] substituents attached directly to phosphorus by a C-P bond have emerged as user-friendly phosphite mimics with the potential for improved catalytic activity and/or longevity. Alcarazo and co-workers have been at the forefront of this cationic phosphine revolution through the introduction and application of various mono-,[9,10] di-[10,11-13] and tri-cationic[14] ligands including very recent examples of chiral forms.[15,16]
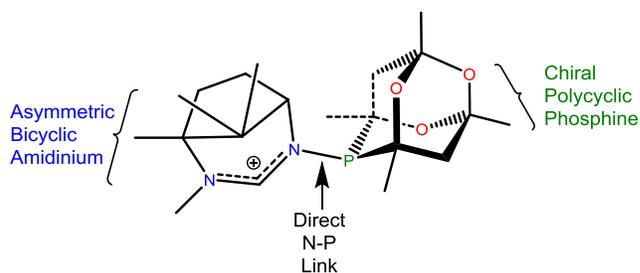

Figure 1. Ligand structure.

Inspired by this elegant work and that of others,[17,18] we sought to combine our interest in polycyclic phosphines and amidinium salts (as precursors to NHCs) to generate cationic phosphines where both constituent units are asymmetric and connected by an N-P bond (figure 1). This is distinct from the reported examples which, without exception, have a C-P bond between the phosphine and cationic organic sub-units. The inclusion of the N-P connection was driven by a desire to see what effect, if any, replacing the established C-P link with an N-P has on the ligand properties. The construction of such ligands requires access to chiral forms of the positively charged organic substituent and the phosphorus-containing component. We[19-24] and Wilhelm[25-27] have already demonstrated the synthetic utility of amidinium species derived from 1,3-diamino-1,2,2-trimethylcyclopentane which made this the obvious candidate for the cationic fragment. The need for a robust, inherently chiral PR$_2$ group capable of supporting a stable N-P bond to the amidinium

led to the selection of 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphatricyclo[3.3.1.1³,⁷]decane or Cagephos (CgP) as it satisfied all of the desired criteria.[28-30] Our preliminary report detailed the synthesis of the ligand as a diastereomeric mixture as our original attempts at resolution were unsuccessful.[31] We have since discovered that, in contrast to slow evaporation at the bench, crystallisation from hot THF under N_2 is a viable route to the isolation of pure [α-CgPAmMe]BF₄ which can be employed as a ligand itself or as a potential precursor to NHC-phosphines. The present paper discusses aspects of the coordination chemistry of the cationic phosphine and attempts at accessing NHC derivatives thereof.

RESULTS AND DISCUSSION

Ligand synthesis
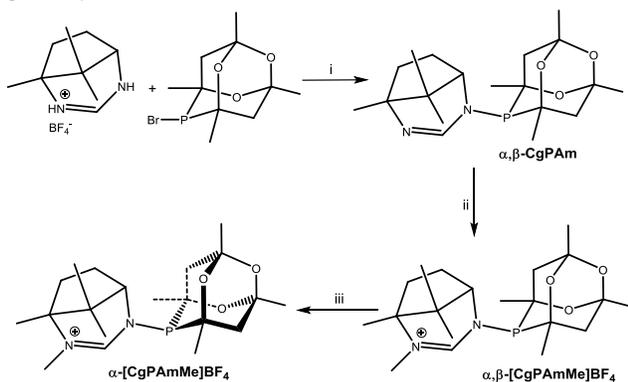
Scheme 1. i) 3K₂CO₃, MeCN, RT; ii) [Me₃O]BF₄, CH₂Cl₂, RT; iii) Hot THF

The [α,β-CgPAmHMe]BF₄ ligand was prepared as previously detailed[31] in an overall yield of 78% by the two-step process shown in scheme 1.[31] Resolution was effected by crystallisation from hot THF under anhydrous O₂-free conditions to give a single isomer of [CgPAmHMe]BF₄. Although these crystals proved unsuitable for structural analysis by single-crystal X-ray techniques, the oxide did crystallize in a form amenable to structure determination (Figure 2). The molecular structure of the oxide confirms the identity of the least soluble diastereomer as α-. In the crystal, the NC*H*N hydrogen is located towards an oxygen of the phosphacycle which may indicate a degree of intramolecular hydrogen bonding (O···C = 3.01 Å). The P1-N1 bond length is somewhat long reflecting little to no π-contribution and the N1-C11 bond is slightly longer than N2-C11 which is a feature common to all the structures reported herein.
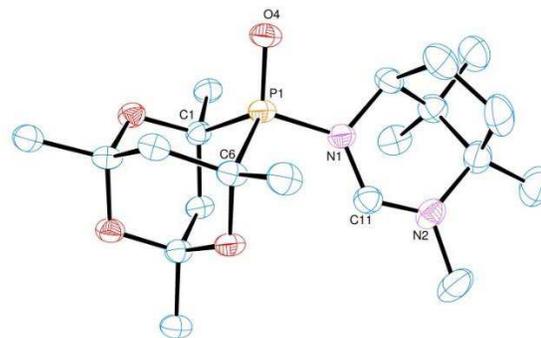
Figure 2. Molecular structure of [α-CgP(O)AmHMe]⁺. The BF₄⁻ anion, hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1-O4 1.474(3); P1–N1 1.716(4); P1–C1 1.823(4); P1–C6 1.827(4); N1–C11 1.343(6); N2–C11 1.292(6); N1–C11-N2 123.5(4); P1–N1-C11 125.0(3); C1–P1–C6 97.98(18); N1–P1–C1 109.28(19); N1–P1–C6 109.17(19); N1-P1-O4 108.31(18).

The ³¹P{¹H} NMR spectrum of [α-CgPAmHMe]BF₄ shows a single peak at 34.9 ppm and the ¹H NMR spectrum is characterized by a single peak for the NCHN hydrogen around 8.5 ppm and a series of singlets and doublets for the methyl groups in the aliphatic region. There is little change in the ¹H NMR spectrum upon oxidation to [α-CgP(O)AmMe]BF₄ other than the observation of a ³$J_{\text{H-P}}$ coupling of 4.3 Hz to the NC*H*N proton and some bunching of the methyl resonances. The oxide shows an upfield shift in the ³¹P{¹H} NMR spectrum of ~7 ppm compared to [α-CgPAmHMe]BF₄.

κ¹-P Coordination Chemistry

A primary driver of the current research was to examine the nature of the coordination of [α-CgPAmHMe]⁺ with particular emphasis on the stability of the N-P link and the effect of complexation on the orientation of the amidinium fragment. This latter point is of import as it influences the stereoelectronic profile of the ligand. A common empirical method for assessing the electronic nature of phosphines is through comparison of carbonyl stretching frequencies in the IR spectra of *trans*-[Rh(L)₂(CO)Cl]⁰,ⁿ⁺ complexes.[32] *Trans*-[Rh(α-CgPAmHMe)₂(CO)Cl](BF₄)₂, **1**, which was prepared as a yellow solid by standard procedures, showed a ν(CO) stretch at 2020 cm⁻¹ which compares with values of 1965, 2016, 2024, 2003 and 2007 cm⁻¹ for the analogous complexes of PPh₃, P(OPh)₃, P(pyrrolyl)₃, 2-(diphenylphosphino)-1,3-dimethylimidazolium and a trans-chelating imidazoliumphosphine ligand.[33-35] This data places the ligand at the strongly π-accepting end of the P-donor range and, whilst accepting that these values can be misleading when a complex is structurally compromised, this is not the case for **1** (Figure 3). The conformity to the square planar ideal is confirmed upon inspection of the structure and associated metrics notably the near-linear Cl-Rh-C and P-Rh-P bond angles of 178.4° and 176.1° and the sum of the angles about the metal which equal 360° with no individual angle more than ±2° from 90°. As expected from the IR data, the Rh-C bond in **1** is relatively long at 1.843(4) Å and both the Rh-Cl and C-O bond lengths are short at 2.3622(10) Å and 1.126(5) Å respectively (cf. 1.824, 2.383 and 1.137 Å for the Rh-C, Rh-Cl and C-O bonds in a similar pyridiniumphosphine complex).[10] The Rh-P bond lengths are comparable

with those to PPh₃, PCy₃ and 2-imidazoliumdiphenylphosphine in similar complexes and intermediate between the two disparate lengths quoted for a related pyridiniumphosphine species.[10] The lack of any significant structural distortion reflects the relatively small steric profile presented by the ligand which is largely a consequence of the 'tied-back' nature of the phosphacycle. The amidinium group is the largest substituent and is the major contributor to the calculated $\%V_{bur}$ of 31.5[36] and cone angle of 153.7⁰ for the complex. These values are comparable to those reported for PPh₃.[32,37-38] The steric impact of the amidinium group does depend on its orientation with respect to the metal and is less when the NC*H*N hydrogen projects towards the metal (as in the Rh complex) than in other orientations (see below).

The ³¹P{¹H} NMR spectrum of *trans*-[Rh(α-CgPAmHMe)₂(CO)Cl](BF₄)₂ shows a doublet at 85.0 ppm with a slightly higher $^1J_{\text{P-Rh}}$ (152.4 Hz) value than that observed for the bidentate imidazoliumphosphine complex of Canac and Chauvin.[35] The carbonyl resonance, seen as a doublet of triplets at 182.7 ppm ($^1J_{\text{C-Rh}}$ = 71.8Hz, $^2J_{\text{C-P}}$ = 15.4 Hz) in the ¹³C{¹H} NMR spectrum, is closely analogous to that for the reported complex. This data combined with the IR data above, confirms [α-CgPAmHMe]⁺ as a strong π-acceptor.

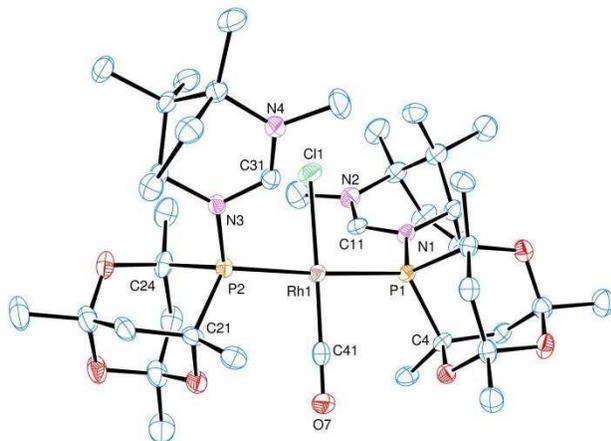**Figure 3.** Molecular structure of [Rh(α-CgPAmHMe)2(CO)Cl]²⁺, **1**. The BF₄⁻ anions, hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-P1 2.3241(11); Rh1-P2 2.3248(11); Rh1-Cl1 2.3622(10); Rh1-C41 1.843(4); C41-O7 1.126(5); P2–N3 1.751(4); P2–C21 1.865(5); P2–C24 1.876(5); N3–C31 1.338(6); N4–C31 1.286(6); P1–Rh1-P2 176.14(4); Cl1–Rh1-C41 178.36(16); P1–Rh1-Cl1 89.12(4); P1–Rh1-C41 91.42(15); P2–Rh1-Cl1 88.10(4); P2–Rh1-C41 91.43(15); N3–C31-N4 124.0(4); P2–N3-C31 115.4(3); C21–P2–C24 94.8(2); N3–P2–C21 106.69(19); N3–P2–C24 108.61(19); N1-P1-O4 108.35(18).

The gold(I) complex [Au(α-CgPAmHMe)Cl]BF₄, **2**, is formed in high yield from the reaction of the ligand with Au(THT)Cl in CH₂Cl₂. The complex was recrystallized as colourless blocks and characterised by single-crystal X-ray diffractometry (Figure 4). The structure is unexceptional, with very similar metrics to those reported for related Au(I) complexes with mono- and di-cationic phosphines.[13] One outstanding feature is the orientation of the amidinium group which assumes a different conformation to that seen in the rhodium complex. In the structure of **2** the NC*H*N hydrogen points away from the metal and towards one of the oxygens of the phosphacycle resulting in an increased $\%V_{bur}$ value of 35.9 (cone angle = 159.1⁰) compared to those of the rhodium complex.

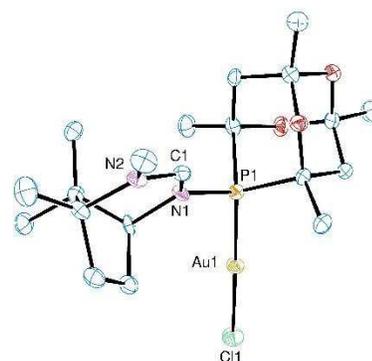**Figure 4.** Molecular structure of [Au(α-CgPAmHMe)Cl]⁺, **2**. The BF₄⁻ anion, hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au1-P1 2.2137(18); Au1-Cl1 2.2704(19); P1–N1 1.724(6); N1–C1 1.332(9); N2–C1 1.300(9); P1–Au1-Cl1 179.18(7); N1–C1-N2 123.1(6).

The ³¹P{¹H} NMR spectrum of **2** shows a singlet at 70.2 ppm, representing a coordination shift of ~35 ppm which is commensurate with that expected for related cationic phosphine complexes of Au(I). The presence of a single signal may indicate a preference for the solid state conformer in solution or, more likely, free rotation about the N-P bond; the observation of a single solution species for **2** would tend to support this. The ¹H and ¹³C{¹H} NMR spectra are unremarkable with the former showing no evidence of a downfield shifted NC*H*N resonance which might be expected if a strong internal hydrogen-bond were present in solution. Efforts to isolate and characterize the bis(ligand) gold species [Au(α-CgPAmHMe)₂]X₃ were universally unsuccessful. Insoluble precipitates predominated that, when encouraged into solution in DMSO, revealed numerous peaks in the ³¹P{¹H} NMR spectrum; this complex was not pursued further as successive attempts proved inconclusive and poorly reproducible.

The synthesis of the Cu(I) analogue to **2** was obtained in a similar manner to give [Cu(α-CgPAmHMe)Cl]BF₄, **3**. The complex showed a broad resonance in its ³¹P{¹H} NMR spectrum at 34.8 ppm (width at half height = 150 Hz) suggesting fluxionality in solution, possibly between the monomeric form and a halide bridged dimer. The MS was inconclusive although the only observable species other than free ligand were at high amu with the nearest formulation being consistent with a dimer (see ESI). The analogous Ag(0) complex containing one coordinated phosphine and a halide proved elusive.

Addition of two equivalents of [α-CgPAmHMe]BF₄ to [Cu(MeCN)₄]BF₄ or AgOTf gave [Cu(α-CgPAmHMe)₂(MeCN)₂](BF₄)₃, **4**, and [Ag(α-CgPAmHMe)₂]OTf.(BF₄)₂, **5**, respectively. The former had a broad singlet at 38.0 ppm in the ³¹P{¹H} NMR spectrum (width at half height = 80 Hz) whereas complex **5** gave a broad doublet at 62.7 ppm with an average $^1J_{\text{P-Ag}}$ coupling constant of 574 Hz. Although the broadening did not allow for accurate

determination of each of the individual couplings to Ag-107 and Ag-109, the fact that a doublet was observed is indicative of relatively slow or precluded ligand exchange. The magnitude of the coupling constant is of the order reported for [Ag(PR$_3$)$_2$]$^+$ complexes but appreciably lower than those for analogous complexes of phosphites.[39] Elemental analyses are consistent with the formulations as given and confirmed by HRMS for **4** and MALDI for **5**.

The strongly electron-withdrawing [α-CgPAmHMe]$^+$ would be expected to compliment low oxidation state metals such as Pt(0). When the ligand was combined with "Pt(dvtms)" (where dvtms is divinyltetramethyldisiloxane) in a 1:1 ratio the complex [Pt(α-CgPAmHMe)(dvtms)]BF$_4$, **6**, was isolated as a white solid. The structure shown in Figure 5 confirms this formulation with a trigonal planar Pt(0) centre supporting the κ^1-P phosphine and the bidentate dvtms ligand. The Pt-P bond length of 2.263Å compares to that of 2.21Å in a similar complex containing a substituted triphenylphosphite[40] and is shorter than the 2.29 Å and 2.384(2) Å reported for the same complex with PPh$_3$[41] and PtBu$_3$[42] respectively. The average Pt-C bond length of 2.17Å compares with those for the reported complexes with the other phosphines and phosphites but are longer than those reported (~2.12Å) for complexes containing strongly donating ligands such as NHCs.
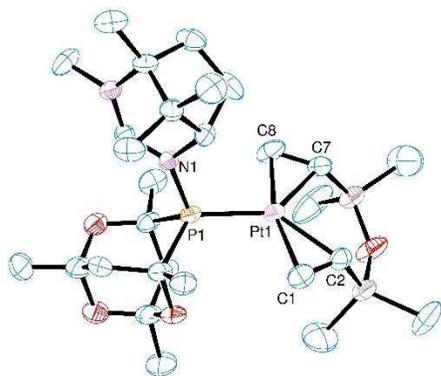

Figure 5. Molecular structure of [Pt(α-CgPAmHMe)(dvtms)]$^+$. The BF$_4^-$ anion and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1-P1 2.263(2); Pt1-C1 2.164(8); Pt1-C2 2.168(8); Pt1-C7 2.166(8); Pt1-C8 2.169(9); P1–N1 1.754(6); P1–Pt1-C1 98.1(3); P1–Pt1-C8 98.2(3).

The ^{31}P{^{1}H} NMR spectrum of **6** shows a singlet at 88.4 ppm with Pt-195 satellites ($^1J_{P-Pt}$ = 4236 Hz). The magnitude of the coupling constant is substantially larger than that reported for a triarylphosphine analogue (3641 Hz) but much lower than those reported for phosphite analogues (> 6300 Hz).[40,41] The ^{1}H NMR spectrum shows all the expected resonances with the NCHN hydrogen appearing as a doublet ($^3J_{H-P}$ = 7.0 Hz) at 8.07 ppm. When a sample of the complex was crystallised from acetone in air, the isolated colourless crystals had spectra quite distinct from those observed for **6**. The ^{31}P{^{1}H} NMR spectrum gave a single broad peak with no discernible Pt-195 satellites and the ^{1}H NMR spectrum had far fewer resonances than expected with no evidence of the bicyclic diaza unit. The nature of the compound was elucidated upon determination of the molecular structure by single-crystal X-ray techniques (Figure 6). Clearly dissolution

of **6** in wet acetone in air has led to hydrolytic degradation of the [α-CgPAmHMe]$^+$ ligands, loss of dvtms and a redistribution so that the platinum now coordinates to three CgPOH ligands. The platinum remains as Pt(0) and retains the expected trigonal planar geometry with an average Pt-P bond length of 2.3448 Å and P-Pt-P angle of 119.81 °. It is obvious that the diaza fragment has been lost and replaced by an OH group on each of the phosphines. The fact that a BF$_4$ molecule is seen in the crystal would suggest that either one of the CgPOH ligands is protonated at the oxygen or that there is HBF$_4$ in the lattice. The oxygen labelled O11 in the figure is in close proximity to the water molecule in the lattice (O$\cdots$O distance 2.997 Å) which may indicate the presence of a hydrogen-bond between these. However, there are also close contacts (2.89 Å) between a fluorine and the oxygen of the water molecule which suggests the same so we are unable to assign unequivocally the proton.
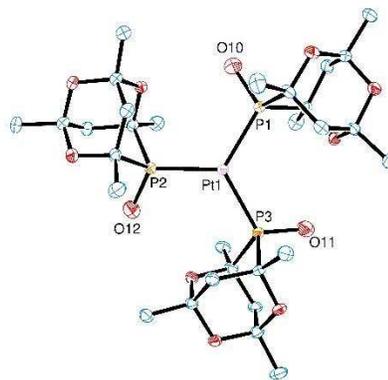
Figure 6. Molecular structure of [Pt(α-CgPOH)$_3$]. The lattice BF$_4$ and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1-P1 2.3411(14); Pt1–P2 2.3468(14); Pt1–P3 2.3466(13); P1–O10 1.658(5); P2–O12 1.667(5); P3–O11 1.662(5); P1–Pt1-P2 119.50(5); P1–Pt1-P3 120.38(5); P2–Pt1–P3 119.56(5).

The observation of hydrolytic P-N bond cleavage is unexpected as the ligands themselves and other metal complexes of [CgPAmHMe]$^+$ are known to be hydrolytically stable.[31] The reasons for the ligand degradation in the current case remain unclear, however, the very observation of N-P breakage does raise questions as to the integrity of the ligand framework. Irrespective of whether the [CgPAmHMe]$^+$ ligand is a single diastereomer or an α,β- mixture, this remains the only example of N-P bond cleavage in a complex of the cationic phosphine observed in our laboratories. While this is a unique observation for the cationic ligand, this apparent integrity does not appear to extend to complexes of the deprotonated form (see below).

Reactions of base with κ^1-P complexes

Part of the remit of the current study was to examine the possibility of generating C,P chelates (or μ-C,P bridges) upon release of the NHC carbon through treatment of the κ^1-P complexes with base. This has not been possible with previous imidazolium phosphines as the NCN carbon is bonded to the phosphorus.[1-16] The in situ ^{31}P{^{1}H} NMR spectrum of a solution of [Ag(α-CgPAmHMe)(OTf)]BF$_4$ in THF after treatment with 1.2 equivalents of KHMDS showed an ex-

tremely broad peak that was barely discernible. After isolation of a solid complex and redissolution, the resultant ^{31}P{^{1}H} NMR spectrum showed a sharp set of doublets at 98.5 ppm ($^1J_{\text{P-Ag}}$ = 481, 416 Hz) and two broad doublets at 64.8 ppm (average $^1J_{\text{P-Ag}}$ = 358 Hz) and 62.2 ppm (average $^1J_{\text{P-Ag}}$ = 359 Hz). Recrystallisation of this mixture by vapour diffusion gave colourless crystals (**8**) which were of sufficient quality for analysis by single-crystal X-ray techniques (Figure 7). It is immediately obvious from the figure that the ligand has fragmented into its phosphacycle and amidine components through scission of the P-N bond. Closer inspection reveals two phosphacycle units connected through an oxygen atom through the formation of a P-O-P link with each P-donor binding a separate silver ion in the dimeric structure. The trigonal planar coordination about each silver ion is completed by an N-bound amidine and a triflate anion (lower part of Figure 7). The lack of any lattice anions reflects the fact that the nitrogen heterocycles are neutral and not cationic. An argentophilic interaction is apparent as the average Ag-Ag distance of 3.177 Å is well within the accepted limit of <3.44 Å (the sum of the van der Waals radii).[43,44] In solution complex **8** gives a broad doublet in the ^{31}P{^{1}H} NMR spectrum at 107.0 ppm with an average $^1J_{\text{P-Ag}}$ of 667 Hz. The ^{1}H NMR spectrum contains all the expected peaks with a singlet at 7.21 ppm for the NC*H*N hydrogen and all peaks assigned to the neutral amidine ligands upfield of those in complexes of [α-CgPAmHMe]$^+$ as expected.

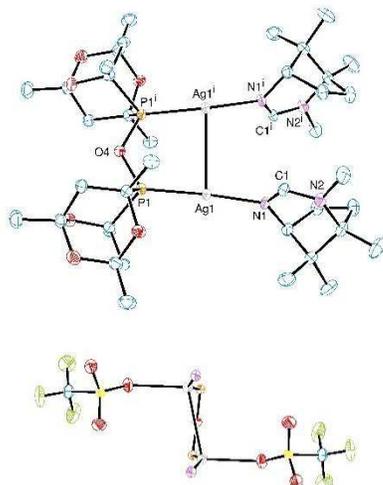**Figure 7.** Molecular structure of [Ag$_2$(α,α-CgPOPCg)(Am)$_2$(OTf)$_2$], **8**. The OTf$^-$ ligands and hydrogen atoms have been omitted for clarity in the top view. The coordination geometry about each silver ion in the bottom view shows only the atoms bound to the metal ions and the OTf$^-$ ligands in full. Selected bond lengths (Å) and angles (°): Ag1-P1 2.3375(13); Ag1-N1 2.120(4); Ag1-Ag1^i 3.0706(6); P1-O4 1.637(3); Ag1-OTf 2.578(8); P1-Ag1-N1 155.31(11); N1-C1-N2 126.2(5).

A simultaneous and contemporaneous reaction to that described for **8** was set up with CuCl to give, after ten days of vapour diffusion with CH$_2$Cl$_2$ / pentane, golden-brown crystals with the molecular structure shown in figure 8. Clearly the original ligand framework has again been disrupted by P-N cleavage releasing the component phosphacycle and amidine fragments. The isolated crystals show

a central Cu$_4$Cl$_6$ adamantyl-type core with an encapsulated oxygen atom sitting in a tetrahedral hole formed by the four Cu(II) ions; this is a relatively common structural motif.[45] The bond lengths and angles in the Cu$_4$Cl$_6$O core are closely analogous to those reported previously.[45,46] The crystal does not contain any lattice anions or cations so the oxidation state of each copper ion is +2 and there is no evidence of the phosphacycle fragment (see later). Each Cu(II) ion is trigonal bipyramidal with the chlorides forming the trigonal plane and the oxide and amidine occupying the axial sites. To our knowledge this is the first reported example of a metal complex of 4,5,8,8-tetramethyl-2,4-diazabicyclo[3.2.1]oct-2-ene.

After isolation of [Cu$_4$(Am)$_4$(μ-Cl)$_6$(O)] the mother liquor was taken to dryness to give a green solid which freely dissolved in toluene. The ^{31}P NMR spectrum of the green solution showed two major peaks at δ$_P$ 49.8 and 29.3 ppm with several minor peaks between 20 and 30 ppm. Attempts to isolate pure material from this solution were unsuccessful but HRMS showed a peak at 857.3776 amu for a species of composition C$_{40}$H$_{68}$O$_8$N$_4$P$_2$Cu which is consistent with the formula [Cu(α,α-CgPOPCg)(Am)$_2$]$^+$ plus an extra oxygen. The MS also shows a peak at 461.16 amu for [(α,α-CgPOPCg) + O − H]$^+$ and 167.16 for [AmH]$^+$ as expected. This suggests reactivity akin to that observed for the Ag(I) complex.
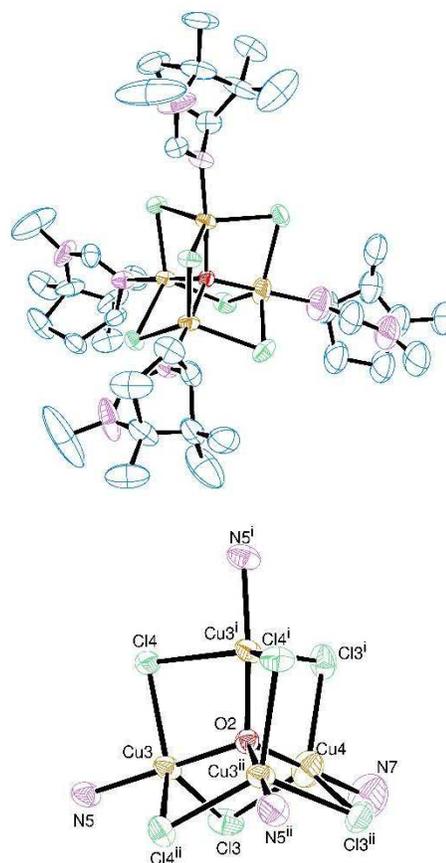
Figure 8. Molecular structure of [Cu$_4$(Am)$_4$(μ-Cl)$_6$(O)] (above) and the coordination core (below). For clarity, the hydrogens and selected atoms at disordered positions atoms have been omitted from the above. All non-Cu bound atoms have been removed in the lower structure. Selected bond lengths (Å) and angles (°): Cu3-O2 1.926(5); Cu4-O2 1.858(14); Cu3-N5

1.975(12); Cu4-N7 1.971(14); Cu3-Cl4 2.360(3), Cu3-Cl3 2.414(5); Cu3-Cl3-Cu4 78.78(15); Cu3-O2-Cu4 109.8(4); N5-Cu3-Cl4 94.7(4); N5-Cu3-Cl3 97.5(4).

Although the vapour diffusion experiments were set-up under nitrogen using dried degassed solvents, it is clear that some adventitious water (and O_2 in the case of copper) must have been present during set-up or had entered the apparatus during the crystallization period which occurred over a period of about ten days. The presence of water is the most likely reason for the cleavage of the P-N bond presumably through catastrophic nucleophilic attack at the P-atom by H_2O. These observations suggest increased fragility of the P-N bond after deprotonation of the amidinium salt (or in the presence of base) as, with the exception of the Pt(0) complex (see above), we have not observed any P-N bond cleavage with [CgPAmHMe]+, whether coordinated or free. In order to assess the susceptibility of the ligand to hydrolysis (and nucleophilic attack more generally), we investigated the reaction of [CgPAmHMe]BF₄ with OH⁻/OD⁻ by ³¹P{¹H} NMR spectroscopy. When a solution of [α-CgPAmHMe]BF₄ in CD₃CN was treated with 0.5 mol equivalents of KOH in D₂O (0.5 M solution) the ³¹P{¹H} NMR spectrum showed, ten minutes after addition of base, two doublets at 41.4 and -20.4 ppm (¹J_{P-P} = 373 Hz) in addition to a residual signal for [α-CgPAmHMe]BF₄ and a resonance at 84.4 ppm for α-CgP(O)H. The doublets are assigned to the P-P bonded dimer [α,α-CgP-P(O)Cg] with the P(V) centre giving the downfield resonance and the P(III) being at -20.4 ppm. When the reaction was performed in d₆-dmso [α-CgP-P(O)Cg] crystallised out from the reaction mixture after several hours of standing. It is noteworthy that both *rac-* and *meso-* forms of [CgP-P(O)Cg] (along with CgP-PCg and CgP(O)-P(O)Cg) have been reported previously by the group of Pringle.[29] The formation of the diphosphine can be explained by initial attack of OH⁻/OD⁻ at [α-CgPAmHMe]BF₄ to cleave the P-N bond releasing CgPOH(D) and the neutral amidine. The CgPOH(D) behaves subsequently as a P-nucleophile and attacks a second [α-CgPAmHMe]BF₄ molecule to generate [α-CgP-P(O)Cg].

The formation of the diphosphoxane in the Ag(I) complex can be explained by the generation of a κ¹-*P* [Ag(CgPOH)]+ species initiated by the ingress of adventitious water. Coordination prevents direct nucleophilic attack of the phosphorus at a second [α-CgPAmHMe]+ (as noted above) but allows O-based attack to generate the observed [α,α-CgPOPCg]. In an effort to deliberately replicate the observations with the Ag(I) complex an NMR experiment was performed whereupon half an equivalent of D₂O was added to a solution of [Ag(α-CgPAmHMe)(OTf)]BF₄ in CD₃CN. The addition of D₂O did not produce any observable change in the ³¹P{¹H} and ¹H NMR spectra and it was concluded that the ligand remained intact under these conditions. The subsequent addition of 0.5 equivalents of KOD gave an immediate dark precipitate but the ³¹P{¹H} and ¹H NMR spectra were unchanged after 30 minutes apart from the loss of the amidinium peak at 8.18 ppm presumably from H/D exchange. Inspection of the solution after 24 hours revealed a significant change in the ³¹P{¹H} NMR spectrum with a broad resonance around 100 ppm dominating. Although no species was isolated from this NMR scale experiment the

similarity between the resonance observed here and that for the isolated complex **8** would appear to support the in situ formation of this complex.

These observations reveal [α-CgPAmHMe]+ to be activated towards nucleophilic attack and while this is a frustration for the potential application of [α-CgPAmHMe]+ as a ligand to support catalysis, it may prove useful as a synthon for the formation of novel asymmetric diphosphines and other derivatives. Thus, the amidinium group acts as a chiral auxiliary for resolution of the α,β-phosphacycle and serves as an activating group for the introduction of various nucleophiles. This may prove to be a viable synthetic protocol and investigations are underway to isolate both [α,α-CgP-P(O)Cg] and [α,α-CgPOPCg] and to explore the production of other asymmetric phosphacycles from [α-CgPAmHMe]BF₄.

Catalytic testing

While the exact nature of the ligand breakdown can only be speculated upon at present, it is patently clear that the P-N link is fragile (especially after deprotonation) and the ligand is unlikely to be sufficiently robust to support any metal-based catalysis involving a base. In order to test such a presumption we undertook some catalysis to assess the performance of the group 11 metal complexes in the asymmetric A³ reaction (AA³, scheme 2). From Table 1 it can be seen that most of the complexes did produce active catalysts for the AA³ reaction (with the unexpected exception of 4-nitrobenzaldehyde) but no enantioselectivity was observed in all cases. This is somewhat surprising as, even if N-P bond cleavage occurred prior to or during the catalysis, the resulting phosphacycle and amidine fragments would retain their inherent chirality and, if one or other or both are still bound to the metal, some stereo-induction would be expected. The observation of racemic products in all cases is therefore, a surprise, and may reflect the presence of active catalytic species that do not contain the original ligand or decomposition fragments therefrom. This information is not available to date and requires further study to confirm or refute. We are continuing to investigate other catalytic processes involving metal ions of both the cationic phosphine and the NHC derivative and will report these in due course.
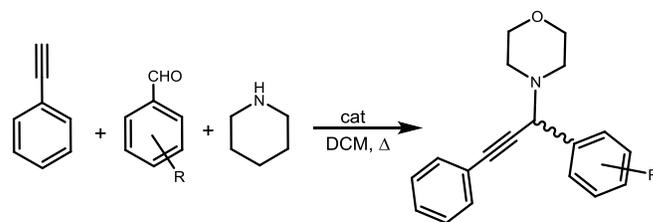
Scheme 2 The asymmetric A³ reaction.

Table 1 Catalytic performance in the AA³ reaction[a]

Complex	Aldehyde	Conversion[b] %	*ee*[c] %
2[d]	C₆H₅CHO	100	0
3	C₆H₅CHO		
4	C₆H₅CHO	80	0

5	C_6H_5CHO	80	0
2[d]	$4\text{-}NO_2C_6H_5CHO$	0	
4	$4\text{-}NO_2C_6H_5CHO$	0	
5	$4\text{-}NO_2C_6H_5CHO$	0	
	$4\text{-}NO_2C_6H_5CHO$	0	
2[d]	$2\text{-}MeOC_6H_5CHO$	81	0
4	$2\text{-}MeOC_6H_5CHO$	75	0
5	$2\text{-}MeOC_6H_5CHO$	45	0
2[d]	$4\text{-}Me_2NC_6H_5CHO$	29	0
4	$4\text{-}Me_2NC_6H_5CHO$	47	0
5	$4\text{-}Me_2NC_6H_5CHO$	5	0
L:Cu[e]	C_6H_5CHO	87	0
3L:Cu[f]	C_6H_5CHO	73	0

[a] CH_2Cl_2, 40 ^0C, 36 hrs; [b] Conversion determined by ^{1}H NMR analysis of the crude reaction mixtures based on benzaldehyde conversion; [c] determined by HPLC analysis using a Phenomonex 5 μm Lux Cellulose-1 (250 x 4.6 mm) column eluted with 95:5 hexane:propan-2-ol at a flow rate of 0.5 ml min^{-1}; [d] with one equivalent of $AgBF_4$; [e] solid catalyst prepared by the addition of one equivalent of [α-CgPAmHMe]BF_4 to [Cu(MeCN)$_4$]BF_4 in CH_2Cl_2 and subsequent removal of volatiles; f solid catalyst prepared by the addition of three equivalents of [α-CgPAmHMe]BF_4 to [Cu(MeCN)$_4$]BF_4 in CH_2Cl_2 and subsequent removal of volatiles.

Conclusion

A single diastereomer of a cationic phosphine has been synthesized through the combination of asymmetric amidinium and phosphacycle fragments and subsequent resolution by recrystallisation. The resultant ligand, as a single isomer, has been coordinated in the κ^1-P mode to a number of metal complexes to allow stereoelectronic profiling. Pertinent empirical data show the ligand to be a powerful π-acceptor, in line with related compounds. Attempts to deprotonate the metal-bound ligands have thus far proved unsuccessful with facile N-P bond cleavage being observed with the Cu(I) and Ag(I) complexes. This would appear to restrict the potential catalytic application of these systems as suggested by an initial exploration of the AA[3] reaction which produced completely racemic products for all the employed complexes. The N-P fragility is an inherent property of the amidinium phosphine which is shown to be susceptible to nucleophilic attack at the P-atom. This surreptitious finding may provide an avenue to a library of novel asymmetric ligands bearing the asymmetric phosphacycle. We are continuing to investigate this possibility and related aspects of ligand integrity and will report our findings in due course.

EXPERIMENTAL SECTION

General considerations. All procedures were carried out under an inert atmosphere (N$_2$) using standard Schlenk line techniques or in an inert atmosphere glovebox (N$_2$). Chemicals were purchased from commercial sources and used without further purification unless otherwise stated.

Solvents were purified using an MBraun solvent purification system except THF and Et_2O which were distilled from potassium and sodium respectively immediately prior to use. NMR spectra were recorded on Bruker Fourier 300, DPX 400 and Avance 500 MHz NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts were referenced relative to the residual solvent resonances in the deuterated solvent. ^{31}P{^{1}H} NMR spectra were referenced relative to 85% H_3PO_4 external standard. Mass spectra (ESI) were recorded on a Waters LCT premier XE spectrometer or, where specified, through the EPSRC UK National Mass Spectrometry Facility at Swansea University. All catalytic samples were analysed by ^{1}H NMR spectroscopy (conversion) and HPLC using a Phenomonex 5 μm Lux Cellulose-1 (250 x 4.6 mm) column eluted with 95:5 hexane:propan-2-ol at a flow rate of 0.5 ml min^{-1} (*ee*).

Synthesis of [α-CgPAmHMe]BF$_4$. A mixture of 1,8,8-trimethyl-4-aza-2-azoniabicyclo[3.2.1]oct-2-ene tetrafluoroborate (1.0 g, 4.2 mmol), α,β-CgPBr[47] (1.24 g, 4.2 mmol) and K_2CO_3 (1.74 g, 12.6 mmol) were stirred in MeCN (20 ml) for 24 hrs. On return, the mixture was filtered and the solvent removed in vacuo to give a cream solid. The solid was dissolved in CH_2Cl_2 (25 ml) whereupon [Me$_3$O]BF$_4$ (0.65 g, 4.40 mmol) was added as a solid and the solution stirred for 30 minutes. The solvent was removed in *vacuo* and the solid residue dissolved in hot THF ($\sim$30 ml) under N$_2$. Upon leaving overnight fine fibrous crystals of [α-CgPAmHMe]BF$_4$ precipitated which were isolated and dried in *vacuo*. Yield = 0.39 g (20%). A second crop (19%) was isolated after leaving the mother liquor at -20 ^{0}C. [31]P{[1]H} (d$_6$-acetone, 145 MHz): 34.9 ppm. [1]H (d$_6$-acetone, 400 MHz): 8.47 (s, 1H), 3.78 (dd, 9.0, 5.3 Hz, 1H), 3.42 (s, 3H), 2.83 (m, 1H), 2.40 (m, 1H), 2.28-1.76 (m, 6H), 1.58 (d, 13.0 Hz, 3H), 1.48 (s, 3H), 1.46 (d, 13.8 Hz, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H) ppm. [13]C{[1]H} (d$_6$-acetone, 100 MHz): 156.7 (CH), 96.5 (C, d, 1.0 Hz), 96.2 (C), 74.9 (C, d, 28.6 Hz), 73.5 (C, d, 16.3 Hz), 71.9 (C), 70.9 (CH, d, 17.6 Hz), 45.1 (CH$_2$, d, 19.7 Hz), 41.8 (C, d, 5.1 Hz), 39.8 (CH$_2$), 39.1 (CH$_3$), 34.8 (CH$_2$), 32.6 (CH$_2$), 26.8 (CH$_3$, d, 22.3 Hz), 26.8 (CH$_3$), 26.4 (CH$_3$, d, 1.1 Hz), 24.9 (CH$_3$, d, 10.1 Hz), 21.0 (CH$_3$), 17.0 (CH$_3$), 13.2 (CH$_3$) ppm. HRMS (ES): m/z 381.2316 (calc. 381.2307) [L]$^+$, 100%. Anal: Calc. for $C_{20}H_{34}N_2O_3PBF_4$: C, 51.30; H, 7.32; N, 5.98%. Found: C, 51.4; H, 7.3; N, 6.1%.

Synthesis of [α-CgP(O)AmHMe]BF$_4$. A solution of [α-CgPAmHMe]BF$_4$ (30 mg) in MeCN was heated close to boiling in air and left to cool. After several days at RT on the bench crystals of the oxide formed which were isolated by filtration. Yield = 20 mg (64%). [31]P{[1]H} (CDCl$_3$, 145 MHz): 28.0 ppm. [1]H (CDCl$_3$, 400 MHz): 8.35 (d, 4.3 Hz, 1H), 4.01 (t, 5.0 Hz, 1H), 3.38 (s, 3H), 2.69 (m, 1H), 2.59 (dd, 13.9, 1.9 Hz, 1H), 2.45 (dd, 15.0, 2.0 Hz, 1H), 2.28 (m, 1H), 2.18-1.92 (m, 4H), 1.45 (s, 3H), 1.40 (s, 3H), 1.36 (d, 7.0 Hz, 3H), 1.34 (d, 13.4 Hz, 3H), 1.15 (s, 3H), 1.14 (s, 3H) ppm. [13]C{[1]H} (CDCl$_3$, 100 MHz): 153.4 (CH, d, 5.6 Hz), 96.4 (C, d, 2.6 Hz), 95.7 (C, d, 2.7 Hz), 73.6 (C, d, 22.2 Hz), 73.1 (C, d, 14.9 Hz), 72.6 (C), 64.2 (CH), 42.2 (CH$_2$, d, 2.7 Hz), 41.2 (C, d, 3.8 Hz), 40.4 (CH$_2$, d, 2.7 Hz), 39.5 (CH$_3$), 38.7 (CH$_2$), 32.3 (CH$_2$), 25.8 (CH$_3$), 25.4 (CH$_3$), 21.1 (CH$_3$), 19.0 (CH$_3$), 18.7 (CH$_3$, d, 2.2 Hz), 16.5 (CH$_3$), 12.8 (CH$_3$) ppm. HRMS (ES): m/z 397.2258 (calc. 397.2256) [L]$^+$, 100%. Anal: Calc. for $C_{20}H_{34}N_2O_4PBF_4$: C, 49.60; H, 7.08; N, 5.79%. Found: C, 49.8; H, 7.0; N, 5.8%.

Synthesis of *trans*-[Rh(α-CgPAm-HMe)$_2$(CO)Cl](BF$_4$)$_2$.CH$_2$Cl$_2$. To a stirred solution of [Rh(CO)Cl]$_2$ (20 mg, 6.0 x 10^{-5} mol) in CH$_2$Cl$_2$ (3 ml) was added, as a solid, [α-CgPAmHMe]BF$_4$ (56 mg, 1.2 x 10^{-4} mol) and the yellow solution left to stir for 2 hrs. The volatiles were removed in *vacuo* and the resultant solid crystallised from CH$_2$Cl$_2$/Et$_2$O in air as fine orange-yellow crystals. Yield = 70 mg (92%). ^{31}P{^{1}H} (CDCl$_3$, 145 MHz): 85.0 (d, $^1J_{\text{P-Rh}}$ 152.3 Hz) ppm. ^{1}H (CDCl$_3$, 400 MHz): 8.80 (t, 3.2 Hz, 1H), 4.49 (br, 1H), 3.48 (dt, 14.8, 3.3 Hz, 1H), 3.32 (s, 3H), 2.89 (m, 1H), 2.40 (m, 1H), 2.32-1.84 (m, 6H), 1.74 (m, 2 x 3H), 1.51 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H), 1.17 (s, 3H) ppm. ^{13}C{^{1}H} (CDCl$_3$, 100 MHz): 182.8 (CO, dt, 71.8, 15.2 Hz), 162.9 (CH, t, 14.5 Hz), 97.5 (C, d, 1.0 Hz), 95.9 (C), 79.3 (C, t, 5.6 Hz), 74.3 (C, t, 11.9 Hz), 72.4 (C), 65.4 (CH), 47.0 (CH2, t, 7.2 Hz), 43.0 (C), 39.4 (CH$_2$), 38.8 (CH$_3$), 34.2 (CH$_2$), 27.7 (CH$_2$), 26.4 (CH$_3$), 26.2 (CH$_3$), 25.9 (CH$_3$, t, 4.2 Hz), 23.0 (CH$_3$), 17.8 (CH$_3$), 13.9 (CH$_3$) ppm. HRMS (ES): m/z 1014.3325 (calc. 1014.3372) [M + BF$_4$$^-$]$^+$, 100%. Anal: Calc. for C$_{41}$H$_{68}$N$_4$O$_7$P$_2$ClRhB$_2$F$_8$.CH$_2$Cl$_2$: C, 42.47; H, 5.94; N, 4.71%. Found: C, 42.1; H, 6.2; N, 4.7%.

Synthesis of [Au(α-CgPAmHMe)Cl]BF$_4$.CH$_2$Cl$_2$. To a stirred solution of [Au(THT)Cl] (40 mg, 1.25 x 10^{-4} mol) in CH$_2$Cl$_2$ (4 ml) was added, as a solid, [α-CgPAmHMe]BF$_4$ (58 mg, 1.25 x 10^{-4} mol) and the resultant solution left to stir for 2 hrs. The volatiles were removed in *vacuo* and the resultant solid crystallised from CH$_2$Cl$_2$ upon slow evaporation in air. Yield = 70 mg (80%). ^{31}P{^{1}H} (d$_6$-acetone, 145 MHz): 70.2 ppm. ^{1}H (d$_6$-acetone, 400 MHz): 8.51 (d, 3.3 Hz, 1H), 4.29 (dd, 9.4, 4.4 Hz, 1H), 3.39 (s, 3H), 2.81 (m, 1H), 2.65 (ddd, 14.5, 6.6, 1.1 Hz, 1H), 2.40-1.88 (m, 6H), 1.65 (d, 16.0, 3H), 1.47 (d, 17.2 Hz, 3H), 1.39 (obs, 6H), 1.31 (s, 3H), 1.21 (s, 3H), 1.18 (s, 3H) ppm. ^{13}C{^{1}H} (d$_6$-acetone, 100 MHz): 155.5 (CH), 97.3 (C, d, 1.9 Hz), 96.9 (C), 76.5 (C, d, 23.7 Hz), 75.3 (C, d, 32.7 Hz), 74.0 (C), 72.8 (CH, d, 6.4 Hz), 45.5 (CH$_2$, d, 11.8 Hz), 42.6 (C, d, 4.3 Hz), 40.7 (CH$_3$), 39.3 (CH$_2$), 35.3 (CH$_2$), 32.8 (CH$_2$), 26.2 (CH$_3$), 26.1 (CH$_3$), 26.0 (CH$_3$), 23.5 (CH$_3$, d, 3.4 Hz), 20.9 (CH$_3$), 16.9 (CH$_3$), 13.1 (CH$_3$) ppm. HRMS (ES): m/z 613.1636 (calc. 613.1662) [M]$^+$, 100%. Anal: Calc. for C$_{20}$H$_{34}$N$_2$O$_3$PClAuBF$_4$.CH$_2$Cl$_2$: C, 32.11; H, 4.62; N, 3.57%. Found: C, 32.0; H, 4.6; N, 3.5%.

Synthesis of [Cu(α-CgPAmHMe)Cl]BF$_4$.CH$_2$Cl$_2$. To a stirred suspension of CuCl (11 mg, 1.1 x 10^{-4} mol) in CH$_2$Cl$_2$ (4 ml) was added, as a solid, [α-CgPAmHMe]BF$_4$ (50 mg, 1.1 x 10^{-4} mol) and the resultant solution left to stir for 12 hrs. The volatiles were removed in *vacuo* to give the desired compound as a white solid. Yield = quantitative. ^{31}P{^{1}H} (d$_6$-acetone, 145 MHz): 34.8 (major) ppm. ^{1}H (d$_6$-acetone, 400 MHz): 8.48 (s br, 1H), 3.81 (br, 1H), 3.31 (s, 3H), 2.73 (m, 2H), 2.40 (m, 1H), 2.28 (m, 1H), 2.10 (m, 2H), 1.88 (m, 2H), 1.61 (d, 14.6 Hz, 3H), 1.48 (d, 15.6 Hz, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H), 1.16 (s, 3H), 1.12 (s, 3H) ppm. ^{13}C{^{1}H} (d$_6$-acetone, 100 MHz): 155.6 (CH, br), 96.9 (C), 96.7 (C), 75.6 (C, d, 4.4 Hz), 74.1 (C, d, 16.2 Hz), 73.1 (C), 71.9 (CH, br), 44.9 (CH$_2$, d, 14.3 Hz), 42.1 (C, d, 4.5 Hz), 40.2 (CH$_3$), 39.3 (CH$_2$), 34.8 (CH$_2$), 34.1 (CH$_2$), 26.5 (CH$_3$), 26.3 (CH$_3$), 24.2 (CH$_3$, d, 5.8 Hz), 21.8 (CH$_3$), 17.2 (CH$_3$), 13.1 (CH$_3$) ppm. MS (ES): m/z 1093.13 (calc. 1093.35) [2L + 2M + Cl + BF$_4$ + 2MeCN]$^+$, 30%. Anal: Calc. for C$_{20}$H$_{34}$N$_2$O$_3$PClCuBF$_4$.CH$_2$Cl$_2$: C, 38.67; H, 5.56; N, 4.30%. Found: C, 38.7; H, 5.7; N, 4.6%.

Synthesis of [Cu(α-CgPAmHMe)$_2$(CH$_3$CN)$_2$](BF$_4$)$_3$.CH$_2$Cl$_2$. To a stirred solution of [Cu(CH$_3$CN)$_4$]BF$_4$ (25 mg, 8.0 x 10^{-5} mol) in CH$_2$Cl$_2$ (4 ml) was added, as a solid, [α-CgPAmHMe]BF$_4$ (75 mg, 1.6 x 10^{-4} mol) and the resultant solution left to stir for 2 hrs. The volatiles were removed in *vacuo* to give the complex as a white solid. Yield = quantitative. ^{31}P{^{1}H} (CDCl$_3$, 145 MHz): 38.0 ppm. ^{1}H (CDCl$_3$, 400 MHz): 8.19 (d, 3.1 Hz, 1H), 3.63 (t, 6.7 Hz, 1H), 3.26 (s, 3H), 2.70 (m, 1H), 2.24 (s, 6H), 2.20-1.76 (m, 7H), 1.47 (d, 13.8 Hz, 3H), 1.41 (d, 13.8 Hz, 3H), 1.39 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.13 (s, 3H), 1.10 (s, 3H) ppm. ^{13}C{^{1}H} (CDCl$_3$, 100 MHz): 156.7 (CH, d, 5.9 Hz), 118.6 (C), 96.5 (C, d, 3.5 Hz), 75.2 (C, d, 8.8 Hz), 73.8 (C, d, 2.1 Hz), 72.3 (C), 70.1 (CH, d, 12.8 Hz), 45.4 (CH$_2$, d, 16.6 Hz), 41.9 (C, d, 3.8 Hz), 39.7 (CH$_3$), 39.6 (CH$_2$), 35.4 (CH$_2$), 33.0 (CH$_2$), 27.2 (CH$_3$), 26.9 (CH$_3$), 26.6 (CH$_3$, d, 17.3 Hz), 24.8 (CH$_3$, d, 7.3 Hz), 21.9 (CH$_3$), 17.5 (CH$_3$), 13.7 (CH$_3$) 2.2 (CH$_3$) ppm. HRMS (ES): m/z 999.3982 (calc. 999.3977) [M – 2MeCN – BF$_4$]$^+$, 100%. Anal: Calc. for C$_{44}$H$_{74}$N$_6$O$_6$P$_2$CuB$_3$F$_{12}$.CH$_2$Cl$_2$: C, 43.10; H, 6.11; N, 6.70%. Found: C, 43.6; H, 6.4; N, 6.7%.

Synthesis of [Ag(α-CgPAmHMe)$_2$](OTf)(BF$_4$)$_2$. To a stirred solution of [Ag(OTf)] (26 mg, 1.0 x 10^{-4} mol) in CH$_2$Cl$_2$ (4 ml) was added, as a solid, [α-CgPAmHMe]BF$_4$ (95 mg, 2.0 x 10^{-4} mol) and the resultant solution left to stir for 2 hrs. The volatiles were removed in *vacuo* to give the complex as a white solid. Yield = quantitative. ^{31}P{^{1}H} (CDCl$_3$, 145 MHz): 62.7 (d br, $^1J_{\text{P-Ag}}$ 574 Hz) ppm. ^{1}H (CDCl$_3$, 400 MHz): 8.29 (s, 1H), 4.22 (d, 4.1 Hz, 1H), 3.26 (s, 3H), 2.85 (m, 1H), 2.76 (d, 14.9 Hz, 1H), 2.27-1.79 (m, 6H), 1.64 (d, 23.7 Hz, 6H), 1.40 (s, 3H), 1.37 (s, 3H), 1.29 (s, 3H), 1.18 (s, 3H), 1.11 (s, 3H) ppm. ^{13}C{^{1}H} (CDCl$_3$, 100 MHz): 161.3 (CH, br), 97.7 (C), 96.1 (C), 77.5 (C), 75.1 (C), 72.1 (C), 66.8 (CH), 46.4 (CH$_2$), 42.2 (C), 39.9 (CH$_3$), 38.9 (CH$_2$), 37.6 (CH$_2$), 33.8 (CH$_2$), 28.5 (CH$_3$), 27.7 (CH$_3$), 26.3 (CH$_3$), 25.1 (CH$_3$), 22.4 (CH$_3$), 17.9 (CH$_3$), 13.9 (CH$_3$) ppm. MALDI: m/z 1043.4 (calc. 1043.37) [M - OTf]$^+$. Anal: Calc. for C$_{40}$H$_{68}$N$_4$O$_9$P$_2$SAgB$_2$F$_{11}$: C, 41.26; H, 5.74; N, 4.69%. Found: C, 41.2; H, 5.9; N, 4.7%.

Synthesis of [Pt(α-CgPAmHMe)(dvtms)]BF$_4$. To a stirred solution of Pt$_2$(dvtms)$_3$ (0.86 x 10^{-4} mol) in THF (4 ml) was added, as a solid, [α-CgPAmHMe]BF$_4$ (80 mg, 1.72 x 10^{-4} mol) and the resultant solution left to stir for 24 hrs. The volatiles were removed in *vacuo* to give a cream coloured solid that was washed with pentane (2 x 4 ml) and dried in vacuo. Yield = quantitative. Crystals suitable for structural analysis by single-crystal X-ray techniques were obtained by slow-diffusion of pentane into a solution of the complex in toluene under N$_2$. ^{31}P{^{1}H} (CD$_2$Cl$_2$ 145 MHz): 88.4 ($^1J_{\text{P-Pt}}$ 4237.5 Hz) ppm. ^{1}H (CD$_2$Cl$_2$, 400 MHz): 8.07 (d, 7.3 Hz, 1H), 4.44 (dd, 5.3, 2.3 Hz, 1H), 3.20 (s, 3H), 3.13 (dd, 12.2, 6.5 Hz, 1H), 2.92 (m, 1H), 2.77 (m, 2H), 2.54 (m, 2H), 2.40-2.00 (m, 6H), 1.83 (m, 1H), 1.63 (d, 15.0 Hz, 3H), 1.47 (d, 13.5 Hz, 3H), 1.38 (s, 3H), 1.30 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.14 (s, 3H), 0.30 (s, 3H), 0.28 (s, 3H), -0.35 (s, 3H), -0.36 (s, 3H) ppm. ^{13}C{^{1}H} (CD$_2$Cl$_2$, 100 MHz): 159.7 (CH, d, 26.6 Hz), 96.6 (C), 96.1 (C), 78.1 (C, d, 11.3 Hz), 73.2 (C), 66.4 (CH, d, 4.1 Hz), 53.6 (CH, d, 11.5 Hz), 53.1 (CH$_2$, d, 5.0 Hz), 52.8 (CH, d, 12.6 Hz), 52.3 (CH, d, 12.7 Hz), 51.0 (CH$_2$, d, 6.2 Hz), 45.4 (CH$_2$, d, 15.0 Hz), 42.2 (C), 39.7 (CH$_3$), 38.6 (CH$_2$), 34.0 (CH$_2$), 27.7 (CH$_3$), 26.9 (CH$_3$), 25.9 (CH$_3$, d, 3.9 Hz), 25.4 (CH$_3$, d, 10.0 Hz), 22.5 (CH$_3$), 18.2 (CH$_3$), 13.8 (CH$_3$), 1.4 (CH$_3$, d, 2.0 Hz), 1.3 (CH$_3$, d, 2.2 Hz), -1.4 (CH$_3$), -1.5 (CH$_3$) ppm.

HRMS (ES): m/z 762.2849 (calc. 762.2851) [M]⁺, 100%. Anal: Calc. for $C_{28}H_{52}N_2O_4PSi_2PtBF_4$: C, 39.56; H, 6.17; N, 3.30%. Found: C, 39.7; H, 6.2; N, 3.2%. During an attempt to recrystallize a sample from acetone in air, colourless crystals were obtained which proved to be [Pt(CgPOH)₃]HBF₄ derived from decomposition of the original ligand and redistribution of the resultant phosphacycle fragments. ³¹P{¹H} (CDCl₃ 162 MHz): 62.3 (br) ppm. ¹H (CD₂Cl₂, 400 MHz): 3.55 (s, 3H), 2.18 (s, 3H), 2.14-2.02 (m, 9H), 1.42 (s, 18H), 1.32 (d, 29.0 Hz, 18H) ppm. MS (ES): m/z 891.29 (calc. 891.22) [M]⁺, 100%.

Synthesis of [Ag₂(α-CgPOPCg)(Am)₂(OTf)₂]. A solution of [Ag(α-CgPAmHMe)(OTf)]BF₄ was prepared in situ by combining 1 equivalent of both Ag(OTf) and [α-CgPAmHMe)]BF₄ (80 mg) in CH₂Cl₂ (4 ml). After stirring for 1 hr, the CH₂Cl₂ was removed in vacuo and the solid residue dissolved in THF (4 ml). Solid KHMDS (1.2 equivs) was added to the stirred solution and the mixture left overnight at RT. On return, the mixture was filtered under N₂, the residue dissolved in CH₂Cl₂ (3 ml), and re-filtered into an apparatus set-up for crystallisation by vapour diffusion. Pentane was added as the precipitating solvent and the apparatus left for 10 days during which time colourless crystals deposited. Yield = 32 mg. The crystals were suitable for structural analysis by single-crystal X-ray techniques ³¹P{¹H} (CDCl₃ 202 MHz): 107.0 (¹J_{P-Ag} 667 Hz) ppm. ¹H (CDCl₃, 500 MHz): 7.21 (s, 2H), 3.20 (s br, 2H), 2.82 (s, 6H), 2.40 (m, 2H), 2.30 (m, 2H), 2.03-1.69 (m, 16H), 1.50 (d, 15.5 Hz, 6H), 1.44 (d, 15.0 Hz, 6H), 1.35 (s, 6H), 1.32 (s, 3H), 1.09 (s, 6H), 100 (s, 6H), 0.97 (s, 6H) ppm. ¹³C{¹H} (CDCl₃, 125 MHz): 157.1 (CH), 96.6 (C), 95.9 (C), 67.8 (C, br), 67.3 (C), 42.6 (CH, br), 40.6 (CH₂), 40.1 (CH₂), 36.1 (CH₃), 34.5 (CH₂), 33.0 (CH₂), 27.6 (CH₃, br), 27.6 (CH₃), 26.7 (CH₃), 25.1 (CH₃, br), 21.9 (CH₃), 17.4 (CH₃), 14.7 (CH₃) ppm. Anal: Calc. for $C_{42}H_{68}N_4O_{13}P_2S_2Ag_2F_6$: C, 39.02; H, 5.30; N, 4.33%. Found: C, 38.7; H, 5.1; N, 4.5%. Unfortunately, despite several attempts, it was not possible to obtain satisfactory MS data for this complex.

Synthesis of [Cu₄(Am)₄(μ-Cl)₆(μ₄-O)]. A solution of [Cu(α-CgPAmHMe)(Cl)]BF₄ was prepared in situ by combining 1 equivalent of both CuCl and [α-CgPAmHMe)]BF4 (80 mg) in CH₂Cl₂ (4 ml). After stirring for 1 hr, the CH₂Cl₂ was removed in *vacuo* and the solid residue dissolved in THF (4 ml). Solid KHMDS (1.2 equivs) was added to the stirred solution and the mixture left overnight at RT. On return, the mixture was filtered under N2, the residue dissolved in CH₂Cl₂ (3 ml), and re-filtered into an apparatus set-up for crystallisation by vapour diffusion. Pentane was added as the precipitating solvent and the apparatus left for 10 days during which time golden-brown crystals deposited. Yield = 25 mg. The crystals were suitable for structural analysis by single-crystal X-ray techniques. Anal: Calc. for $C_{40}H_{72}N_8OCu_4Cl_6$: C, 41.85; H, 6.32; N, 9.76%. Found: C, 41.8; H, 6.2; N, 9.7%. Unfortunately, despite several attempts, it was not possible to obtain satisfactory MS for this complex; only unbound, protonated amidine being observed in all cases at 167.16 amu.

Crystal structure determination. Single-crystal XRD data were collected on an Agilent SupaNova Dual Atlas diffractometer with a mirror monochromator using either Cu (λ = 1.5418 Å) or Mo (λ = 0.7107 Å) radiation. Sample temperature was controlled using an Oxford Cryosystems cooling apparatus. Crystal structures were solved and refined using SHELXS and refined using SHELXL.[48] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealized positions, and a riding model was used with Uiso set at 1.2 or 1.5 times the value of Ueq for the atom to which they are bonded. One of the ligands in [Cu₄(Am)₄(μ-Cl)₆(O)] (Figure 8) shows disorder over the three fold axis and refinement was carried out with constrained geometry and displacement parameters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR, MS and where appropriate IR spectra for all the compounds. Tables of relevant crystallographic data and figures for the compounds (PDF)

Accession codes

CCDC 1558895, 1558896, 1561527, 1845379-1845382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENT

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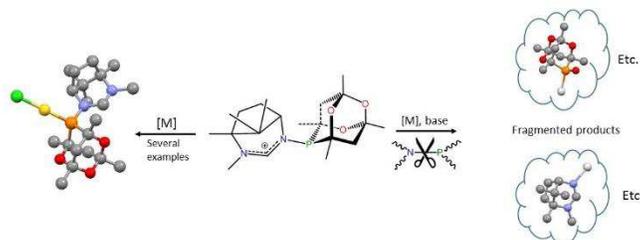
A single enantiomer of a cationic phosphine, [α-CgPAmHMe]BF$_4$ has been synthesised and coordinated to Rh(I), Au(I), Ag(I), Cu(I) and Pt(0). Analysis of pertinent empirical data reveals the ligand to be highly electron-withdrawing due to the cationic amidinium group directly bound to the phosphorus. The N-P bond connecting the amidinium and the phosphacycle is susceptible to attack by nucleophiles (H$_2$O, OH$^-$) when coordinated leading to bond rupture and release of the neutral amidine group. These fortuitous observations suggest that [α-CgPAmHMe]BF$_4$ may be a very useful synthon for the production of novel asymmetric phosphines.

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