Amidine functionalized phosphines: tuneable ligands for transition metals

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Attachment of racemic 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphatricyclo[3.3.1.1^{3,7}]decane (α,β-CgP) to (1*R*,5*S*)-1,8,8-trimethyl-2,4-diazabicyclo[3.2.1]oct-2-ene gave a diastereomeric mixture of a novel amidine-phosphine ligand, α,β-CgPAm. The phosphination was completely selective for the 4-position of the bicyclic amidine and there was no subsequent 1,2-migration of the α,β-CgP group. Methylation of the non-phosphinated nitrogen gave the amidinium salt [α,β-CgPAmMe]BF_4 as a diastereomeric mixture. The donating ability of α,β-CgPAm and [α,β-CgPAmMe]$^+$ has been assessed through the synthesis and characterization of appropriate Rh(I), Au(I) and Pt(II) complexes. As expected α,β-CgPAm is a better net donor than the cationic derivative as shown by the magnitude of the υCO stretches in the IR spectra of the [Rh(L)(CO)(acac)]0/+ complexes and through determination of the relative energies of the HOMO and LUMO orbitals for both ligands by DFT. Attempts to resolve [Au(α,β-CgPAmMe)Cl]BF_4, [Pt(α,β-CgPAmMe)Cl_3], [Rh(α,β-CgPAmMe)(acac)(CO)]BF_4 and [Rh(α,β-CgPAmH)(acac)(CO)]BF_4 by fractional crystallization were unsuccessful as diastereomeric mixtures were obtained in every case; the structures of the last three complexes have been determined by single-crystal X-ray techniques and compared with related literature complexes.

Introduction

Much of the appeal of the highly utilized phosphorus-donating ligands derives from the ease with which their stereoelectronic character can be tuned through appropriate choice of substituent and/or supporting molecular framework. In crude terms, the use of alkyl groups at the P-donor promotes σ-donation but compromises π-acceptance while substituents containing electronegative atoms directly bonded to the phosphorus generate ligands that display the opposite behavior. This simple delineation dictated much of the early application of P-ligands in catalysis with phosphines (particularly trialkylphosphines) being employed when net donors were desired and phosphites when acceptors were necessary. The use of phosphites is often beset with problems of stability,[1] especially under forcing or acidic conditions, and hence more robust surrogates have been sought.

One way to generate electron-deficient phosphines and potentially circumvent the aforementioned stability issues is to use positively charged substituents directly bonded to the P-donor.[2] The positively charged substituents currently employed include cyclopropenium,[3] pyridinium[4] and imidazolinium[2,5] groups and the resultant phosphines can be mono-,[2] di-[2b,6] or tri-cationic[7] depending on the number of these substituents bound to the P atom. As expected, the inclusion of cationic groups at phosphorus generates strongly electrophilic ligands that deplete electron density at the metal center upon coordination enabling enhanced π-activation of electron-rich substrates such as alkynes to enable hitherto unknown or difficult reaction chemistry.[2-7] Alcarazo and coworkers have been at the vanguard of this exciting field and have been responsible for the development of several frameworks, including recent asymmetric examples,[8] showing highly electrophilic character at phosphorus. The electronic character of the ligand need not be pre-set and electron-deficient systems can be derived through alkylation, protonation or binding of Lewis acids to appropriate substituents on the phosphorus atom as identified recently by Hofmann.[9] The reported bidentate systems can be neutral or cationic at the extremes or display additive-dependent chameleonic behavior upon addition of certain (usually Lewis acidic) agents.[9] These examples show that, with appropriate design, an electronically diverse range of ligands can be derived from a single framework through judicious choice of receptor group and activating agent.

Our combined interest in cyclic phosphines[10] and ring-expanded NHC[11] ligands prompted us to explore the possibility of using phosphines with amidine substituents as latent cationic ligands. The elegant work of Alcarazo and others[2-9] has focused on cationic phosphines where the positively charged fragment(s) is usually attached *via* a C–P bond with examples of P-donors containing a cationic nitrogen heterocycle attached by an N–P link being rare in the literature.[12] Such compounds do exist but they have been primarily used as precursors to P-functionalized NHCs[12b-e,13] and the coordination chemistry of the cationic phosphines has not been explored. Furthermore, we have been unable to find a single example of an amidinium substituted phosphine that contains an asymmetric element(s) and chiral cationic phosphines containing an N–P bond are necessarily absent. This is an obvious omission in a burgeoning and exciting research field which we are seeking to address through the development of selected *N*-phosphinated amidines(iniums) and/or tetrahydrodiazepine(iniums) with stereogenic centers. The current paper details our initial foray in the area through the preparation and characterization of a phosphine-amidine hybrid with a polycyclic framework which undergoes ready methylation to generate a cationic amidiniophosphine. Changes in the electronic character induced upon methylation have been assessed through the preparation of a number of pertinent metal complexes of both the neutral and

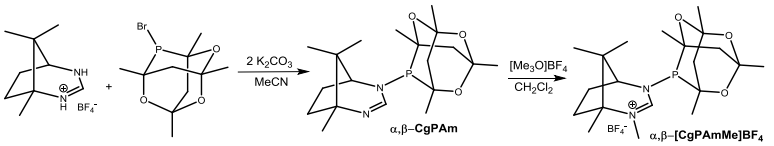
cationic phosphines in concert with DFT calculations.

Results and Discussion

Ligand synthesis and characterisation

Although a number of imidazolium-phosphine compounds are known, they have usually been employed as precursors to the corresponding mixed donor NHC ligands.[13] The reaction of appropriate imidazoles with halophosphines is the usual route to *N*-phosphinated derivatives, however many R_2P fragments tend to undergo a 1,2-migration during synthesis to give the C–P derivative either in the salt or the neutral carbene. This extends to amidines and, although the C-P forms are interesting systems in their own right, we were focused on examining cyclic amidines where the phosphorus group could be introduced and retained at one of the nitrogen atoms. Previous studies on imidazole and tetrahydropyrimid-2-ylidene derivatives showed the P(*t*Bu)$_2$ unit to be resistant to migration,[9,12b-e,14] attributable, in part, to its large steric profile; less bulky phosphines do not appear to be as stable in the N–P form and are susceptible to N → C migration. This information, allied with our longstanding interest in phosphacycles, led us to choose a cyclic mimic of P(*t*Bu)$_2$, namely 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphatricyclo[3.3.1.13,7]decane or Cagephos (α,β-CgP), as our PR_2 moiety. Although substitutionally similar, α,β-CgP is not as strongly donating as P(*t*Bu)$_2$ which is also an advantage for developing electrophilic phosphines. The α,β- prefix refers to the two enantiomeric forms of the phosphacycle which, for the secondary phosphine CgPH, are separable.[15]

There are very few reports of *N*-functionalization of 6-membered amidines/amidiniums with PR_2 groups[12] and none concerning 7-membered rings or asymmetric derivatives. Our previous work on ring-expanded NHCs has concentrated on inherently chiral, fused-ring systems derived from camphoric acid.[11] Thus, we sought to combine this framework with the α,β-CgP unit to access hybrid ligands of the form highlighted above. The synthetic procedure for the preparation of the amidine-Cagephos and amidinium-Cagephos ligands, α,β-CgPAm and [α,β-CgPAmMe]$^+$, is shown in Scheme 1. As indicated, the ligands were acquired as 1:1 diastereomeric mixtures as, although the amidinium salt was a single isomer, the CgPBr was racemic. Our intention was to use the amidinium framework as primary source of asymmetry and as a chiral auxiliary to assist in separation of the diastereomers post-synthesis. The initial phosphination reaction proceeds in high yield from the reaction of the cyclic amidinium salt [AmH$_2$]BF$_4$ with α,β-CgPBr in the presence of potassium carbonate. The differential reactivity of the two distinct nitrogen atoms in the amidine allows complete control over the regioselectivity so that the addition occurs only at the 4-position. The reaction can be followed by ^{31}P NMR spectroscopy which, in the early stages, shows the expected decrease in the intensity of the peak at δ_P ~55 ppm (α,β-CgPBr) with the contemporaneous appearance of two new peaks at ~42 and ~33 ppm. These peaks represent the two diastereomers of the initially formed amidinium phosphine, [α,β-CgPAmH]X. As the reaction continues to completion, the intensity of the α,β-CgPBr and the amidinium phosphine peaks decrease as the desired deprotonated α,β-CgPAm compound is formed; the two diastereomers being observed at 29.0 and 21.5 ppm in the ^{31}P NMR spectrum. As noted there is no diastereoselectivity observed during the addition and α,β-CgPAm is obtained as a cream solid which is a mixture of the two possible isomers. This leads to quite complicated ^{1}H and ^{13}C NMR spectra as every resonance is duplicated in both spectra (see ESI). The lack of N→C migration of the α,β-CgP fragment is confirmed by both the ^{31}P{^{1}H} chemical shift (C-bound derivatives are further upfield) and the observation of the NC*H*N hydrogen in the ^{1}H NMR spectrum. Isolation of the *N*-phosphinated compound indicates that α,β-CgPAm does mimic the behavior observed for the di-(*t*Bu)P group in related imidazole-phosphines.[9,12b-e] Efforts to resolve the diastereomers by crystallization have so far proved unsuccessful.



Scheme 1. Synthesis of α,β-CgPAm and [α,β-CgPAmMe]BF$_4$.

Selective methylation of the amidine nitrogen atom is achieved by the reaction of α,β-CgPAm with trimethyloxonium tetrafluoroborate in dichloromethane. The reaction goes to completion within one hour at room temperature and is easily monitored by ^{31}P NMR spectroscopy as the signals for the neutral phosphines disappear and those for the amidinium species appear at 45.0 and 36.5 ppm respectively. The magnitude of the downfield shift is commensurate with the alkylation of the amidine group with no evidence of competitive methylation at the phosphorus. Recrystallization of the salt from THF by slow evaporation under air gave colorless crystals suitable for structure determination by single-crystal X-ray techniques. The asymmetric unit contains two molecules, one of each of the two diastereomers, with one isomer being shown in Figure 1. The molecular structure of each is as expected with almost exactly equivalent metrics between the two diastereomers. The P–N bond lengths at 1.760(5) and 1.764(5) Å compare with values of 1.796(3), 1.752(4) and 1.766(5) Å quoted by Bertrand for his onio- and dionio-substituted phosphanes coordinated by DBU and DBN.[12a] The N–C6 bond lengths are comparable and lie between the values expected for single and double bonds reflecting conjugation across all three atoms and the N3–C6–N4 angle is typical of amidinium salts with this bicyclic framework.[16] The orientation of the phosphorus lone pair is *trans* to the amidinium NC*H*N hydrogen in both cases and the C–P–C angle in the phosphacycle is compressed to ~94° with wider N–P–C angles of around 104° (sum of angles about P ~ 303°) typical for this phosphacycle.[15]

Interestingly, after isolation the ^{31}P{^{1}H} NMR spectrum of the salt showed the expected two major peaks in a 1:1 ratio and two minor peaks at similar chemical shift to the major peaks. Closer inspection of the ^{31}P{^{1}H} spectrum of the original reaction mixture also revealed the presence of these minor peaks. One possibility is rotameric isomers derived from restricted rotation about the P–N bond with the major species being the two diastereomeric forms present in the solid-state structure and the minor components the alternative structures resulting from a 180° rotation about the N–P bond. DFT calculations suggest that the geometric isomer with the P-lone pair *cis* to the NC*H*N hydrogen is 12 KJ mol^{-1} less stable than that observed in the solid-state, with a barrier to

interconversion of *ca.* 40 kJ mol^{-1} (see ESI). However, there was no NMR evidence of interconversion of the forms upon heating to 80 °C as would be expected for a barrier of this magnitude. Whatever the exact nature of these minor species their removal prior to the preparation of the coordination compounds was not necessary. The ^{1}H NMR spectrum of [α,β-CgPAmMe]BF_4 shows the amidinium hydrogen downfield of its position when compared to the spectrum of the precursor α,β-CgPAm, commensurate with the introduction of a formal positive charge. The *N*-methyl resonances are seen at 3.27 and 3.25 ppm and all the expected shifts are evident in the ^{13}C NMR spectrum (see experimental and ESI).

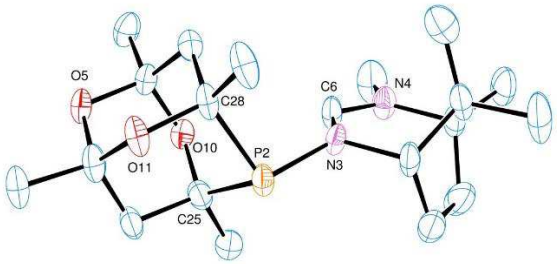


Figure1. Ortep view of the molecular structure of one of the two diastereomers of [α,β-CgPAmMe]BF_4. The second isomer, BF_4^- anion and hydrogen atoms have been omitted for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (º): P2–N3 1.764(5); P2–C25 1.864(6); P2–C28 1.868(7); N3–C6 1.327(8); N4–C6 1.297(8); N3–C6-N4 122.9(5); P2–N3-C6 125.4(4); C25–P2–C28 93.6(3); N3–P2–C25 103.3(3); N3–P2–C28 105.4(3).

DFT calculations on both α,β-CgPAm and [α,β-CgPAmMe]$^+$ reveal the expected trends where both the HOMO and LUMO are lower in energy in the cationic ligand (Figure 2). In both cases the HOMO has a large orbital coefficient on the P atom for the lone pair which has substantial p-character that is most pronounced in the cationic ligand. The relative distribution of the HOMO varies between the two ligands with a greater component on the phosphacycle unit in [α,β-CgPAmMe]$^+$ as opposed to the amidine moiety in the neutral ligand. The LUMOs of both ligands are more closely similar with substantial p-character at P shared across the N-P bond (bonding π-orbital) as well as some delocalization over the Am fragment. The existence of a bonding N-P component in the LUMO suggests that the strength of this link would not be compromised upon occupancy of this orbital. NBO analysis shows that methylation affects hybridisation at P: in CgPAm the orbital make up is $3s^{1.45}$ $3p^{2.49}$, and [CgPAmMe]$^+$ the equivalent values are $3s^{1.51}$ $3p^{2.44}$. Moreover, NBO also indicates that in CgPAm the lone pair on P has 55% s-character, and 45% p, while in [CgPAmMe]$^+$ these values are 60/40%, such that the lone pair in the latter is expected to have slightly more s-character.

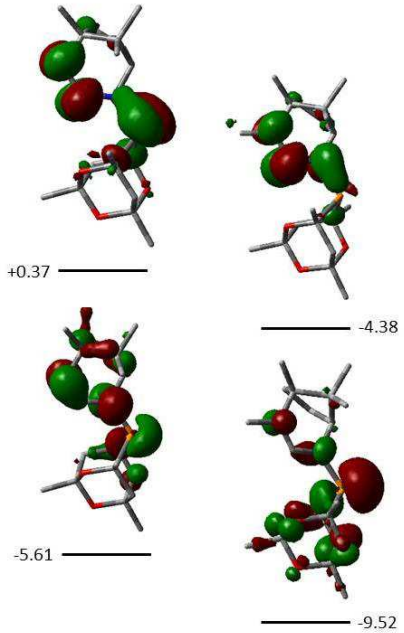


Figure 2. Frontier orbitals with energies in eV for the LUMO (top) and HOMO (bottom) of α,β-CgPAm (left) and [α,β-CgPAmMe]$^+$ (right).

Although stable in air, in the solid-state and in solution at RT, heating solutions of the salt in THF or MeCN under air does lead to P-oxidation. When a solution of [α,β-CgPAmMe]BF_4 in MeCN was heated near boiling for five minutes and then left to stand at RT, crystals were observed to form which proved to be the phosphine oxide derivative [α,β-CgP(O)AmMe]BF_4 (Figure 3). As expected, the P–N bond in the oxide is appreciably shorter at 1.712(4) Å than the value of 1.764(5) Å observed in [α,β-CgPAmMe]BF_4.[17] The P–C bonds are also shorter in the oxide but the C–P–C angle in the phosphacycle is expanded compared to that in the unoxidized form. The P=O bond length is typical and averages 1.475(4) Å. The metrics are closely similar to the imidazolium-P(O)^{t}Bu$_2$ salt of Ogoshi et al[18] with the exception of the N-P bond which is appreciably shorter here at 1.712(4) Å compared to 1.768(5) Å in the reported complex. The strong intramolecular hydrogen-bonding between the phosphoryl oxygen and the NC*H*N hydrogen observed in Ogoshi's compound is not evident in [α,β-CgP(O)AmMe]BF_4 as the hydrogen is directed away from the oxygen atom (Figure 3). Aside from the mild susceptibility to oxidation upon heating in solution, the ligand is robust and does not show any degradation from N-P cleavage upon heating in wet THF, MeCN or MeOH.

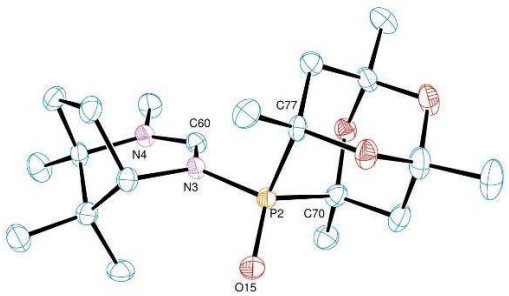


Figure 3. Ortep view of the molecular structure of one of the two diastereomers of [α,β-CgP(O)AmMe]BF_4. The second isomer and the

BF_4^- anions have been omitted for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (º): P2–O15 1.479(4); P2–N3 1.712(4); P2–C70 1.837(5); P2–C77 1.839(5); N3–C60 1.349(7); N4–C60 1.306(7); C70–P2–C77 97.8(2); N3–P2–C70 110.1(3); N3–P2–C77 106.5(2).

Metal complexes of α,β-CgPAm and [α,β-CgPAmMe]$^+$

In order to assess bonding differences between coordinated α,β-CgPAm and [α,β-CgPAmMe]$^+$, we required appropriate reference compounds with one or more spectroscopic handles. Tolman examined the variation in CO stretching frequencies in a series of $Ni(CO)_3(PR_3)$ complexes (derived from highly toxic $Ni(CO)_4$) in his seminal study.[19] More recently, *trans*-$[M(PR_3)_2(CO)Cl]$ complexes have been established as user-friendly alternatives for the assessment of the electronic character of P-donors.[20] However, these latter complexes contain two bound phosphines and are not ideal for our systems as the diastereomeric nature of the ligands will lead to undesirable isomeric complications. To circumvent the formation of overly complex isomeric mixtures but allow useful electronic benchmarking, $[Rh(acac)(L)(CO)]^{0/+}$ complexes were chosen as spectroscopic markers. The 1:1 reaction of α,β-CgPAm with $[Rh(acac)(CO)_2]$ led to the release of CO gas and the formation of a bright yellow solution from which yellow [Rh(α,β-CgPAm)(acac)(CO)] was isolated. The $^{31}P\{^1H\}$ spectrum of the complex consisted of two doublets for the two diastereomers at 85.9 and 84.7 ppm with $^1J_{P\text{-}Rh}$ coupling constants of 199.7 and 202.1 Hz respectively. These values compare with related complexes containing P-donors with two carbon atoms and one nitrogen bound to the phosphorus such as $P(NC_4H_4)Ph_2$ ($^1J_{P\text{-}Rh}$ = 194 Hz).[21] Characteristic features in the ^1H NMR spectrum include the two peaks for the amidine hydrogens around 7.90 ppm, two acac CH resonances at ~5.44 ppm and the hydrogens from the amidine methine groups close to 4 ppm. The CO stretch is observed at 1988 cm^{-1} in the IR spectrum which compares to values of 1978 cm^{-1} for $[Rh(acac)(PPh_3)(CO)]$ and 2006 cm^{-1} for $[Rh(acac)\{P(OPh)_3\}(CO)]$.[21,22]

Substituting α,β-CgPAm for [α,β-CgPAmMe]BF_4 gave [Rh(α,β-CgPAmMe)(acac)(CO)]BF_4 in similar fashion. The $^{31}P\{^1H\}$ NMR spectrum had the two doublets for each diastereomer at 111.9 and 107.3 ppm with $^1J_{P\text{-}Rh}$ values of 206.6 and 208.8 Hz respectively. The increased values of the coupling constants are commensurate with the greater electron-withdrawing ability of [α,β-CgPAmMe]$^+$ compared to α,β-CgPAm. This is further exemplified in the IR spectrum of [Rh(α,β-CgPAmMe)(acac)(CO)]BF_4 where the CO stretch is observed at 2005 cm^{-1}. The solid-state structure of the complex was determined from crystals grown by vapor diffusion of Et_2O into a solution of the complex in CH_2Cl_2 and the molecular structure of one of the two diastereomers present in the unit cell is shown in Figure 4. The metrics accord with those expected when compared with electron-donating phosphines or electron-withdrawing phosphites with a Rh–P bond length of 2.2174(13) Å and a slightly elongated Rh-O_{acac} bond *trans* to the phosphine.[21] The bond angles about the metal are, allowing for constrictions imposed by the chelating acac$^-$, close to the expected 90º. Additionally, there is a slight distortion from linearity (6.3(6)–7.8(6)°) evident in the Rh1–C32–O1 link away from the impacting phosphacycle. The N3–C51–N4 angle of 124.7(5)º is towards the high end for this amidinium scaffold and, unlike in the uncoordinated ligand, the amidinium hydrogen and the P-lone pair (albeit bonded to the Rh) are mutually *cis*.

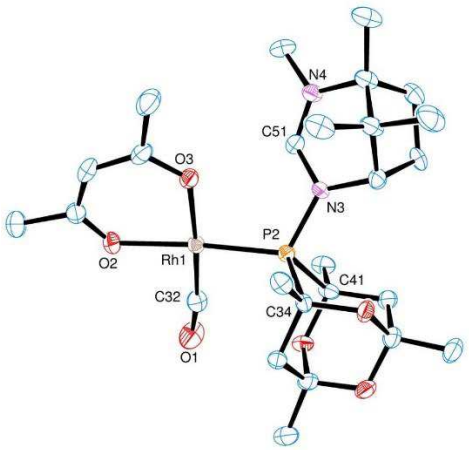


Figure 4. Ortep view of the molecular structure of one of the two diastereomers of [Rh(α,β-CgPAmMe)(acac)(CO)]BF_4. The second isomer, BF_4^- anion, CH_2Cl_2 solvent molecule and hydrogen atoms have been omitted for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (º): Rh1–P2 2.2174(13); Rh1–C32 1.833(6); Rh1–O2 2.053(4); Rh1–O3 2.033(3); P2–N3 1.739(4); P2–C34 1.873(5), P2–C41 1.869(5); N3–C51 1.337(6); N4–C51 1.299(6); C(32)-O(1) 1.134(7); N3–C51–N4 124.7(5); C34–P2–C41 94.4(2); Rh1–P2–N3 113.73(15); P2–Rh1–C32 92.22(17); P2–Rh1–O3 91.37(10); P2–Rh1–O2 174.17(11); Rh1–C32–O1 172.2(5).

Methylation of the amidine nitrogen clearly leads to enhanced electron-withdrawing capability in [α,β-CgPAmMe]$^+$ compared to α,β-CgPAm. However, it remained to be seen what effect, if any, the addition of Lewis acids had on the electronic nature of α,β-CgPAm in [Rh(α,β-CgPAm)(acac)(CO)]. In order to explore how the electronic properties of α,β-CgPAm could be altered without having to formally alkylate to the amidinium species, we examined the solution properties of [Rh(α,β-CgPAm)(acac)(CO)] in the presence of selected Lewis acids. When one equivalent of BCl_3 or $AlCl_3$ were added to [Rh(α,β-CgPAm)(acac)(CO)] a downfield shift was observed in the ^{31}P NMR spectra with two new doublets being observed at 109.0 and 105.1 ppm. Somewhat unexpectedly, the magnitude of the shift and indeed the $^1J_{P\text{-}Rh}$ coupling was equivalent in each case. Removal of the volatiles gave light tan (BCl_3) and yellow ($AlCl_3$) solids respectively with the ^1H NMR spectra of both crude samples being very similar, presenting two broad peaks and two triplets in the aromatic region; inexplicably there were no resonances assignable to the coordinated acac$^-$. Crystallization of the product from the reaction with BCl_3 enabled an understanding of this behavior as shown from the molecular structure in Figure 5.

It is immediately obvious from Figure 5 that the acac$^-$ ligand has been lost and replaced by two chlorides to give an overall zwitterionic structure; the absence of a counterion reflects protonation of the N4 atom to generate the zwitterion. The peaks in the aromatic region of the ^1H NMR spectrum alluded to above can now be assigned as the NH (broad peaks) and NC*H*N (triplets) hydrogens of the two diastereomers of [Rh(α,β-CgPAmH)$(Cl)_2$]. Clearly the influence of the Lewis acid extends beyond simple association to the amidine nitrogen and leads to removal of the acac$^-$ and the introduction of a second chloride ligand. The provenance of the H^+ can only be speculated upon at this stage but the only likely source is the solvent (CH_2Cl_2). This reactivity

remains of interest but is beyond the remit of the current paper and will be addressed in detail in a subsequent publication.

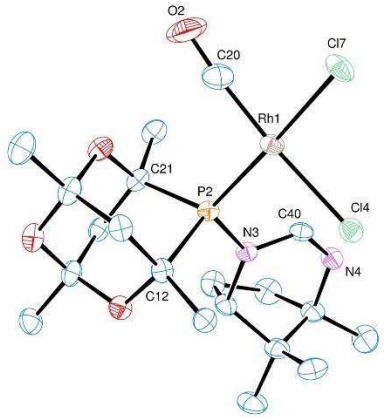


Figure 5. Ortep view of the molecular structure of one of the two diastereomers of [Rh(α,β-CgPAmH)(Cl)$_2$]. The second isomer, residual solvent and hydrogen atoms have been omitted for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (º): Rh1–P2 2.2176(7); Rh1–C20 1.795(5); Rh1–Cl4 2.3839(11); Rh1–Cl7 2.3904(8); P2–N3 1.749(3); P2–C12 1.871(3), P2–C21 1.868(3); N3–C40 1.345(4); N4–C40 1.275(4); N3–C40–N4 122.8(3); C12–P2–C21 93.93(15); Rh1–P2–N3 113.99(9); P2–Rh1–C20 94.12(12); P2–Rh1–Cl4 90.59(3); P2–Rh1–Cl7 174.78(3); Rh1–C20–O2 175.0(3).

The Rh(I) complexes were prepared to allow an initial assessment of the influence of the amidine/amidinium unit on the donating properties of the phosphine. The inability to resolve the diastereomeric mixtures led us to prepare other coordination compounds that might enable this separation. For relevant comparison with reported systems, we sought to prepare Au(I) and Pt(II) complexes of both α,β-CgAmP and [α,β-CgPAmMe]$^+$. [Au(α,β-CgPAm)Cl] was isolated in good yield as a cream solid from the reaction of the ligand with Au(THT)Cl in THF. The ^{31}P{^{1}H} NMR confirmed complexation with coordination shifts (Δδ) of 35.8 and 37.6 ppm for the two diastereomers. The identity of the complex was fully confirmed by ^{1}H, ^{13}C and HRMS as detailed in the ESI. [Au(α,β-CgPAmMe)Cl]BF$_4$ was isolated as a white solid in a similar manner and gave two broad resonances in the ^{31}P{^{1}H} spectrum with coordination shifts of 31.9 and 33.5 ppm and peak half-height widths of 237 and 324 Hz respectively. The origin of the broadening is speculative but is likely a consequence of restricted rotation about the N–P bond. The broadening does not extend to the ^{1}H NMR spectrum where the peaks are largely resolved (see ESI). Attempts to separate the two isomers of either [Au(α,β-CgPAm)Cl] or [Au(α,β-CgPAmMe)Cl]BF$_4$ by crystallization from common organic solvents and solvent mixtures were unsuccessful with only the diastereomeric mixture being acquired on every occasion. Structural analysis for either complex was not possible as the crystals obtained were not of sufficient quality for single-crystal X-ray diffraction.

The reaction of α,β-CgPAm with K$_2$[PtCl$_4$] gave a yellow solid which proved to be largely insoluble in all common solvents precluding full characterization. Fortunately, the similarly prepared [Pt(α,β-CgPAmMe)(Cl)$_3$] complex was more amenable to analysis. Although not freely soluble in most solvents, it was sufficiently soluble in acetone to allow the isolation of yellow crystals suitable for structural determination to enable structural comparison with the limited number of crystallographically characterized complexes bearing cationic phosphines.[2c,4,5] The molecular structure of one of the two diastereomers is shown in Figure 6. The zwitterionic complex has the expected square planar geometry about the Pt center with 90 ± 5° angles (sum of angles about Pt = 359.96°). The Pt–P bond length is typical and compares with those of 2.2122(13) and 2.224(4) Å reported by Alcarazo for related [Pt(PR$_3$)Cl$_3$] complexes containing cationic phosphines.[5] The Pt–Cl bond trans to the P-donor is marginally longer than the other two as expected from the greater *trans* directing effect of the cationic donor again in accordance with the observations of Alcarazo.[4,5] As for the other complexes reported here, the orientation of the amidinium group with respect to the P–M bond is *cis* and there is complementarity between the metrics reported for this complex and the others above. This projection of the NCHN unit towards the other ligands in each of the complexes may reflect a small degree of H-bonding between the NC*H*N hydrogen and one or more of the other ligands bound to the metals but is most likely the least sterically encumbered orientation for the amidinium group. Analysis of the sterics (excluding hydrogens) presented by the [α,β-CgPAmMe]$^+$ ligand using the SambVca 2.0 program[23] gave %V_{bur} values of 33.2, 32.9 and 32.5% for the [Rh(α,β-CgPAmMe)(acac)(CO)]BF$_4$, [Rh(α,β-CgPAmH)(Cl)$_2$] and [Pt(α,β-CgPAmMe)(Cl)$_3$] complexes, respectively. These values are not dissimilar to those for PPh$_3$.[21]

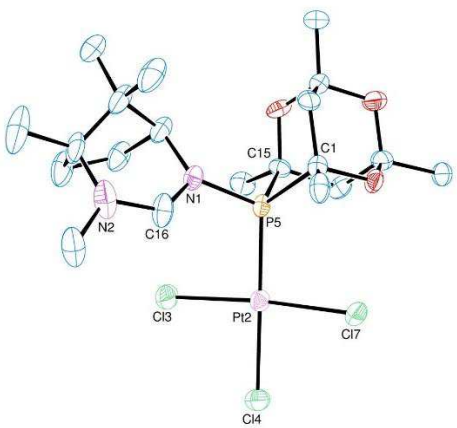


Figure 6. Ortep view of the molecular structure of one of the two diastereomers of [Pt(α,β-CgPAmMe)(Cl)$_3$]. The second isomer, residual solvent and hydrogen atoms have been omitted for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (º): Pt2–P5 2.219(3); Pt2–Cl3 2.309(3); Pt2–Cl4 2.351(3); Pt2–Cl7 2.297(3); P5–N1 1.768(8); P5–C1 1.879(11), P5–C15 1.885(11); N1–C16 1.320(17); N2–C16 1.334(14); N1–C16–N2 124.3(12); C1–P5–C15 95.6(5); Pt2–P5–N1 111.7(3); P5–Pt2–Cl3 91.12(11); P5–Pt2–Cl7 94.40(10); P5–Pt2–Cl4 178.24(11).

The ^{31}P{^{1}H} NMR spectrum of [Pt(α,β-CgPAmMe)(Cl)$_3$] contains two major peaks for each of the two diastereomers with ^{195}Pt ($^1J_{P\text{-}Pt}$ = 4284 and 4334 Hz). These values are appreciably larger than those quoted for related imidazolium-2-phosphine and pyridiniumphosphine complexes of the type [(PRPh$_2$)PtCl$_3$] where values of 3420 and 1953 Hz were reported[4,24] but close to those (3942 Hz) seen with another imidazolium-2-phosphine complex[5] and related complexes of Cagephos derivatives where the phosphine is *trans* to chloride (4101 and 4198 Hz).[25] Aside from the major species in solution, the ^{31}P{^{1}H} spectrum reveals the

presence of two minor species which are believed to be rotameric isomers resulting from restricted rotation about the P–N bond. The ^{1}H NMR spectrum also shows the presence of these minor species. Unfortunately the poor solubility of the complex prevented acquisition of an acceptable ^{13}C NMR spectrum.

DFT calculations on [Pt(α,β-CgPAmMe)(Cl)$_3$] were performed to further explore the behavior of the cationic ligand. Geometry optimization yielded a Pt—P distance of 2.276 Å, in reasonable agreement with experimental data and almost identical to that in [Pt(PPh$_3$)(Cl)$_3$] at the same level of calculation. Natural bond orbital (NBO) analysis indicates a strong Pt—P bond made up of donation of the P lone pair into a hybrid of Pt s, p and d-orbital and back-donation from a filled d-orbital on Pt to empty (predominantly d type) orbitals on P. The latter contribution equates to 35 kcal mol^{-1} which is substantially greater than that of 24 kcal mol^{-1} calculated for [Pt(PPh$_3$)(Cl)$_3$] (see ESI for full details). This data therefore suggests that [α,β-CgPAmMe]$^{+}$ has similar σ-donation to, but is a rather better π-acceptor ligand than, PPh$_3$.

Conclusions

A novel cationic phosphine ligand [α,β-CgPAmMe]$^{+}$ composed of a chiral amidinium substituent and a racemic phosphacycle has been prepared and aspects of its coordination chemistry explored relative to the neutral parent phosphine α,β-CgPAm. IR analysis of the [Rh(L)(acac)(CO)Cl]$^{0,1+}$ complexes together with DFT analysis of the free ligands reveal the cationic ligand to be a poorer donor but better acceptor than the neutral form. Attempts to form simple Lewis acid/base pairs between [Rh(α,β-CgPAm)(acac)(CO)] and BCl$_3$ or AlCl$_3$ were unsuccessful due to facile acac^{-} abstraction by the Lewis acids. The validity of the phosphines as ligands was further confirmed through coordination to Au(I) and Pt(II) and analysis of the resultant complexes. The acquisition of single diastereomers of either of the ligands or the reported complexes have proved unsuccessful but efforts towards accessing useable quantities of both diastereomers either through improved separation techniques or *via* synthetic protocols using pre-resolved α- and/or β-CgPBr are in progress. Once realized, the single diastereomers will be examined as ligands for various catalytic asymmetric transformations which will be reported in due course.

Experimental

General information: Unless stated otherwise, all reactions were performed under a nitrogen atmosphere using standard Schlenk techniques and, where appropriate, an inert atmosphere glovebox. Solvents were dried and degassed by refluxing over standard drying agents under dinitrogen and distilled immediately prior to use or obtained from an MBraun SPS system. Infrared spectra were recorded as solid samples on a Shimadzu ATR spectrophotometer. Mass spectra were carried out on a VG Platform II Fisons mass spectrometer. The NMR spectra were recorded on Bruker Avance 400, 500 or 600 MHz instruments at the frequencies indicated. α,β-CgPBr was prepared as detailed in the literature.[26]

Crystallography

Single-crystal XRD data were collected on single crystals mounted in paratone on an Agilent SuperNova Dual Atlas three-circle diffractometer with a mirror monochromator [using either Cu (λ = 1.5418 Å) or Mo (λ = 0.7107 Å) radiation], equipped with an Oxford Cryosystems cooling apparatus. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on gaussian integration over a multifaceted crystal model within CrysAlisPro.[27] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[28] A summary of crystallographic data are available as ESI and the structures deposited with the Cambridge Structural Database (CCDC deposition numbers 1550609–1550613). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

α,β-CgPAm.
A mixture of 1,8,8-trimethyl-4-aza-2-azoniabicyclo[3.2.1]oct-2-ene tetrafluoroborate (0.5 g, 2.1 mmol), α,β-CgPBr (0.62 g, 2.1 mmol) and K$_2$CO$_3$ (0.87 g, 6.3 mmol) were stirred in MeCN (10 ml) for 24 hrs. The mixture was subsequently filtered and the filtrate concentrated to small volume whereupon a cream solid precipitated. The solid was isolated by filtration and dried *in vacuo*. Yield = 0.44 g (57%). A second crop (20%) was isolated after cooling the mother liquor to -20 °C overnight. ^{31}P{^{1}H} (CDCl$_3$, 145 MHz): 28.8, 21.3 ppm. ^{1}H (CDCl$_3$, 400 MHz): 7.51 (s, 0.5H), 7.47 (s, 0.5H), 3.11 (dd, 9.6, 5.2 Hz, 0.5H), 2.97 (dd, 9.8, 4.6 Hz, 0.5H), 1.97 (m, 3H), 1.77 (m, 4H), 1.63 (m, 1H), 1.38 (d, 2.8 Hz, 1.5H), 1.36 (d, 3.5 Hz, 1.5H), 1.27 (obs, 9H), 1.05 (d, 3.2 Hz, 3H), 0.95 (s, 1.5H), 0.93 (s, 3H), 0.91 (s, 1.5H) ppm. ^{13}C{^{1}H} (CDCl$_3$, 100 MHz): 146.4 (CH, d, 4.7 Hz), 146.1 (CH, d, 4.3 Hz), 94.4 (C), 96.2 (C), 95.8 (C), 95.7 (C), 75.5 (C, d, 25.8 Hz), 74.8 (C, d, 25.1 Hz), 73.7 (C, d, 15.2 Hz), 73.5 (C, d, 17.5 Hz), 70.9 (CH, d, 27.0 Hz), 70.1 (CH, d, 27.8 Hz), 63.4 (C), 63.2 (C), 46.1 (CH$_2$, d, 12.4 Hz), 45.9 (CH$_2$, d, 12.3 Hz), 41.7 (CH$_2$), 41.0 (CH$_2$), 40.6 (C, d, 5.7 Hz), 40.0 (C, d, 3.7 Hz), 36.1 (CH$_2$), 35.9 (CH$_2$), 34.0 (CH$_2$), 33.9 (CH$_2$), 27.8 (CH$_3$, d, 1.8 Hz), 27.7 (CH$_3$, d, 23.0 Hz), 27.3 (CH$_3$, d, 5.0 Hz), 27.0 (CH$_3$, d, 22.4 Hz), 26.4 (CH$_3$, d, 10.5 Hz), 25.5 (CH$_3$, d, 10.5 Hz), 22.7 (2 x CH$_3$), 19.9 (CH$_3$), 19.5 (CH$_3$), 18.4 (CH$_3$), 17.8 (CH$_3$) ppm. HRMS (ES): *m/z* 367.2158 (calc. 367.2151) [L + H]$^{+}$, 100%.

[α,β-CgPAmMe]BF$_4$
A mixture of α,β-CgPAm (0.5 g, 1.37 mmol) and [Me$_3$O]BF$_4$ (0.21 g, 1.40 mmol) were stirred in CH$_2$Cl$_2$ (25 ml) for 2 hrs. The solvent was removed *in vacuo* and the solid residue dissolved in the minimum amount of THF (~5 ml) in air. Upon leaving overnight fine crystals of [α,β-CgPAmMe]BF$_4$ precipitated which were isolated and air-dried. Yield = 0.34 g (53%). A second crop (18%) was isolated after leaving the mother liquor to stand. ^{31}P{^{1}H} (CDCl$_3$, 145 MHz): 44.0, 35.4 ppm. ^{1}H (CDCl$_3$, 400 MHz): 8.17 (s, 0.5H), 8.13 (s, 0.5H), 3.43 (t, 6.7 Hz, 0.5H), 3.37 (t, 5.8 Hz, 0.5H), 3.27 (s, 1.5H), 3.25 (s, 1.5H), 2.90 (m, 0.5H), 2.61 (m, 0.5H), 2.25-1.65 (m, 7H), 1.42 (obs, 6H), 1.39 (br, 1.5H), 1.37 (s, 1.5H), 1.33 (s, 1.5H), 1.31 (s, 3H), 1.28 (s, 1.5H), 1.11 (obs, 6H), 1.05 (s, 3H) ppm. ^{13}C{^{1}H} (CD$_3$CN, 100 MHz): 156.8 (CH), 156.3 (CH), 97.1 (C, d, 1.1 Hz), 96.9 (C), 96.7 (2 x C), 75.7 (C, d, 30.2 Hz), 75.4 (C, d, 28.8 Hz), 73.9 (C, d, 17.5 Hz), 73.8 (C, d, 16.5 Hz), 73.3 (C), 72.5 (C), 71.3 (CH, d, 20.7 Hz), 70.3 (CH, d, 21.8 Hz), 45.4 (CH$_2$, d, 19.8 Hz), 45.3 (CH$_2$, d, 19.8 Hz), 42.2 (C, d, 4.6

Hz), 41.6 (C, d, 2.4 Hz), 40.2 (CH_2), 39.8 (CH_2), 39.6 (CH_3), 39.0 (CH_3), 35.3 (CH_2), 35.0 (CH_2), 33.0 (CH_2), 32.2 (CH_2), 27.6 (CH_3, d, 28.3 Hz), 27.4 (CH_3, d, 22.0 Hz), 26.9 (2 x CH_3), 26.2 (CH_3, d, 1.2 Hz), 26.1 (CH_3, d, 1.2 Hz), 25.3 (CH_3, d, 10.3 Hz), 25.2 (CH_3, d, 10.3 Hz), 21.3 (2 x CH_3), 17.3 (CH_3), 17.0 (CH_3), 13.7 (CH_3), 13.2 (CH_3) ppm. HRMS (ES): *m/z* 381.2316 (calc. 381.2307) $[L]^+$, 100%.

[α,β-CgP(O)AmMe]BF_4

A solution of [α,β-CgPAmMe]BF_4 (30 mg) in MeCN (2 ml) was heated near boiling for 2 mins and left to stand at RT whereupon the compound crystallized. The crystals were isolated by filtration and air-dried. Yield = 12 mg (39%). $^{31}P\{^1H\}$ (CD_3CN, 145 MHz): 27.2, 26.4 ppm. ^1H (CD_3CN, 400 MHz): 8.28 (s, 1H), 4.21 (t, 5.6 Hz, 0.5H), 4.11 (t, 4.6 Hz, 0.5H), 3.33 (s, 1.5H), 3.32 (s, 1.5H), 2.70 – 1.94 (m, 9H), 1.47 (s, 3H), 1.43 (s br, 6H), 1.40 (s, 1.5H), 1.34 (s, 1.5H), 1.22 (s, 1.5H), 1.21 (s, 1.5H), 1.15 (s, 1.5H), 1.10 (s, 1.5H) ppm. $^{13}C\{^1H\}$ (CD_3CN, 100 MHz): 155.1 (CH, d, 5.6 Hz), 154.8 (CH, d, 5.4 Hz), 97.6 (C, d, 2.5 Hz), 97.4 (C, d, 2.7 Hz), 97.3 (C, d, 2.8 Hz), 97.2 (C, d, 2.6 Hz), 75.2 (C, d, 27.8 Hz), 75.2 (C, d, 18.8 Hz), 75.1 (C), 74.8 (CH, d, 18.7 Hz), 74.6 (CH, d, 23.5 Hz), 74.3 (C, d, 8.3 Hz), 74.2 (C), 66.0 (C), 63.6 (C), 43.4 (C, d, 6.6 Hz), 43.3 (C, d, 5.4 Hz), 43.0 (CH_2, d, 11.8 Hz), 43.0 (CH_2, d, 11.8 Hz), 40.8 (CH_2), 40.5 (CH_2), 39.7 (CH_2), 38.8 (CH_2), 33.7 (CH_2), 31.9 (CH_2), 26.7 (CH_3, d, 14.6 Hz), 21.5 (CH_3), 21.4 (CH_3), 20.3 (CH_3, d, 1.3 Hz), 20.0 (2 x CH_3), 19.9 (CH_3, d, 1.3 Hz), 17.4 (CH_3), 17.1 (CH_3), 13.7 (CH_3), 13.3 (CH_3) ppm.

[Rh(α,β-CgPAm)(acac)(CO)]

To a stirred solution of [Rh(acac)$(CO)_2$] (70 mg, 2.73 x 10^{-4} mol) in CH_2Cl_2 was added α,β-CgPAm (100 mg, 2.73 x 10^{-4} mol) as a solid. After an initial effervescence and color change to a light yellow, the solution was left to stir for 1 hr. The solvent was subsequently removed *in vacuo* and the solid residue dissolved in a small amount of Et_2O. After filtering, all volatiles were removed to give a bright yellow solid. Yield = 140 mg (86%). $^{31}P\{^1H\}$ ($CDCl_3$, 145 MHz): 88.8 (d, $^1J_{P\text{-}Rh}$ 198.6 Hz), 81.8 (d, $^1J_{P\text{-}Rh}$ 201.8 Hz) ppm. ^1H ($CDCl_3$, 400 MHz): 7.90 (s, 0.5H), 7.86 (d, 3.8 Hz, 0.5H), 5.44 (s, 0.5H), 5.43 (s, 0.5H), 4.10 (t, 4.1 Hz, 0.5H), 4.05 (t, 6.6 Hz, 0.5H), 3.44 (dd, 13.4, 5.7 Hz, 0.5H), 3.22 (dd, 13.8, 5.9 Hz, 0.5H), 2.38-1.64 (m, 7H), 2.02 (s, 3H), 1.88 (s, 1.5H), 1.82 (s, 1.5H), 1.59 (d, 12.5 Hz, 1.5H), 1.55 (d, 12.8 Hz, 1.5H), 1.40 (s, 1.5H), 1.36 (s, 1.5H), 1.33 (s, 1.5H), 1.32 (s, 1.5H), 1.30 (s, 3H), 1.07 (d, 5.8 Hz, 3H), 1.01 (s, 1.5H), 0.98 (s, 1.5H), 0.97 (s, 3H) ppm. $^{13}C\{^1H\}$ ($CDCl_3$, 100 MHz): 188.6 (C, dd, 74.6, 24.2 Hz), 187.8 (C, dd, 75.3, 24.3 Hz), 186.8 (C), 186.6 (C), 184.5 (C), 183.9 (C), 146.9 (CH, d, 14.9 Hz), 144.6 (CH), 100.1 (CH, d, 2.3 Hz), 100.1 (CH, d, 2.4 Hz), 95.7 (C), 95.3 (C), 94.9 (C, d, 1.2 Hz), 94.8 (C, d, 1.1 Hz), 75.4 (C, d, 20.6 Hz), 72.5 (C, dd, 17.3, 3.0 Hz), 72.2 (C, dd, 17.5, 3.1 Hz), 67.1 (CH, d, 3.1 Hz), 63.2 (C), 63.1 (C), 45.8 (CH_2, d, 12.7 Hz), 45.4 (CH_2, d, 13.4 Hz), 40.0 (C, d, 2.5 Hz), 39.8 (CH_2), 39.7 (CH_2), 39.6 (C), 37.3 (CH_2), 36.6 (CH_2), 33.0 (CH_2), 32.9 (CH_2), 26.7 (CH_3), 26.6 (CH_3), 26.5 (CH_3, d, 0.9 Hz), 26.5 (CH_3), 26.4 (CH_3, d, 0.9 Hz), 26.1 (CH_3), 26.0 (CH_3), 25.9 (CH_3), 24.8 (CH_3, d, 3.9 Hz), 24.7 (CH_3, d, 7.4 Hz), 24.2 (CH_3, d, 7.9 Hz), 23.1 (CH_3, d, 3.4 Hz), 22.1 (CH_3), 21.9 (CH_3), 18.5 (CH_3), 18.4 (CH_3), 18.2 (CH_3), 18.0 (CH_3), ppm. IR (solid): 1988 cm^{-1} (C≡O). HRMS (ES): *m/z* 597.1619 (calc. 597.1601) $[M + H]^+$, 100%.

[Au(α,β-CgPAm)Cl]

To a stirred solution of [Au(THT)Cl] (32 mg, 1.03 x 10^{-4} mol) in THF (5 ml) was added α,β-CgPAm (38 mg, 1.03 x 10^{-4} mol) as a solid. The solution was left to stir for 1 hr and the solvent removed *in vacuo* to yield a cream solid. Yield = 55 mg (90%). $^{31}P\{^1H\}$ (C_6D_6, 145 MHz): 64.6, 58.9 ppm. ^1H (C_6D_6, 400 MHz): 7.72 (s, 0.5H), 7.68 (s, 0.5H), 3.80 (dd, 12.2, 2.4 Hz, 0.5H), 3.67 (s br, 1H), 3.48 (d, 10.2 Hz, 0.5H), 2.62 (br, 1H), 2.14 (m br, 2H), 1.66-1.06 (m br, 4H), 1.26 (s, 3H), 1.22 (s, 3H), 1.15 (s, 3H), 1.12 (s, 3H), 0.85 (s, 1.5H), 0.75 (s, 1.5H), 0.72 (d, 20.0 Hz, 1.5H), 0.40 (s, 1.5H) ppm. $^{13}C\{^1H\}$ (C_6D_6, 100 MHz): 139.8 (CH), 139.6 (CH), 95.6 (C), 95.4 (C), 95.2 (2 x C), 75.0 (C, d, 28.7 Hz), 74.5 (C, d, 29.2 Hz), 73.4 (C, d, 37.7 Hz), 73.2 (C, d, 35.6 Hz), 71.4 (CH, d, 8.2 Hz), 70.2 (CH, d, 8.3 Hz), 64.0 (C), 63.4 (C), 44.6 (CH_2, d, 12.0 Hz), 44.3 (CH_2, d, 12.1 Hz), 40.1 (CH_2), 39.9 (CH2), 39.7 (C), 39.3 (C), 35.4 (CH_2), 35.1 (CH_2), 32.9 (CH_2), 32.0 (CH_2), 29.9 (CH_3), 26.2 (CH_3), 26.1 (CH_3), 25.7 (CH_3), 25.1 (CH_3, d, 8.3 Hz), 24.7 (CH_3), 23.6 (CH_3, d, 3.5 Hz), 22.6 (CH_3, d, 3.4 Hz), 21.3 (CH_3), 21.2 (CH_3), 18.7 (CH_3), 18.0 (CH_3), 17.1 (CH_3), 16.9 (CH_3) ppm. HRMS (ES): *m/z* 599.1509 (calc. 599.1505) $[M + H]^+$, 100%.

[Au(α,β-CgPAmMe)Cl]BF_4

To a stirred solution of [Au(THT)Cl] (66 mg, 2.14 x 10^{-4} mol) in CH_2Cl_2 (10 ml) was added [α,β-CgPAmMe]BF_4 (100 mg, 2.14 x 10^{-4} mol) as a solid and the resultant solution left to stir for 2 hrs. The solvent was removed *in vacuo* and the cream solid crystallized from $CHCl_3$/Et_2O by vapor diffusion. Yield = 102 mg (68%). $^{31}P\{^1H\}$ ($CDCl_3$, 145 MHz): 75.9 (br), 68.9 (br) ppm. ^1H ($CDCl_3$, 400 MHz): 8.34 (s, 0.5H), 8.31 (s, 0.5H), 4.18 (dd, 10.4, 4.3 Hz, 0.5H), 3.86 (br, 0.5H), 3.37 (s, 3H), 2.94 (m, 0.5H), 2.59 (d, 15.4 Hz, 0.5H), 2.50 (dd, 16.1, 6.5 Hz, 1H), 2.25 (m, 3H), 2.04 (m, 4H), 1.60 (s, 1.5H), 1.56 (s, 1.5H), 1.52 (s, 1.5H), 1.49 (s, 1.5H), 1.48 (s, 1.5H), 1.44 (s, 1.5H), 1.37 (s, 3H), 1.34 (s, 1.5H), 1.16 (obs, 6H) ppm. $^{13}C\{^1H\}$ (CD_3CN/$CDCl_3$, 100 MHz): 155.0 (CH), 154.7 (CH), 97.1 (C), 96.9 (C), 96.6 (C), 96.4 (C), 76.1 (C, d, 18.8 Hz), 74.8 (C, d, 19.6 Hz), 74.5 (C), 73.5 (C), 72.4 (CH, d, 7.2 Hz), 71.2 (CH, d, 7.6 Hz), 45.4 (CH_2, d, 12.9 Hz), 44.9 (CH_2, d, 12.2 Hz), 42.2 (C, d, 4.2 Hz), 41.6 (C), 40.6 (CH_3), 40.3 (CH_3), 39.2 (CH_2), 37.9 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 32.6 (CH_2), 31.0 (CH_2), 26.2 (obs, 6 x CH_3), 24.5 (CH_3, d, 3.4 Hz), 23.8 (CH_3, d, 3.8 Hz), 21.4 (CH_3), 21.3 (CH_3), 17.3 (CH_3), 16.9 (CH_3), 13.4 (CH_3), 12.8 (CH_3) ppm. HRMS (ES): *m/z* 613.1674 (calc. 613.1661) $[M - BF_4]^+$, 100%.

[Rh(α,β-CgPAmMe)(acac)CO]BF_4

To a stirred solution of [Rh(acac)$(CO)_2$] (55 mg, 2.73 x 10^{-4} mol) in CH_2Cl_2 was added [α,β-CgPAmMe]BF_4 (100 mg, 2.14 x 10^{-4} mol) as a solid. After an initial effervescence and color change to a light yellow the solution was left to stir for 2 hrs. The solvent was subsequently removed *in vacuo* and the solid residue triturated with dry Et_2O. Recrystallization was effected by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the complex. Yield = 122 mg (64%). $^{31}P\{^1H\}$ (d_6-acetone, 145 MHz): 113.3 (d, $^1J_{P\text{-}Rh}$ 204.1 Hz), 105.8 (d, $^1J_{P\text{-}Rh}$ 207.3 Hz) ppm. ^1H (d_6-acetone, 400 MHz): 9.00 (s br, 1H), 5.59 (s, 0.5H), 5.55 (s, 0.5H), 4.54 (s br, 1H), 3.34 (s, 1.5H), 3.33 (s, 1.5H), 3.27 (dd, 13.9, 6.0 Hz, 0.5H), 3.00 (dd, 14.1, 6.0 Hz, 0.5H), 2.75-1.80 (m, 7H), 1.98 (s, 1.5H), 1.96 (s, 1.5H), 1.93 (s br, 3H), 1.61 (d, 10.4 Hz, 1.5H), 1.59 (d, 11.8 Hz, 1.5H), 1.43 (d, 15.9 Hz, 1.5H), 1.37 (s, 3H), 1.34 (s, 1.5H), 1.25 (s, 3H), 1.16 (s, 3H) ppm. $^{13}C\{^1H\}$ (d_6-acetone, 100 MHz): 188.8 (dd, 74.1, 23.9 Hz, CO) 188.6 (s, CO_{acac}), 188.5 (s, CO_{acac}), 188.1 (dd, 74.6, 23.7 Hz, CO), 160.2 (d, 7.4 Hz, CH), 159.9 (d, 3.7 Hz, CH), 101.3

(d, 2.4 Hz, CH), 101.3 (d, 2.4 Hz, CH), 96.8 (C), 96.5 (C), 96.3 (C), 96.2 (C), 77.9 (d, 16.3 Hz, C), 77.1 (d, 16.8 Hz, C), 73.8 (dd, 12.4, 2.8 Hz, C), 73.5 (dd, 11.7, 2.8 Hz, C), 67.1 (d, 2.6 Hz, CH), 65.3 (d, 5.5 Hz, CH), 46.3 (d, 13.8 Hz, CH_2), 45.4 (d, 13.3 Hz, CH_2), 42.3 (C), 41.8 (C), 39.5 (CH_2), 39.2 (CH_3), 38.7 (CH_2), 38.6 (CH_3), 38.0 (CH_2), 37.3 (CH_2), 33.3 (CH_2), 32.5 (CH_2), 26.8 (CH_3), 26.7 (CH_3), 26.2 (CH_3), 26.0 (CH_3), 25.5 (d, 3.9 Hz, CH_3), 24.9 (d, 8.1 Hz, CH_3), 24.7 (d, 8.4 Hz, CH_3), 24.2 (d, 3.2 Hz, CH_3), 21.6 (CH_3), 21.5 (CH_3), 17.9 (CH_3), 17.7 (CH_3), 12.9 (CH_3), 12.8 (CH_3) ppm. IR (solid): 2005 cm^{-1} (C≡O). HRMS (ES): *m/z* 611.1757 (calc. 611.1757) $[M - BF_4]^+$, 100%.

[Rh(α,β-CgPAmH)(CO)Cl$_2$]

To a stirred solution of [Rh(α,β-CgPAm)(acac)CO] (120 mg, 2.01 x 10^{-4} mol) in CH_2Cl_2 (10 ml) was added one equivalent of BCl_3 (0.2 ml of a 1M solution in CH_2Cl_2). The yellow solution darkened considerably upon addition of the BCl_3. After stirring overnight the volatiles were removed *in vacuo* and the residue crystallized from CH_2Cl_2 by vapor diffusion with Et_2O. Crystallization from acetone in air was also effective giving yellow crystals of the complex. The same procedure using $AlCl_3$ instead of BCl_3 gave the same complex in similar yield. Yield = 60 mg (53%). $^{31}P\{^1H\}$ ($CDCl_3$, 145 MHz): 109.0 (d, $^1J_{P\text{-}Rh}$ 199.9 Hz), 105.1 (d, $^1J_{P\text{-}Rh}$ 205.8 Hz) ppm. ^1H ($CDCl_3$, 400 MHz): 9.88 (s br, 0.5H), 9.64 (s br, 1H), 9.09 (t, 7.1 Hz, 0.5H), 4.50 (d, 4.4 Hz, 0.5H), 4.46 (d, 5.1 Hz, 0.5H), 3.55 (dd, 14.0, 6.0 Hz, 0.5H), 3.22 (dd, 14.2, 6.1 Hz, 0.5H), 3.06 (m, 1H), 2.40 (m, 0.5H), 2.22-1.76 (m, 5.5H), 1.75 (s, 1.5H), 1.71 (s, 1.5H), 1.69 (d, 16.0 Hz, 1.5H), 1.61 (d, 15.5 Hz, 1.5H), 1.53 (s, 1.5H), 1.37 (d, 5.4 Hz, 3H), 1.33 (s, 1.5H), 1.31 (s, 1.5H), 1.29 (s, 1.5H), 1.24 (s, 1.5H), 1.19 (s, 1.5H), 1.08 (s, 1.5H), 1.05 (s, 1.5H) ppm. $^{13}C\{^1H\}$ ($CDCl_3$, 100 MHz): 184.3 (dd, 73.2, 15.0 Hz, CO) 183.8 (dd, 73.5, 15.3 Hz, CO), 162.8 (d, 29.0 Hz, CH), 159.8 (d, 24.1 Hz, CH), 97.0 (C), 96.5 (C), 95.9 (C), 95.8 (C), 73.9 (d, 26.4 Hz, C), 73.7 (d, 25.6 Hz, C), 66.7 (s, C), 66.5 (s, C), 66.1 (d, 7.8 Hz, CH), 65.8 (d, 7.1 Hz, CH), 46.8 (d, 14.1 Hz, CH_2), 45.6 (d, 14.0 Hz, CH_2), 42.4 (CH_3), 41.9 (CH_2), 41.0 (CH_2), 39.5 (CH_2), 37.9 (CH_2), 34.7 (CH_2), 32.1 (CH_2), 31.0 (CH_2), 27.7 (CH_3), 26.9 (CH_3), 26.7 (CH_3), 26.6 (d, 3.4 Hz, CH_3), 26.0 (d, 8.2 Hz, CH_3), 25.8 (d, 8.2 Hz, CH_3), 25.7 (d, 2.8 Hz, CH_3), 21.9 (s, CH_3), 21.8 (s, CH_3), 19.1 (s, CH_3), 17.9 (CH_3), 16.0 (CH_3), 15.6 (CH_3) ppm. IR (solid): 1990 cm^{-1} (C≡O). HRMS (ES): *m/z* 574.1081 (calc. 574.1109) $[M - Cl + MeCN]^+$, 100%.

[Pt(α,β-CgPAmMe)Cl$_3$]

A mixture of finely ground $K_2[PtCl_4]$ (107 mg, 2.57 x 10^{-4} mol) and [α,β-CgPAmMe]BF_4 (120 mg, 2.57 x 10^{-4} mol) in MeCN (5 ml) was stirred for 24 hrs. The mixture was subsequently filtered and the volatiles removed to give a yellow solid which was crystallized from acetone by vapor diffusion of Et_2O. Yield = 100 mg (57%). $^{31}P\{^1H\}$ (CD_3CN, 145 MHz): 55.2 (s, $^1J_{P\text{-}Pt}$ 4284.3 Hz), 49.2 (s, $^1J_{P\text{-}Pt}$ 4334.1 Hz) ppm. ^1H (CD_3CN, 400 MHz): 9.36 (d, 7.4 Hz, 0.5H), 8.98 (d, 7.9 Hz, 0.5H), 4.52 (d, 5.1 Hz, 0.5H), 4.48 (s br, 0.5H), 3.48 (dd, 14.3, 6.2 Hz, 0.5H), 3.32 (s, 1.5H), 3.28 (s, 1.5H), 3.26 (dd, 14.6, 6.4 Hz, 0.5H), 2.94 (m, 1H), 2.60-1.90 (m, 6H), 2.19 (s, 1.5H), 2.11 (s, 3H), 1.80 (d, 13.9 Hz, 1.5H), 1.78 (d, 5.4 Hz, 1.5H), 1.75 (d, 5.0 Hz, 1.5H), 1.60 (d, 15.0 Hz, 1.5H), 1.42 (s, 1.5H), 1.37 (s, 1.5H), 1.34 (s, 3H), 1.18 (s, 1.5H), 1.15 (1.5H), 1.13 (1.5H) ppm. The poor solubility of the sample precluded acquisition of acceptable ^{13}C NMR data. HRMS (ES): *m/z* 686.1601 (calc. 686.1576) $[M - Cl + MeCN]^+$, 100%.

Conficts of Interest

There are no conflicts of interest to declare.

Notes and references

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† Electronic Supplementary Information (ESI) available: NMR spectra for all the complexes together with crystallographic details for those compounds characterized by single crystal X-ray techniques are provided in a single pdf file in the Supporting Information. The Supporting Information is available free of charge on the RSC Publications website.

‡ 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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