# Dalton Transactions

Accepted Manuscript






ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Mono- and dimeric complexes of an asymmetric heterotopic P,$C_{NHC}$,pyr ligand

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***Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX***
**DOI: 10.1039/b000000x**

An asymmetric heterotopic ligand (*S*-$N^{Me}$CP) containing a central bicyclic, expanded-ring NHC with one pyridyl and one phosphine *exo*-substituent has been synthesised and its coordination chemistry with selected late transition metals investigated. The amidinium precursor [*S*-$N^{Me}$CHP]$PF_6$ shows variable coordination modes with Ag(I), Cu(I) and Au(I) depending on the L:M ratio. The reaction of two mols of [*S*-$N^{Me}$CHP]$PF_6$ with $[Cu(MeCN)_4]BF_4$, $AgBF_4$ or Au(THT)Cl gives the *bis*-ligand complexes [Cu(κ-*P*-$N^{Me}$CHP)$_2$($CH_3CN$)$_2$]$BF_4$.$(PF_6)_2$, **1**, and [M(κ-*P*-$N^{Me}$CHP)$_2$]X.$(PF_6)_2$ (**3**: M = Ag, X = $BF_4$; **6**: M = Au, X = Cl) respectively. The 1:1 reaction of [*S*-$N^{Me}$CHP]$PF_6$ with AgOTf gave the head-to-tail dimer *H,T*-[$Ag_2$(μ-*N,P*-$N^{Me}$CHP)$_2$(μ-OTf)$_2$]$(PF_6)_2$, **2**, whereas the analogous reaction with Au(THT)Cl gave monomeric [Au(κ-*P*-$N^{Me}$CHP)Cl]$PF_6$, **5**. Complex **2** was converted to *H,T*-[$Ag_2$(μ-*C,P*-$N^{Me}$CP)$_2$]$(PF_6)_2$, **4**, upon addition of base, while **6** gave [Au(κ-*C*-$N^{Me}$CP)$_2$]Cl, **8**, when treated likewise. Reaction of [*S*-$N^{Me}$CHP]$PF_6$ with Ni(1,5-COD)$_2$ gave the oxidative addition / insertion product [Ni($\kappa^3$-*N,C,P*-$N^{Me}$CP)($\eta^3$-$C_8H_{13}$)]$PF_6$, **9**, which converted to [Ni($\kappa^3$-*N,C,P*-$N^{Me}$CP)Cl]$PF_6$, **10**, upon exposure of a $CHCl_3$ solution to air. Complex **10** showed conformational isomerism that was also present in [Rh($\kappa^3$-*N,C,P*-$N^{Me}$CP)(CO)]$PF_6$, **14**, prepared from the precursor complex [Rh(κ-*P*-$N^{Me}$CHP)(acac)(CO)]$PF_6$, **13**, upon heating in $C_6H_5Cl$. [Pt($\kappa^3$-*N,C,P*-$N^{Me}$CP)(Cl)]$PF_6$, **12**, derived from *trans*-[Pt(κ-*P*-$N^{Me}$CHP)$_2$(Cl)$_2$]$(PF_6)_2$, **11**, was isolated as a single conformer.

## Introduction

The combination of two or more donor atoms of disparate character in a bi- or multi-dentate ligand can generate complexes with unusual properties as each distinct donor will show variable binding to any given metal ion. Ligands that bind strongly through one or more primary donors with weak secondary donation are usually termed hemi-labile and the transient coordination of the weak donor can assist catalytic processes through stabilization of reactive intermediates.[1] There are numerous examples of this type of ligand with many different donor sets to include N/O, P/O, P/N, P/S and S/O combinations as heterotopic bidentate examples.[2] Examples of N-Heterocyclic carbenes (NHCs) with other donors are also numerous[3] but very few combine an expanded-ring N-heterocyclic carbene (ER-NHC) with a phosphine,[4] and of this extremely rare class, only those reported by our group feature an asymmetric element.[4d,e] Although often advantageous from a catalytic viewpoint, hemi-labile behavior is not always desirable (or possible) when employing heterotopic ligands. While we have an interest in hemi-labile systems, our main focus is on the development of heterotopic ligands as frameworks for the control of metal-centered chirality in stereogenic-at-metal complexes and/or to enable construction of homo and hetero bi- and tri-metallic species. Both these aims require robust metal-donor bonding to maintain configurational integrity.

We have been investigating the coordination of linear tridentate systems with central expanded-ring N-heterocyclic carbene (ER-NHC) donors in an effort to understand what ligand-metal combinations favour chelate and/or bridging coordination modes. Our initial studies in the field focused on symmetrically substituted ligands of the type shown in figure 1 where the other donors are pyridines (NCN' framework) or phosphines (PCP' framework) respectively.[4d,e,5] The distinctions between these two ligands are not solely confined to the different secondary donor atoms but extend to variations in the chelate ring sizes with the NCN' systems forming two six-membered, and the PCP' type two seven-membered, chelates upon $\kappa^3$-complexation. These discrepancies result in significant differences in their coordination chemistry with tetrahedral $d^{10}$ metals preferring the PCP' tridentates and square planar and five-coordinate $d^8$ metal ions favoring the NCN' tridentates.[4d,e,5] Configurational preferences were dictated by the nature of the halide in [Cu($\kappa^3$-PCP')X] and were insignificant in $[M(NCN')(1,5\text{-}COD)]^+$ complexes where M = Rh, Ir. In addition, no conformational partiality was seen in square planar $[Ni(NCN')Cl]^+$ where a 1:1 mixture of isomers was obtained.[5] From this we deduced that the unadorned NCN' and/or PCP' frameworks were poor candidates for exerting the conformational control necessary for defining

configuration, and hence absolute stereochemistry, at a metal center. In order to promote the latter a further modification to one or both of the flanking arms was deemed necessary. The introduction of an additional stereo-center in one pyridyl arm of the NCN' ligand to give the $N^{Me}CN$' derivative (Figure 1) was sufficient to achieve this.[5a]

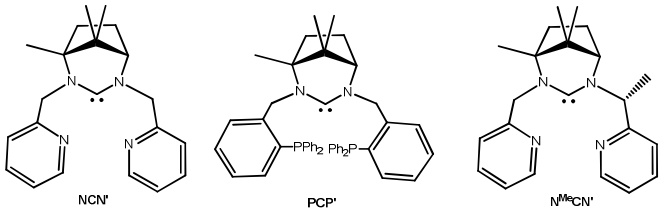



Figure 1. Previous examples of donor-functionalized ER-NHCs.

The aforementioned ligands are of the ABA' type where The A donors are equivalent and the discrimination between them lies at a (relatively) remote point. This is not the ideal as a ligand that contains three completely disparate donors (ABC type) and/or forms chelate rings of two different sizes is preferred. This combination is offered by the hybrid ligand $N^{Me}CP$ (figure 2) which has one pyridyl and one phosphine arm in addition to the central NHC group. The ligand also offers two different chelate ring sizes (a 6- and a 7-membered) to embellish the chiral environment about the metal ion. The current paper reports some initial studies on the complexation of [*S*-$N^{Me}$CHP]$PF_6$ and *S*-$N^{Me}CP$ to metal ions of groups 9, 10 and 11.

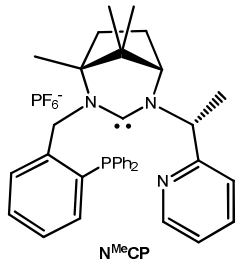


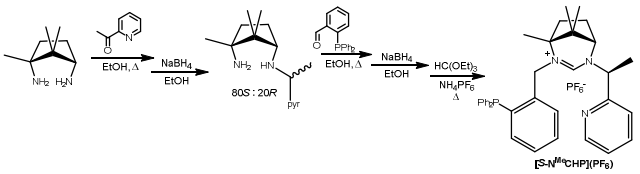

Figure 2. The $N^{Me}CP$ hybrid ligand

## Results and Discussion

### ligand synthesis

Although a number of symmetrical PCP and NCN tridentate ligands are known,[6,7] mixed donor ligands of the $NC_{NHC}P$ type discussed here are extremely rare.[3a] The inclusion of a single $sp^3$ carbon in each of the chelates of *S*-$N^{Me}CP$ was necessary to alleviate some of the strain associated with a $sp^2$-rich ligand backbone and to aid flexibility to encourage facial coordination. Residual strain does still exist so that facile breakage of one or both of the chelate ring(s) can occur and be exploited for the formation of bridged di(tri)metallic species. The nature of the coordination will be highly metal ion-dependent and the current work seeks to establish how both $[N^{Me}CHP]^+$ and $N^{Me}NCP$ behave towards a select number of transition metal ions.

In order to restrict possible isomeric complexity during the coordination chemistry study (and to explore the limitations of stereo-control in the metal systems), a single diastereomer(s) of the ligand was required. We have shown previously that 1,2,2-trimethyl-$N^3$-[1*S*-(pyridin-2-yl)ethyl]cyclopentane-1,3-diamine can be prepared stereoselectively through reduction of the mono-imine produced from condensation of 1,2,2-trimethylcyclopentane-1,3-diamine with (2-pyridyl)acetophenone[5a] and the synthesis of [*S*-$N^{Me}$CHP]$PF_6$ was achieved through extension of this existing chemistry (scheme 1). The initial 80:20 mixture of *S*-[$N^{Me}$CHP]$PF_6$ : *R*-[$N^{Me}$CHP]$PF_6$ was improved to > 9:1 after a single recrystallization from MeOH. The *dr* was deduced from close inspection of pertinent resonances in the $^1$H NMR spectrum where all bar one of the methyl resonances, the bridgehead hydrogens and the methine hydrogens on the chiral carbon in the pyridyl arm of the two diastereomers are well separated. A small amount of analytically pure *S*-[$N^{Me}$CHP]$PF_6$ could be isolated upon repeated recrystallization but for the purposes of convenience, and to avoid the large compound loss associated with complete isomer separation, the majority of the coordination chemistry was performed with the 9:1 *S:R* mixture of [$N^{Me}$CHP]$PF_6$ which, for simplicity, is abbreviated as *S*-[$N^{Me}$CHP]$PF_6$.



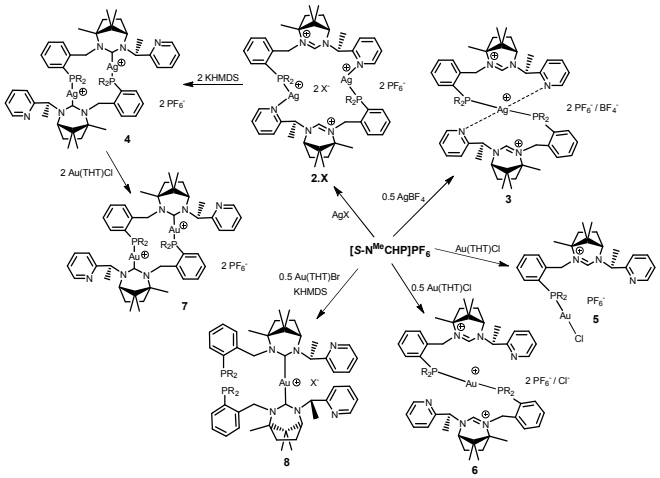

Scheme 1. Synthesis of *S*-[$N^{Me}$CHP]$PF_6$.

### Copper(I), Silver(I) and Gold(I) complexes

Tridentate coordination to Cu(I) was observed previously with the PCP' ligand but aggregates predominated with the NCN' ligand. Although the reasons for this disparate behaviour are not known precisely, the combination of a phosphine donor and a larger chelate in the PCP' system was better able to support $\kappa^3$-coordination at pseudo-tetrahedral Cu(I). As *S*-$N^{Me}CP$ is a hybrid of the aforementioned NCN' and PCP' ligands it was of initial interest to know how it behaved upon coordination to Cu(I). The synthetic procedure was analogous to that used for the preparation of the [Cu($\kappa^3$-PCP')X] complexes with a 1:1 solution of *S*-[$N^{Me}$CHP]$PF_6$ and CuCl in THF being treated with 1.1 equivalents of KHMDS. The resultant solution was examined *in situ* by $^{31}P\{^1H\}$ NMR spectroscopy which showed a number of phosphorus-containing species suggesting a lack of coordination control of the *S*-$N^{Me}CP$ ligand and behavior more akin to that seen with NCN' than PCP'. In an effort to better understand the coordination chemistry of *S*-$N^{Me}CP$ with Cu(I) it seemed expedient to prepare and characterize a precursor complex containing *S*-$[N^{Me}CHP]^+$, with the ideal pre-complex having a *S*-[$N^{Me}$CHP]$PF_6$ : Cu(I) ratio of 1:1. However, the only pure compound isolated from 1:1 reaction mixtures with either CuX or $[Cu(MeCN)_4]^+$ was the phosphine-bound complex [Cu(κ-*P*-$N^{Me}CHP)_2(MeCN)_2]BF_4.(PF_6)_2$, **1**, which was prepared in high yield when the stoichiometry was increased to 2:1 in favor of the ligand. The $^{31}P\{^1H\}$ NMR spectrum of **1** showed a broadened peak (width at half height 43 Hz) at -7.1 ppm reflecting a coordination shift of around 10 ppm which is typical for Cu(I) phosphine complexation.[8] The $^1$H NMR spectrum revealed an unchanged $\delta_H$ for the ortho hydrogen of the pyridine as expected

for an uncoordinated pyridine, and also confirmed the presence of a minor isomer which was not evident from the $^{31}P\{^{1}H\}$ NMR spectrum (this was presumably a complex containing the *R* form of the ligand). Examination of a THF solution of **1** after the addition of KHMDS by $^{31}P\{^{1}H\}$ NMR spectroscopy revealed the presence of a mixture very similar to that observed from the direct *in situ* reaction above except in this case there was clearly some free ligand generated as indicated by the sharp peak at $\delta_P$ = – 17 ppm. Attempts to isolate a pure compound from this mixture were unsuccessful and it was clear that the coordination chemistry of *S*-N$^{Me}$CP with Cu(I) was neither simple nor appropriate for the formation of desired stereogenic-at-metal complexes.

The 1:1 complexation of Ag(I) with NCN' and PCP' mimicked that observed with Cu(I) in that numerous intractable species were observed with the former while a single species was isolated for the latter. The formation of a single species for the PCP' ligand was partly assisted by the prior synthesis of a discrete, pre-complex of the amidinium precursor, namely $[Ag(\kappa^2\text{-PCHP'})_2]^{3+}$. This pathway was denied for the NCN' donor as the related $[Ag(\kappa^2\text{-NCHN'})_2]^{3+}$ proved elusive. The success of the amidinium pre-complex route for the PCP' system prompted an initial focus on *S*-[N$^{Me}$CHP]$PF_6$ to see how the phosphine and/or pyridine donors coordinate to Ag(I) when the NHC anchor is unavailable. When a THF solution containing *S*-[N$^{Me}$CHP]$PF_6$ and one equivalent of Ag(OTf) was stirred overnight a white solid (**2.OTf**) was deposited which was subsequently recrystallised from THF/$Et_2O$ at 4 °C as large colourless blocks (scheme 2). Identification of **2.OTf** was aided by determination of the molecular structure by single crystal X-ray techniques as shown in Figure 3.




Scheme 2. Synthesis of complexes **2-8**.

The complex is a head-to-tail dimer where each silver center is coordinated by a phosphine from one [*S*-N$^{Me}$CHP]$^+$ ligand and a pyridine from a second ligand so that the overall structure can be described as a 22-membered di-silver macrocycle. The dimeric structure is further supported by two bridging triflates each of which use separate oxygen atoms to coordinate to the two silver ions (for the purposes of clarity the $CF_3SO_3^-$ groups are excluded from the figure). Each silver ion has a pseudo-tetrahedral geometry where the extent of the distortion from the tetrahedral ideal is exemplified by the intra-metal bond angles that range from 67° to 141°. The Ag-P bond lengths of 2.367(3) and 2.386(3) Å are shorter than the values of 2.441(2) and 2.464(2) Å reported for a related μ-dppm complex[9] but the Ag-N distances are similar. Closer correlation is observed with the complexes of Espinet[10] where an average Ag-P bond length of 2.378(1) was reported along with Ag-N lengths of 2.334(4) Å and those of 2.39 and 2.24 Å reported by Gimeno.[11] Although the Ag-P and Ag-N bond lengths are similar for both parts of the dimer, it is not symmetric as the Ag-O bond lengths are quite disparate with values of 3.066(11) and 2.464(11) Å for one of the silver ions and 2.776(11) and 2.538(11) Å for the other. The bridging triflates appear to be further supported by hydrogen-bonding contacts between the RNC*H*NR hydrogens and selected oxygen atoms of the $CF_3SO_3^-$ groups. The chiral carbon atoms in the pyridyl arms show the expected *S* stereochemistry and the two pyridine groups are mutually *trans*.

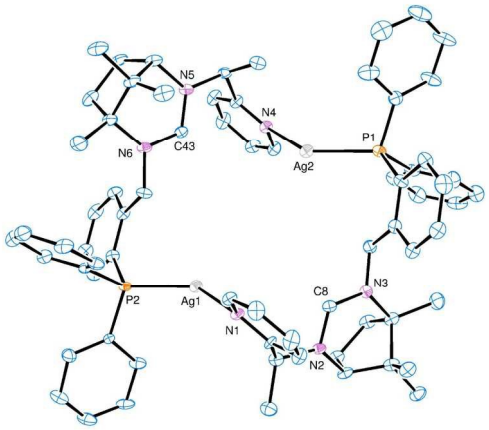



**Figure 3.** The molecular structure of **2**.**OTf**. Hydrogen atoms, lattice solvent, $PF_6^-$ counterions and bridging triflates (one of which sits above the $Ag_2P_2N_2$ plane and the other below) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-P2 2.367(3); Ag1-N1 2.247(10); Ag2-P1 2.386(3); Ag2-N4 2.319(10); N1-Ag1-P2 140.5(3); N4-Ag2-P1 138.1(3); N2-C8-N3 121.8(12); N5-C43-N6 123.2(12).

The $^{31}P\{^{1}H\}$ NMR spectrum of **2.OTf** consists of two doublets centered at 14.2 ppm for the two silver isotopomers with $^{1}J_{P\text{-}Ag(107)}$ and $^{1}J_{P\text{-}Ag(109)}$ values of 650 and 751 Hz respectively. The chemical shift is downfield of the $^{31}P\{^{1}H\}$ resonance for *S*-[N$^{Me}$CHP]$PF_6$ and the observation of P-Ag coupling is indicative of slow phosphine exchange at room temperature. The magnitude of the coupling constants suggests two coordinate, presumably linear, Ag(I) indicating loss of the weakly bound bridging triflates upon dissolution.[12] The pyridine groups remain coordinated as evidenced by the downfield shifted (8.95 ppm) *ortho* proton resonance in the $^{1}H$ NMR spectrum which is better resolved for the mixed $PF_6^-/BF_4^-$ salt as some broadening is evident with the $PF_6^-/CF_3SO_3^-$ compound (see supplementary material). The $^{13}C\{^{1}H\}$ NMR spectrum is fully consistent with these conclusions but only monomeric species were observed in the HRMS.

When the reaction of *S*-[N$^{Me}$CHP]$PF_6$ with AgOTf was repeated in a 2:1 L:M ratio the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture in THF showed a broad doublet at ~ 5 ppm. Removal of the solvent gave a white solid, $[Ag(\kappa\text{-}P\text{-}N^{Me}CHP)_2]OTf.(PF_6)_2$, **3**, that was sparingly soluble in $CHCl_3$ and MeCN but more soluble

in acetone and dichloromethane. The $^1$H NMR spectrum recorded in $CD_2Cl_2$ was similar to the uncoordinated ligand with the amidinium hydrogen being very evident as a singlet at $\delta_H$ = 8.06 ppm. It is noteworthy that the position of the *ortho*-pyridine hydrogen(s) is little shifted from its position in the spectrum of *S*-[N$^{Me}$CHP]PF$_6$ and it would appear that the coordination of the pyridine donors is transient or completely absent in **3**.

When **2.OTf** was treated with a slight excess of KHMDS in THF the $^{31}$P{$^1$H} NMR spectrum changed from the pair of doublets at 14.2 ppm for **2.OTf** to a new pair of doublets centered at 3.40 ppm. The reaction was clean by $^{31}$P{$^1$H} NMR spectroscopy as no other phosphorus containing species were detected in solution and, after work-up, complex **4** was isolated as feathery crystals. Although spectroscopically pure (see below) the crystals were not of sufficient quality to allow the determination of the solid-state structure by single-crystal X-ray diffraction and it was unclear, at this stage, whether the compound was a monomer or a dimer. The two doublets in the $^{31}$P{$^1$H} NMR spectrum had $^1J_{P\text{-}Ag}$ coupling constants of 467 and 539 Hz for $^{107}$Ag and $^{109}$Ag respectively, appreciably smaller than those observed for **2.OTf** which may reflect a coordination number >2 or simply be a consequence of the different nature of the donor *trans* to the phosphine (ER-NHC vs pyridine). The magnitude of the $^1J_{P\text{-}Ag}$ coupling constants compare with related, well-defined, linear 2-coordinate complexes containing phosphines *trans* to NHCs which supports the notion of two-coordinate silver in solution.[13] This relative orientation of donors is not possible for a monomeric complex containing $\kappa^2$- or $\kappa^3$-N$^{Me}$CP and it would appear that the $C_{NHC}$ donor has replaced the pyridine upon addition of base to give dimeric [Ag$_2$(μ-*C,P*-N$^{Me}$CP)$_2$](PF$_6$)$_2$. The lack of a coordinated pyridine is supported by the position of the *ortho* pyridine resonance in the $^1$H NMR spectrum of **4** where it is observed close to its position in the spectrum of the uncoordinated *S*-[N$^{Me}$CHP]PF$_6$ pro-ligand. Comparison of the $^1$H NMR spectrum of **4** with **2.OTf** reveals further distinctions, notably the absence of the characteristic singlet for the amidinium hydrogen and a significant downfield shift of ≥ 1 ppm for one of the methylene hydrogens in the phosphine arm. The NHC carbon appears as a doublet of doublets at 208.7 ppm for each Ag isotopomer in the $^{13}$C{$^1$H} NMR spectrum with coupling constants of 195, 224 and 54 Hz for $^1J_{C\text{-}Ag(107)}$, $^1J_{C\text{-}Ag(109)}$ and $^2J_{C\text{-}P}$ respectively. The observation of the latter coupling confirms that each silver ion is coordinated by an NHC and a phosphorus donor and the fact that all three coupling constants have values that closely mimic those for a related linear [Ag(phosphine)(NHC)]$^+$ complex ($\delta_C$ = 200.5 ppm, $^1J_{C\text{-}Ag(107)}$, $^1J_{C\text{-}Ag(109)}$, $^2J_{C\text{-}P}$ = 199.5, 233.2, 64.6 Hz)[13] does suggest that **4** is the head-to-tail [Ag$_2$(μ-*C,P*-N$^{Me}$CP)$_2$](PF$_6$)$_2$ dimer. The observed chemical shift and the magnitude of the Ag-$C_{NHC}$ coupling constants also accord with data reported previously for 6/7-membered ER-NHC complexes[14] although further comparison with closely analogous systems with a carbene donor *trans* to a phosphine is limited by the scarcity of such compounds. Other than the aforementioned complexes of Tapu,[13] $^2J_{C\text{-}P}$ data for similar compounds is lacking due to poor solubility,[15] complicating secondary couplings or the complete absence of an observed signal and/or C-P coupling.[16] Hofmann has observed a $^2J_{C,P}$ value of 76.7 Hz for a related Cu(I) dimer.[17] Unfortunately, although species of molecular mass > 1250 were observed by mass spectrometry, formulations for these proved elusive and consequently high resolution data is only available for monomeric fragmentation species (see experimental). While the absence of qualifying crystallographic and/or mass spectrometric data prevents an unequivocal assignment of the molecular structure, the spectroscopic data does provide strong circumstantial evidence for the H-T dimer which is further supported by structural determination of the analogous digold complex (see below).

Unlike Ag(I) the coordination chemistry of gold(I) is dominated by the 2-coordinate linear geometry and it was anticipated that the Au(I) complexes of both *S*-[N$^{Me}$CHP]$^+$ and *S*-N$^{Me}$CP would subscribe to this preference. This proclivity is not conducive to the formation of stereogenic-at-metal complexes but can be useful for the construction of multimetallic systems as $\kappa^1$-coordination at gold frees up the remaining donors for coordination to other metals. The 1:1 reaction of *S*-[N$^{Me}$CHP]PF$_6$ with Au(THT)Cl gave, after work-up, a white solid (**5**) with a $^{31}$P{$^1$H} NMR spectrum that consisted of one major (~90%) and one minor (~10%) peak at 25.0 and 24.8 ppm respectively for the two possible isomers resulting from the 9:1 diastereomeric composition of the ligand. The $^1$H NMR spectrum is unremarkable and resembles quite closely the spectrum of *S*-[N$^{Me}$CHP]PF$_6$ suggesting an unbound pyridine group and a formulation of [Au(κ-*P*-N$^{Me}$CHP)Cl]PF$_6$. Likewise the $^{13}$C{$^1$H} NMR is predictable as might be expected for the simple coordination of the P-donor and the formulation is confirmed by HRMS where a peak at 764.2230 amu is observed. When the reaction was performed with a 2:1 ratio of *S*-[N$^{Me}$CHP]PF$_6$ to Au(I) a white solid [Au(κ-*P*-N$^{Me}$CHP)$_2$]Cl.(PF$_6$)$_2$ (**6**) was isolated which gave two broad singlets for the major and minor isomers at 9.6 and 10.7 ppm in the $^{31}$P{$^1$H} NMR spectrum. The upfield shift of the $^{31}$P{$^1$H} resonance for both isomers compared to those of **5** is commensurate with that expected upon replacement of a chloride ligand *trans* to the phosphine by a second phosphine and the broadening is likely the result of some restricted rotation about the Au-P bonds or a relatively slow, undiscerned fluxional process. The $^1$H NMR spectrum of the diastereomeric mixture confirmed the presence of the amidinium hydrogen at $\delta_H$ = 8.7 ppm but was otherwise of little diagnostic value. The formulation was confirmed by mass spectrometry where a peak at m/z = 1441.4806 for the complex trication plus one $PF_6^-$ and one $Cl^-$ was observed.

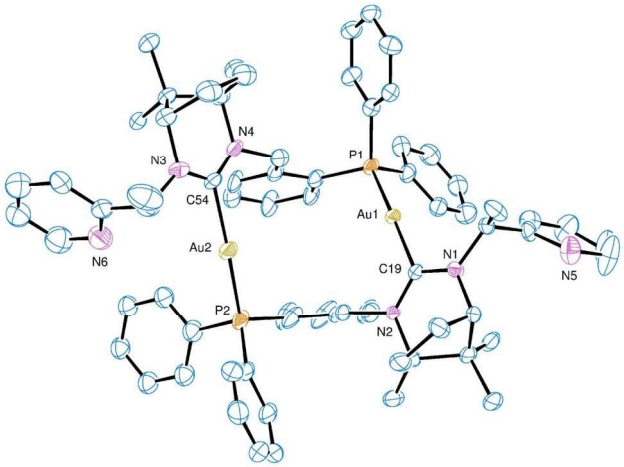



**Figure 4.** The molecular structure of *H,T*-[$Au_2$(μ-*C,P*-$N^{Me}CP)_2$]$(PF_6)_2$, **7**. Hydrogen atoms, lattice solvent and $PF_6^-$ counterions are omitted for clarity. Selected bond lengths (Å) and angles (°): Au1-P1 2.296(5); Au1-C19 2.108(17); Au2-P2 2.281(6); Au2-C54 2.091(17); P1-Au1-C19 171.6(5); P2-Au2-C54 171.0(6); N1-C19-N2 120.1(15); N3-C54-N4 120.2(16).

Transmetallation of *H,T*-[$Ag_2$(μ-*C,P*-$N^{Me}CP)_2$]$(PF_6)_2$ with two equivalents of Au(THT)Cl gave the analogous bimetallic gold complex *H,T*-[$Au_2$(μ-*C,P*-$N^{Me}CP)_2$]$(PF_6)_2$, **7**, the structure of which was confirmed by single-crystal X-ray diffraction (Figure 4). The complex could also be prepared by prior *in situ* deprotonation of *S*-$[N^{Me}CHP]^+$ and subsequent addition of the gold starting complex or from complex **5** upon addition of base. The molecular structure, shown in figure 4, is a head-to-tail dimer where the two gold ions are coordinated to one NHC and one phosphine donor from the two bridging *S*-$N^{Me}CP$ ligands respectively. The geometry at the metal is linear two coordinate as expected with a slightly acute average P-Au-C bond angle of 171.3° and a distance of 4.871 Å between the two gold atoms. The Au-P and Au-C bond lengths of 2.281(6), 2.296(5) and 2.091(17), 2.108(17) Å respectively, largely align with those reported for related complexes although the latter are towards the longer end of the reported range.[16,18] The NCN angle of the carbene unit averages 120.2° which is towards the upper end of the range for 6/7-membered ER-NHCs.[18c,d] The overall structure of the digold macrocycle is puckered with the two P-Au-C vectors orientated at an angle of ~63° to one another. Such an orientation results in (or is possibly the result of) aromatic stacking of the two phenyl rings fused to the 14-membered macrocyclic ring although the distance between the centroids of each ring is relatively long at 4.228 Å. Of the two possible conformations, δ and λ, defined by the relation of the two P-Au-C vectors, only the δ form occurs in the solid-state. Although the structure shown in figure 4 is of a rare type, *H-T* gold dimers of phosphine-NHC heterotopic ligands are known for systems where the P donor is directly connected to one or both of the nitrogens of the NHC.[6i,16] Symmetrically substituted *bis*(diphenylphosphinoethyl)NHCs do form gold trimers but the coordination at each of the gold atoms is through solely phosphine or carbene donors.[6i]

When [Au(κ-*P*-$N^{Me}CHP)_2$]Cl.$(PF_6)_2$ (generated in situ in THF) was treated with 2.2 equivalents of KHMDS the peak in the $^{31}P\{^1H\}$ NMR spectrum for the major diastereomer changed from a broad singlet (width at half height 78 Hz) at $\delta_P$ ~10 ppm to a slightly broadened singlet (width at half height 24 Hz) at $\delta_P$ = -17.0 ppm. The similarity between this latter chemical shift and that of *S*-$[N^{Me}CHP]^+$ indicates that the phosphines have been displaced by the NHC donors upon deprotonation of the amidinium groups to generate [Au(κ-*C*-$N^{Me}CP)_2$]$PF_6$, **8**. Dangling phosphines have been observed previously in related Ag(I) systems.[19] The $^1H$ NMR spectrum of the complex lacks the amidinium hydrogen as expected and shows some broadening particularly for the $CH_2(C_6H_4)PPh_2$ methylene resonances which may reflect some restricted rotation about the Au-C or N-C/C-$C_{Ar}$ bond or possible transient coordination of the phosphine donors (accepting that the $^{31}P$ NMR spectrum indicates a predominantly unbound state). Coordination of the carbenic carbon is confirmed on inspection of the $^{13}C\{^1H\}$ NMR spectrum which shows a signal at $\delta_C$ 202.8 ppm for these carbons, which is a similar position to the chemical shifts reported for analogous ER-NHC complexes of Au(I).[16,18]

The molecular structure of **8** shows the gold bound to two *S*-$N^{Me}CP$ ligands solely through the NHC carbons to produce the expected linear complex (Figure 5). As deduced from the NMR measurements the phosphine and pyridine donors play no part in the coordination and each is arranged mutually *trans* to the like donor of the other ligand in the solid-state. The C-Au-C bond angle is close to linear at 175.0(6)° and the Au-C bond lengths are very typical for *bis*-NHC complexes of this type. There is some disparity in the N-C-N bond angles where one, at 118.6(9)°, is typical of an ER-NHC, but the other is somewhat compressed at 115.4(10)°. The two NCN planes are canted with respect to one another with a relatively small skew angle of ~ 23°. The uncoordinated phosphine and pyridine donors are available for binding to other metal ions to make heterometallic dimers and trimers as is being investigated currently in our laboratories.

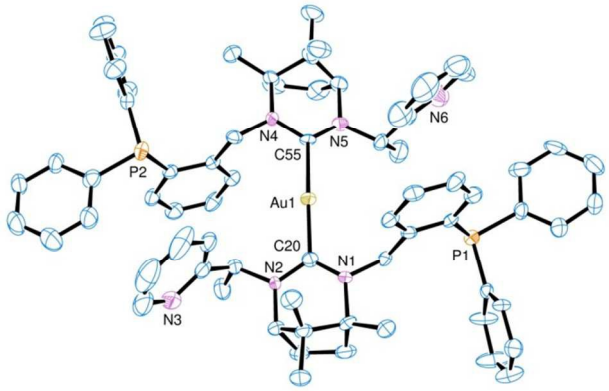


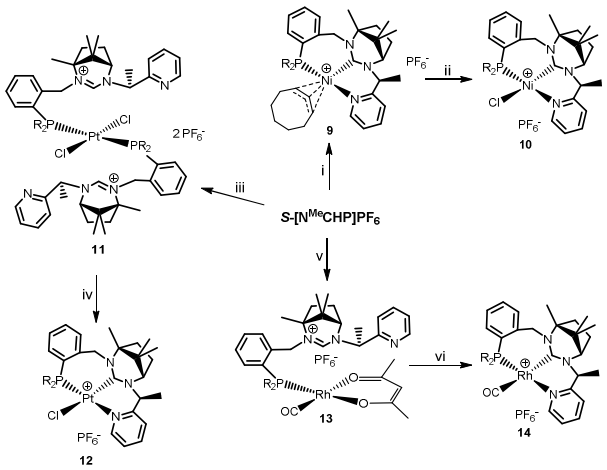

**Figure 5.** The molecular structure of [Au(κ-*C*-$N^{Me}CP\}_2$]$PF_6$, **8**. Hydrogen atoms, lattice solvent and $PF_6^-$ counterions are omitted for clarity. Selected bond lengths (Å) and angles (°): Au1-C20 2.029(12); Au1-C55 2.071(10); C20-Au1-C55 175.0(6); N1-C20-N2 115.4(10); N4-C55-N5 118.6(9).

### Nickel(II), Platinum(II) and Rhodium(I) complexes

The failure to acquire any $\kappa^2$- or $\kappa^3$- complexes of the monovalent group 11 metals prompted an inspection of other metal ions where such modes are expected. Ni(II), Pd(II), Pt(II) and Rh(I) formed $\kappa^3$-complexes with one or other or both of the previously reported NCN' and PCP' ligands and were thus chosen as good

candidates for the formation of complexes of the type $[M(\kappa^3\text{-}N^{Me}CP)X]^{n+}$. Although the resultant square planar complexes would be neither labile (with the possible exception of $Ni^{2+}$) nor stereogenic-at-metal, they did provide an opportunity to investigate any conformational preference of the fully chelated ligand in the absence of configurational complications. It is well known that NHCs coordinate with a preference for the NCN plane to lie at an angle to the coordination plane, *e.g.* in square planar complexes of Pt(II), Rh(I) etc, it is typically canted at an angle of ~50° to the square $ML_4$ plane. For unsymmetrically substituted NHCs, the drop (conformation) can then be described as δ or λ depending upon the relative orientation of the two planes.[20] There is usually little to no conformational selectivity observed for monodentate NHCs but overall ligand conformations of δ and/or λ can be adopted in complexes of tridentate ligands with central NHC donors. Part of the remit of our study is to examine conformational selectivity in certain complexes of $\kappa^3\text{-}N^{Me}CP$ and to attempt to understand what factors, other than preferential NHC binding, influence the δ/λ isomer distribution.

When a 1:1 mixture of $[S\text{-}N^{Me}CHP]PF_6$ and $Ni(COD)_2$ in THF was monitored by $^{31}P\{^1H\}$ spectroscopy, a gradual loss of signal for the pro-ligand ($\delta_P$ = -16.2 ppm) was observed commensurate with the growth of a new resonance at $\delta_P$ = 13.1 ppm. After approximately 24 hours only the signal at 13.1 ppm remained. The resultant complex, $[Ni(\kappa^3\text{-}N^{Me}CP)(\eta^3\text{-}C_8H_{13})]PF_6$, **9**, was isolated as an orange-yellow solid upon removal of all volatiles. The $^1H$ NMR spectrum of **9** showed resonances at 5.22 (t, $^3J_{H\text{-}H}$ = 8.5 Hz), 4.36 (m) and 3.91 (m) ppm characteristic of the formation of the $\eta^3$-cyclooctenyl ligand concordant with the structural assignment of $[Ni(\kappa^3\text{-}N^{Me}CP)(\eta^3\text{-}C_8H_{13})]PF_6$. This is analogous to the reactivity observed previously with $[NCHN']PF_6$.[5] The coordination of both the NHC carbon and the phosphine was confirmed by $^{13}C\{^1H\}$ NMR spectroscopy where the carbenic carbon was observed as a doublet ($^2J_{C\text{-}P}$ = 16.5 Hz) at 202.1 ppm. This compares with a shift of 189.3 ppm and a $^2J_{C\text{-}P}$ of 32 Hz in the related PCP pincer complex of Fryzuk[8e] and 162.8 ppm ($^2J_{C\text{-}P}$ = 35.5 Hz) for a *trans*-$[Ni(P\text{^}NHC)_2]$ complex;[21] it should be noted that both of these reported ligands contain normal 5-membered NHCs. The $^1H$ NMR spectrum of **9** also shows a high field doublet for the methyl group attached to the chiral carbon of the pyridyl arm at 0.33 ppm. This is shifted 1.2 ppm upfield of its position in the spectrum of $S\text{-}[N^{Me}CHP]PF_6$ and is reminiscent of the chemical shift of the analogous methyl group in the 5-coordinate complexes of the type $[M(\kappa^3\text{-}NCN')(C_8H_{12})]^+$ (M = Rh, Ir). The shift likely results from the $CH_3$ group residing in the shielding region of an aromatic ring but attempts to confirm this by single crystal X-ray diffraction were unsuccessful. Although two isomers of $[Ni(\kappa^3\text{-}NCN')(\eta^3\text{-}C_8H_{13})]^+$ were produced, this does not appear to be the case for **9** as only a single peak is observed at $\delta_P$ = 13.1 ppm in the $^{31}P\{^1H\}$ spectrum. There is evidence of a second species in the $^1H$ NMR spectrum but the majority of the sample (>90%) is a single isomer and the minor isomer is likely to be the complex from the coordination of the small amount of $R\text{-}N^{Me}CP$ present. The large chemical shift difference between the two methylene protons of the phosphine arm is characteristic of the formation of the P^C chelate which is confirmed upon inspection of the $^{13}C\{^1H\}$ NMR spectrum where a peak at $\delta_C$ = 202.1 ($^2J_{C\text{-}P}$ = 16.5 Hz) for the carbenic carbon is observed. Although the structure of **9** cannot be confirmed unequivocally, a geometry grossly similar to $[Ni(\kappa^3\text{-}NCN')(\eta^3\text{-}C_8H_{13})]^+$ with an axial pyridine and the phosphine in the pseudo-equatorial plane is most likely.




Scheme 3. Synthesis of complexes **9-14**. i) $Ni(1,5\text{-}COD)_2$, THF, RT, 24 hrs; ii) $CHCl_3$, air; iii) 0.5 $K_2[PtCl_4]$, EtOH, Δ, 18 hrs; iv) 2 KHMDS, THF; v) 0.5 $[Rh(acac)CO]_2$, THF, RT; vi) PhCl, 120 °, 2 hrs.

Exposure of a $CHCl_3$ solution of **9** to air gave, after several hours, a solution containing two peaks in the $^{31}P\{^1H\}$ NMR spectrum at 8.0 and 5.2 ppm. After filtering off a slight gelatinous precipitate the compound could be crystallized in low yield from MeOH. The structure of the complex determined by single-crystal x-ray techniques is shown in figure 6. It is clear from the figure that the allyl ligand has been lost and the metal has acquired a chloride in an analogous manner to that already observed for $[Ni(\kappa^3\text{-}NCN')(\eta^3\text{-}C_8H_{13})]^+$.[5c] The nickel centre is square planar with four different donors defining the corners of the plane. The asymmetric unit of the solid-state structure contains two independent molecules which are conformational isomers (δ and λ). There are a number of metric differences between the two conformers including an expanded N-Ni-P bond angle of 176.9° in the δ form compared to 170.1° for the λ which mainly results from the larger C-Ni-P angle in the former (92.53° vs 87.57°). There is no such discrepancy in the N-Ni-C angles which are 86.54±0.04°. The six-membered N-Ni-C ring has a boat conformation in both isomers and the stereochemistry of the chiral carbon in the pyridyl arm is the anticipated *S*. Somewhat surprisingly the orientation of the methyl group attached to the stereogenic carbon in the N-Ni-C4 ring is different for each isomer with an axial projection being seen in the δ conformer and equatorial in the λ as highlighted in figure 6. There are several other structural differences between the two conformers, notably the orientation of one of the methyl groups of the dimethylmethylene bridge which approaches a phosphorus-bound phenyl in the δ isomer but projects towards the pyridine group in the λ conformer. The Ni-L bond lengths are largely invariant between the two forms and are within the ranges expected for a square planar Ni(II) complex of this type.

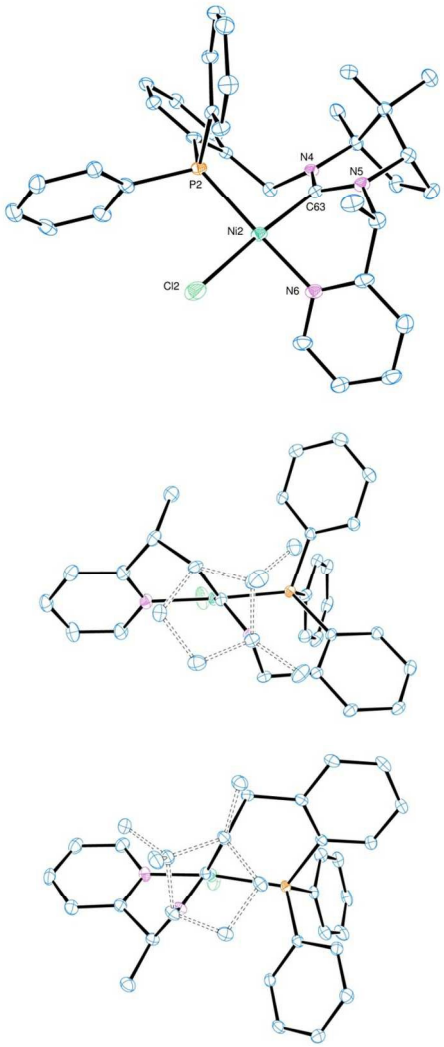



**Figure 6.** The molecular structure of one (δ) of the two conformers of [Ni(κ$^3$-*N,C,P*-NCP)Cl]$^+$, **10** (upper view) and the orientation of the ligand backbone in the two conformers, δ (middle) and λ (lower). Hydrogen atoms, lattice solvent and $PF_6^-$ counterions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni2-C63 1.895(7); Ni2-P2 2.2242(18); Ni2-N6 1.940(6); C63-Ni2-P2 92.53(19); C63-Ni2-N6 86.5(3); P2-Ni2-Cl2 91.36(8); N6-Ni2-Cl2 89.62(19); N4-C63-N5 118.2(6).

The low isolated yield of this complex is largely due to its decomposition in solution. Repeated efforts to improve the yield were unsuccessful with only small amounts of crystalline material being acquired from any given synthesis. The $^{31}P\{^1H\}$ spectrum of the complex recorded immediately after dissolution in normal aerated $CD_3OD$ showed the two peaks noted above in ratios that varied from 1:1 to 1:3 from batch to batch. The $^1H$ NMR spectrum was also complicated by the presence of duplicate signals for the isomeric mixture. After a short period of time the spectra started to show the presence of another complex which, within a matter of hours, was the sole species present in solution. This decomposition product was defined by a single peak at $\delta_P$ 32 ppm in the $^{31}P\{^1H\}$ spectrum which is characteristic of an oxidized phosphine group and it appeared that the phosphine donor in **10** is hemi-labile allowing competitive oxidation on phosphine release. This suggests a relatively large degree of strain in the seven-membered chelate which appears to destabilize the nickel complex. The poor yield of the complex coupled with its instability in solution prevented acquisition of a $^{13}C$ NMR spectrum for **10**.

The isolation of **10** as a mixture of two conformers showed a lack of conformational control akin to that observed for [Ni(κ$^3$-NCN')Cl]$^+$. This was surprising as only a single isomer was seen for the precursor cyclooctenyl complex **9**, and inclusion of the additional chiral centre in the pyridyl chelate had previously led to complete coordination control albeit in five-coordinate Rh(I)/Ir(I) systems.[5a] Irrespective of the unstable nature of **10** in aerated solution, the fact that two conformational isomers were observed does suggest that the current ligand system is poorly selective for square planar Ni(II). In an effort to establish whether this was a general trend or simply the result of the nature of the conversion of **9** to **10** and/or the binding sequence upon addition of *S*-N$^{Me}$CP to Ni(dme)Cl$_2$, we sought to examine other systems of the type [M(κ$^3$-*N,C,P*-N$^{Me}$CP)L]$^+$ (M = Pt, Rh). The preferred route to the platinum complex was through initial P,N-coordination of *S*-[N$^{Me}$NCHP]$PF_6$ to give [Pt(κ$^2$-*P,N*-N$^{Me}$CHP)Cl$_2$]$PF_6$ followed by treatment with base to promote κ$^3$ coordination. However when *S*-[N$^{Me}$CHP]$PF_6$ was reacted with $K_2[PtCl_4]$ or [Pt(COD)Cl$_2$] in a 1:1 ratio, the only complex isolated was *trans*-[Pt(κ-*P*-N$^{Me}$NCHP)$_2$Cl$_2$](PF$_6$)$_2$ (**11**); the yield of which was improved, as expected, upon repeating the reactions with a 2:1 L:M ratio. The structure of the complex was confirmed as *trans* upon analysis by single-crystal X-ray crystallography (figure 7).

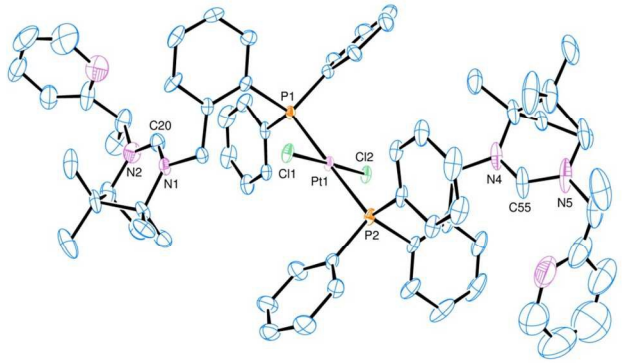



**Figure 7.** The molecular structure of *trans*-[Pt(κ-*P*-N$^{Me}$CHP)$_2$Cl$_2$](PF$_6$)$_2$, **11**. Hydrogen atoms, lattice solvent and $PF_6^-$ counterions are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1-P1 2.3068(17); Pt1-P2 2.3102(17); Pt1-Cl1 2.3026(19); Pt1-Cl2 2.2983(19), P1-Pt1-Cl1 93.15(7); P1-Pt1-Cl2 86.68(7); P2-Pt1-Cl1 86.73(7); P2-Pt1-Cl2 93.46(7); P1-Pt1-P2 179.09(17).

Addition of 1.1 equivalents of KHMDS to *trans*-[Pt(κ-*P*-N$^{Me}$CHP)$_2$Cl$_2$](PF$_6$)$_2$ in THF gave, upon leaving open on the bench for several days, large crystals of the complex [Pt(κ$^3$-*N,C,P*-N$^{Me}$CP)Cl]$PF_6$, **12**, the molecular structure of which is shown in figure 8. Unlike the Ni(II) analog, **12** crystallises as a single isomer with an overall ligand conformation of δ. All other gross structural features are closely analogous to those already described for the δ conformer of **10**. The $^{31}P\{^1H\}$ NMR spectrum of **12** consists of a singlet at $\delta_P$ -7.8 ppm with platinum satellites ($^1J_{P\text{-}Pt}$ = 3655 Hz). The chemical shift is > 20 ppm upfield of its position in **11** but this is not unexpected for the formation of a seven-membered chelate and the one-bond metal-phosphorus

coupling constant is typical.[22] The observation of a single species in the solid-state extends to the solution as relatively simple NMR spectra are observed for compound **12**. It is likely that the δ conformer observed in the solid-state persists in solution as there is no evidence for rapid δ↔λ exchange as the complex shows temperature invariant $^{31}$P and $^{1}$H NMR spectra over the 200-350K range. Complex **12** could also be prepared by transmetallation using **4** and 2 equivalents of $Pt(COD)Cl_2$ or through direct coordination of *in situ* generated *S*-N$^{Me}$CP with the same platinum precursor in a 1:1 ratio, however the products from these approaches were more difficult to purify than the synthesis using **11**.

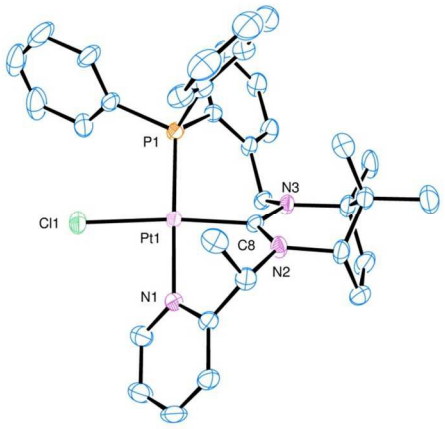



**Figure 8.** The molecular structure of [Pt(κ$^3$-*N,C,P*-N$^{Me}$CP)Cl]$^+$, **12**. Hydrogen atoms, lattice solvent and $PF_6^-$ counterions are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1-C8 1.991(5); Pt1-P1 2.2579(15); Pt1-N1 2.072(5); Pt1-Cl1 2.3471(15), P1-Pt1-C8 92.84(15); N1-Pt1-C8 86.1(2); P1-Pt1-Cl1 93.85(6); N1-Pt1-Cl1 87.12(14); N2-C8-N3 118.6(5).

The Ni(II) and Pt(II) complexes above showed completely disparate behavior so that ambiguity surrounded the ability of *S*-N$^{Me}$CP to bind stereoselectively to square planar complexes. In an effort to increase our understanding of this conformational complexity, we sought to prepare [Rh(κ$^3$-*N,C,P*-N$^{Me}$NCP)(CO)]$PF_6$, **14**, as a further example. The complex [Rh(κ-*P*-N$^{Me}$CHP)(acac)(CO)]$PF_6$, **13**, was chosen as the precursor to **14** as it presented an internal base ($acac^-$) capable of an intramolecular deprotonation of the pendant amidinium group that is pre-disposed for coordination of the carbene upon its release. Addition of solid *S*-[N$^{Me}$CHP]$PF_6$ to a solution of $[Rh(acac)(CO)_2]$ in THF at room temperature gave immediate effervescence suggesting rapid replacement of one CO group by the phosphine donor. This was confirmed upon inspection of the $^{31}$P{$^{1}$H} NMR spectrum of the reaction mixture which consisted of a doublet ($^{1}J_{P\text{-}Rh}$ = 170.4 Hz) at 43.3 ppm consistent with the formation of complex **13**. Removal of volatiles gave an orange-yellow solid which showed the presence of the amidinium hydrogen at 7.88 ppm in the $^{1}$H NMR spectrum in addition to a largely unshifted ortho-pyridine proton resonance at 8.46 ppm reflecting the lack of pyridine coordination. Heating a solution of **13** to 140 °C in chlorobenzene over a period of 2 hours led to the disappearance of the signal for **13** in the $^{31}$P{$^{1}$H} NMR spectrum commensurate with the appearance of two new doublets at δ = 28.8 ($^{1}J_{P\text{-}Rh}$ = 166 Hz, minor) and 27.1 ($^{1}J_{P\text{-}Rh}$ = 165 Hz, major) ppm respectively for the two isomeric forms of complex **14**. The presence of the two isomers in a roughly 1:3 ratio indicated a degree of selectivity during the change from κ$^1$-*P* to κ$^3$-*C,N,P* coordination but this is far from absolute. The upfield shift in $\delta_P$ compared to **13** is indicative of the change in coordination mode from monodentate to tridentate as observed in the platinum complexes. Attempts to form crystals of the complex suitable for structural characterization by single-crystal x-ray techniques were thwarted by the solution instability of the complex. Although the ultimate fate of the compound was not determined, **14** appears to undergo a similar κ$^3$ to κ$^2$ conversion to that described for **10**. This conversion led to very poor yields of pure complex being obtained (as essentially 1:1 isomeric mixtures) and hence the $^{13}$C NMR spectrum given in the SI is for the crude reaction product before attempted purification.

## Conclusions

The coordination chemistry of an asymmetric, potentially bidentate N,P donor with a central amidinium core (*S*-[N$^{Me}$CHP]$^+$) and its deprotonated, tridentate $N_{py}C_{NHC}P$ derivative, *S*-N$^{Me}$CP, has been explored with selected group 9, 10 and 11 metal ions. The chemistry with the monovalent group 11 metal ions is dominated by bridged species with the formation of head-to-tail dimers through μ-*N,P* and μ-*C,P* binding using *S*-[N$^{Me}$CHP]$^+$ and *S*-N$^{Me}$CP, respectively. The isolation of such species points to reduced chelate stability in these complexes. This did not extend to Ni(II), Pt(II) and Rh(I) systems where κ$^3$-coordinated complexes of *S*-N$^{Me}$CP were readily formed and isolated. Although both [Pt(κ$^3$-*N,C,P*-N$^{Me}$CP)Cl]$^+$ and [Rh(κ$^3$-*N,C,P*-N$^{Me}$CP)(CO)]$^+$ were prepared from precursors containing [κ-*P*-N$^{Me}$CHP]$^+$, only the former showed conformational selectivity upon establishment of tridentate coordination. The related [Ni(κ$^3$- *N,C,P*-N$^{Me}$CP)Cl]$^+$ was accessed by a different route and showed little conformational preference. Although it is evident that *S*-N$^{Me}$CP is a flexible ligand able to accommodate metal ions that desire chelating modes as well as those that tend to form bi-metallic (and higher) species, it remains unclear what conditions are required to promote conformational (and ultimately configurational) control in chelated forms. We are currently working to further understand these factors and are seeking to extend the bridged chemistry towards the controlled formation of mixed metal complexes.

## Experimental

**General information**: All synthetic procedures and manipulations were performed under dry nitrogen using standard Schlenk line techniques. Solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. All other chemicals were obtained commercially and used as received. The $^{31}$P{$^{1}$H}, $^{1}$H and $^{13}$C NMR spectra were recorded on a Jeol Eclipse 300 MHz or Bruker Avance 400, 500 or 600 MHz spectrometers and referenced to tetramethylsilane or $H_3PO_4$(δ = 0 ppm). Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer or at the EPSRC UK National Mass Spectrometry Facility at Swansea University.

**Crystallography**

Single-crystal XRD data for compounds **2**, **7**, **8**, **11** and **12** were collected on an Agilent SuperNova Dual Atlas 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. Generally, the crystal structures were solved and refined using SHELX.[23] 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. Data collection and structure solution for compound **10** were performed at the EPSRC National Crystallography Service as detailed.[24] Further details and the relevant CIF files for all structurally characterized complexes are included in the SI.

## Syntheses

### *S*-[N$^{Me}$CHP]PF$_6$.

A solution of 1*R*,3*S*-1,2,2-trimethyl-1,3-diaminocyclopentane, *R,S*-tmcp (1.00 g, 7 mmol), and 2-acetylpyridine (0.85 g, 1 mol equiv) in EtOH (50 ml) was heated close to boiling for 4 hrs. After cooling, the solvent was removed on a rotary evaporator and the residue redissolved in EtOH (50 ml). To this solution was added solid $NaBH_4$ (0.40 g, 10.5 mmol) portionwise over 20 mins. The resulting mixture was stirred overnight before adding conc. HCl (1 ml) carefully with stirring. After stirring for a further 30 mins the volatiles were removed in *vacuo*, the residue dissolved in water (50 ml) and the mixture made strongly basic by addition of solid NaOH. The diamine that oiled out of solution was extracted into $CH_2Cl_2$ (3 x 50 ml), which was subsequently dried over $MgSO_4$, filtered and all volatiles removed in *vacuo* to give the monopyridyl diamine as a pale yellow oil. $^1$H NMR analysis of this intermediate showed it to be a mixture of two isomers in a 3.5:1 ratio. The oil was dissolved in degassed EtOH (50 ml) under nitrogen and 2-(diphenylphosphino)carboxaldehyde (2.03 g, 7 mmol) added thereto. The solution was heated close to boiling for 12 hrs before cooling and removing the solvent in *vacuo*. The residue was dissolved in EtOH (50 ml) and solid $NaBH_4$ (0.40 g, 10.5 mmol) added portionwise over 20 mins. The resulting mixture was stirred overnight then conc. HCl (1 ml) added carefully with stirring. After stirring for a further 30 mins the volatiles were removed in *vacuo*, the residue dissolved in water (50 ml) and the mixture made strongly basic by addition of solid NaOH. The product that oiled out of solution was extracted into $CH_2Cl_2$ (3 x 50 ml), which was subsequently dried over $MgSO_4$, filtered and all volatiles removed in *vacuo* to give a pale yellow oil. The oil was taken into triethylorthoformate (15 ml), $NH_4PF_6$ (1.26 g, 1.1 equivs) added and the mixture heated at 120 °C for 2 hrs whereupon a white solid deposited. After standing overnight the mixture was filtered and the solid washed carefully with MeOH. Yield = 2.56 g (54%). A pure sample of the *S*-isomer could be obtained by recrystallization from MeOH, however, this was accompanied by appreciable loss of material so the complexation chemistry was performed with the original 9:1 *S*:*R* mixture. The compound is air-stable in the solid-state but was kept under $N_2$ as a precaution. The following spectroscopic details are for the *S* isomer. $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, *J* 4.4 Hz, 1H), 7.81 (s, 1H), 7.67 (dt, *J* 7.7, 1.8 Hz, 1H), 7.45-7.05 (m, 15H), 6.89 (dd, *J* 7.4, 4.4 Hz, 1H), 4.84 (q, *J* 6.9 Hz, 1H), 4.71 (m, 2H), 3.74 (d, *J* 5.1 Hz, 1H), 2.42 (m, 1H), 2.04 (m, 1H), 1.90 (m, 1H), 1.78 (m, 1H), 1.56 (d, *J* 7.0 Hz, 3H), 1.18 (s, 3H), 0.96 (s, 3H), 0.54 (s, 3H) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 100 MHz) δ 156.2 (C), 152.2 (d, *J* 2.6 Hz, CH), 149.8 (CH), 137.0 (d, *J* 5.5 Hz, C), 136.8 (d, *J* 3.6 Hz, C), 135.0 (d, *J* 2.5 Hz, C), 134.9 (d, *J* 2.7 Hz, C), 133.9 (d, *J* 9.7 Hz, CH), 133.7 (d, *J* 9.5 Hz, CH), 130.3 (d, *J* 4.6 Hz, CH), 130.1 (CH), 129.7 (CH), 129.5 (d, *J* 9.2 Hz, CH), 129.0 (d, *J* 2.8 Hz, CH), 128.9 (d, *J* 2.4 Hz, CH), 124.0 (CH), 122.4 (CH), 72.4 (C), 66.1 (CH), 63.9 (CH), 51.7 ($CH_2$, d, *J* 25.9 Hz), 40.9 (C), 39.8 ($CH_2$), 32.1 ($CH_2$), 21.2 ($CH_3$), 18.3 ($CH_3$), 16.7 ($CH_3$), 14.4 ($CH_3$) ppm. HRMS (ES): *m/z* 532.2880 (calc. 532.2882) [L – $PF_6$]$^+$, 100%. Anal. Calcd for $C_{35}H_{39}N_3P_2F_6$: C, 62.02; H, 5.81; N, 6.20. Found: C, 61.9; H, 5.8; N, 6.3.

### [Cu(κ-*P*-N$^{Me}$CHP)$_2$(MeCN)$_2$]BF$_4$.(PF$_6$)$_2$, 1

A solution of *S*-[N$^{Me}$CHP]PF$_6$ (100 mg, 0.15 mmol) and $[Cu(MeCN)_4]BF_4$ (24 mg, 0.075 mmol) in THF (5 mL) was stirred at RT overnight and the volatiles subsequently removed in *vacuo* to give a white solid that was dissolved in $CH_2Cl_2$, filtered and taken to dryness to give **1** as a white solid. Yield: 80 mg, 68%. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ (major isomer) 8.54 (d, *J* 4.2 Hz, 2H), 7.84 (s, 2H), 7.73 (dt, *J* 7.4, 1.6 Hz, 2H), 7.52 (t, *J* 7.4 Hz, 2H), 7.45 – 7.05 (m, 30H), 4.86 (q, *J* 6.9 Hz, 2H), 4.75 (d, *J* 16.7 Hz, 2H), 4.61 (d, *J* 16.7 Hz, 2H), 3.35 (d, *J* 4.8 Hz, 2H), 2.01 (m, 6H), 1.63 (d, *J* 6.9 Hz, 6H), 1.49 (m, 2H), 0.81 (s, 6H), 0.79 (s, 6H), 0.43 (s, 6H), ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 125.8 MHz) δ 155.4 (C), 154.1 (CH), 148.9 (CH), 138.0 - 122.1 (20 x aromatics), 71.4 (C), 63.4 (CH), 63.2 (CH), 50.9 (d, *J* 14.1 Hz, $CH_2$), 40.2 (C), 38.7 ($CH_2$), 31.3 ($CH_2$), 20.5 ($CH_3$), 16.2 ($CH_3$), 15.9 ($CH_3$), 13.0 ($CH_3$) ppm. $^{31}$P{$^1$H} NMR (121.7 MHz, $CD_2Cl_2$) δ -7.1 (br) ppm. HRMS (ES): *m/z* 1417.4324 (calc. 1417.4343) [M + $2PF_6$ - 2MeCN]$^+$, 100%. Unfortunately, despite multiple attempts, acceptable analytical data could not be obtained for this complex. Analyses were consistently low in carbon and, to some extent, nitrogen which may relate to MeCN loss prior to combustion.

### *H,T*-[Ag$_2$(μ-*N,P*-N$^{Me}$CHP)$_2$(μ-O$_3$SCF$_3$)$_2$](PF$_6$)$_2$, 2.OTf

A solution of *S*-[N$^{Me}$CHP]PF$_6$ (100 mg, 0.15 mmol) and AgOTf (38 mg, 0.15 mmol) in THF (5 mL) was stirred overnight at RT whereupon the desired complex precipitated as a white solid. The product was isolated by filtration, dried at the pump and recrystallized by the slow diffusion of diethyl ether into a chloroform solution of the complex. Yield: 88 mg, 64%. $^1$H NMR (250 MHz, $CD_2Cl_2$) δ 8.79 (d, *J* 4.5 Hz, 2H), 7.99 (t, *J* 7.7 Hz, 2H), 7.86 (s, 2H), 7.64 (d, *J* 7.7 Hz, 2H), 7.56 – 7.36 (m, 24H), 7.27 (t, *J* 7.6 Hz, 2H), 7.15 (br, 2H), 6.87 (dd, *J* 10.9, 8.1 Hz, 2H), 5.12 (q, *J* 6.9 Hz, 2H), 4.69 (br, 2H), 4.46 (br, 2H), 3.50 (br, 2H), 2.42 (m, 2H), 2.08 (br, 4H), 1.61 (d, *J* 6.9 Hz, 6H), 0.98 (s, 6H), 0.88 (s, 6H), 0.64 (s, 6H) ppm. $^{31}$P{$^1$H} NMR (121.7 MHz, Acetone-$d_6$) δ 14.1 (2 x d, $^1J_{P\text{-}Ag109}$ 751 Hz, $^1J_{P\text{-}Ag107}$ 650 Hz) ppm. MS (EI): *m/z* 1461.31 [L + LH + 2Ag + $PF_6$ + MeCN]$^+$, 55%.

### *H,T*-[Ag$_2$(μ-*N,P*-N$^{Me}$CHP)$_2$](BF$_4$)$_2$.(PF$_6$)$_2$, 2.BF$_4$

A solution of *S*-[N$^{Me}$CHP]PF$_6$ (100 mg, 0.15 mmol) and $AgBF_4$ (29 mg, 0.15 mmol) in THF (5 mL) was stirred overnight at RT whereupon the desired complex precipitated as a white solid. The product was isolated by filtration, dried at the pump and recrystallized by the slow diffusion of diethyl ether into a chloroform solution of the complex. Yield: 67 mg, 52%. $^1$H NMR (250 MHz, Acetone-$d_6$) δ 9.08 (d, *J* 5.2 Hz, 2H), 8.26 (s, 2H),

8.26 (t, *J* 7.8, 1.5 Hz, 2H), 8.20 – 7.55 (m, 30H), 7.08 (ddd, *J* 11.7, 7.7, 1.2 Hz, 2H), 5.44 (q, *J* 6.8 Hz, 2H), 4.80 (d, *J* 14.7 Hz, 2H), 4.36 (d, *J* 14.7 Hz, 2H), 2.97 (br, 2H), 2.71 (m, 2H), 2.25 (m, 2H), 1.84 (d, *J* 6.8 Hz, 6H), 1.01 (s, 12H), 0.79 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, $CD_2Cl_2$) δ 156.5 (C), 153.6 (CH), 149.7 (CH), 137.7 (C), 137.3 (d, *J* 12.6 Hz, C), 134.1 (d, *J* 17.5 Hz, C), 134.0 (d, *J* 16.6 Hz, C), 133.5 (d, *J* 4.9 Hz, CH), 131.5 (d, *J* 9.8 Hz, CH), 131.2 (CH), 129.6 (d, *J* 8.6 Hz, CH), 129.5 (d, *J* 8.5 Hz, CH), 129.0 (d, *J* 7.3 Hz, CH), 128.9 (d, *J* 6.4 Hz, CH), 123.9 (CH), 122.5 (CH), 72.0 (C), 65.0 (CH), 63.6 (CH), 50.8 ($CH_2$, d, *J* 21.2 Hz), 40.6 (C), 39.1 ($CH_2$), 31.4 ($CH_2$), 20.4 ($CH_3$), 16.9 ($CH_3$), 16.1 ($CH_3$), 13.7 ($CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.7 MHz, $CD_3CN$) δ 14.1 (2 x d, $^1J_{P\text{-}Ag109}$ 750.6 Hz, $^1J_{P\text{-}Ag107}$ 650.1 Hz) ppm. HRMS (ES): *m/z* 784.1578 (calc. 784.1574) [LH + Ag + $PF_6$]$^+$, 95%. Anal. Calcd for $C_{70}H_{78}N_6P_4B_2F_{20}Ag_2.0.5CH_2Cl_2$: C, 47.20; H, 4.47; N, 4.72. Found: C, 47.1; H, 4.5; N, 4.7.

**[Ag(κ-*P*-N$^{Me}$CHP)$_2$]BF$_4$.(PF$_6$)$_2$, 3**

A solution of *S*-[N$^{Me}$CHP]$PF_6$ (100 mg, 0.15 mmol) and $Ag(BF_4)$ (15 mg, 0.075 mmol) in THF (5 mL) was stirred overnight at RT and the volatiles removed in *vacuo* to give a white solid that was dissolved in $CH_2Cl_2$, filtered and taken to dryness to give **3** as a white solid. Yield: 99 mg, 86%. $^1H$ NMR (500 MHz, $CD_2Cl_2$) δ (major isomer) 8.62 (d, *J* 4.4 Hz, 2H), 8.06 (s, 2H), 7.79 (dt, *J* 7.7, 1.7 Hz, 2H), 7.64 – 7.29 (m, 30H), 7.07 (d, *J* 7.7, 2H), 5.06 (d, *J* 17.5 Hz, 2H), 4.86 (q, *J* 7.0 Hz, 2H), 4.47 (d, *J* 17.5 Hz, 2H), 3.73 (d, *J* 5.0 Hz, 2H), 2.30 (m, 2H), 2.13 (m, 2H), 2.06 (m, 2H), 1.67 (d, *J* 7.0 Hz, 6H), 1.55 (m, 2H), 0.92 (s, 6H), 0.65 (s, 6H), 0.52 (s, 6H), ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 125.8 MHz) δ 155.3 (C), 154.7 (br, CH), 149.0 (CH), 137.2 (CH), 134.1 (br, C), 133.3 (br, C), 132.7 (CH), 131.5 (CH), 130.8 (d, *J* 15.5 Hz, CH), 129.2 (br, CH), 129.0 (br, CH), 123.4 (CH), 121.9 (CH), 71.4 (C), 63.7 (CH), 63.2 (CH), 50.6 ($CH_2$, br), 40.6 (C), 38.5 ($CH_2$), 31.2 ($CH_2$), 20.6 ($CH_3$), 16.2 ($CH_3$), 16.1 ($CH_3$), 13.1 ($CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.7 MHz, $CD_2Cl_2$) δ 4.5 (vbr d, *J* ~ 475 Hz) ppm. For reasons unknown it proved impossible to obtain MS of the compound as, in all cases, only [N$^{Me}$CHP]$^+$ was observed. Anal. Calcd for $C_{70}H_{78}N_6P_4BF_{16}Ag$: C, 54.24; H, 5.07; N, 5.42. Found: C, 54.5; H, 5.3; N, 5.2.

***H,T*-[Ag$_2$(μ-*C,P*-N$^{Me}$CP)$_2$](PF$_6$)$_2$, 4**

*S*-[N$^{Me}$CHP][$PF_6$] (100 mg, 0.15 mmol) and AgOTf (38 mg, 0.15 mmol) were dissolved in THF (10 mL) and the solution cooled to -40 °C whereupon solid KHMDS (33 mg, 0.16 mmol) was added and the solution left to slowly warm to RT. After stirring at RT for 24 hrs the mixture was filtered and the solvent removed *in vacuo* to yield an off-white solid that was washed with diethyl ether (2 x 10 mL) and dried at the pump. Recrystallization was achieved via the slow diffusion of diethyl ether into a solution of the complex in THF to give solvent-dependent acicular crystals. Yield: 57 mg, 52%. $^1H$ NMR (500 MHz, $CD_2Cl_2$) δ 7.69 (dt, *J* 7.8, 1.7 Hz, 2H), 7.62 (dt, *J* 7.5, 1.7 Hz, 2H), 7.57 – 7.37 (m, 20H), 7.09 (m, 10H), 6.47 (dd, *J* 10.9, 7.9 Hz, 2H), 5.30 (m, 4H), 4.19 (d, *J* 17.7 Hz, 2H), 3.35 (d, *J* 4.4 Hz, 2H), 2.07 (m, 6H), 1.84 (d, *J* 7.4 Hz, 6H), 1.55 (m, 2H), 0.87 (s, 6H), 0.47 (s, 6H), 0.40 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CD_2Cl_2$) δ 208.9 (ddd, $J_{(Ag107/109)}$ 194.6, 225.3 Hz, $J_{C\text{-}P}$ 53.6 Hz, C), 158.0 (C), 149.3 (CH), 141.8 (d, *J* 12.1 Hz, C), 138.2 (CH), 134.7 (d, *J* 16.4 Hz, CH), 132.6 (CH), 131.8 (CH), 130.8 (CH), 130.1 (d, *J* 11.0 Hz, CH), 129.5 (d, *J* 10.3 Hz, CH), 127.7 (d, *J* 6.6 Hz, CH), 127.7 (d, *J* 40.2 Hz, C), 127.2 (d, *J* 40.6 Hz, C), 126.9 (d, *J* 32.0 Hz, C), 126.1 (d, *J* 7.2 Hz, CH), 124.1 (CH), 120.8 (CH), 70.1 (C), 68.2 (CH), 64.1 (CH), 55.6 (d, *J* 21.1 Hz, $CH_2$), 41.0 (C), 39.4 ($CH_2$), 32.2 ($CH_2$), 21.8 ($CH_3$), 18.3 ($CH_3$), 15.9 ($CH_3$), 14.4 ($CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.7 MHz, $CD_2Cl_2$) δ 3.39 (2 x d, $^1J_{P\text{-}Ag109}$ 539 Hz, $^1J_{P\text{-}Ag107}$ 468 Hz) ppm. HRMS (ES): *m/z* 784.1583 (calc. 784.1574) [LH + Ag + $PF_6$]$^+$, 95%; 638.1871 (calc. 638.1854) [L + Ag]$^+$, 90%. Anal. Calcd for $C_{70}H_{76}N_6P_4F_{12}Ag_2$: C, 53.59; H, 4.88; N, 5.36. Found: C, 53.4; H, 4.8; N, 5.3.

**[Au(κ-*P*-N$^{Me}$CHP)Cl]PF$_6$, 5**

A solution of *S*-[N$^{Me}$CHP]$PF_6$ (100 mg, 0.15 mmol) and Au(THT)Cl (48 mg, 0.15 mmol) in THF (5 mL) was stirred overnight at RT and the volatiles removed in *vacuo* to give a white solid that was triturated with dry diethyl ether and dried at the pump. Yield: 138 mg, 93%. $^1H$ NMR (400 MHz, $CD_2Cl_2$) δ (major isomer) 8.47 (d, *J* 4.3 Hz, 1H), 7.85 (s, 1H), 7.72 (dt, *J* 7.7, 1.7 Hz, 1H), 7.65 – 7.27 (m, 14H), 7.25 (ddd, *J* 7.7, 4.9, 1.0 Hz, 1H), 6.78 (ddd, *J* 13.0, 7.8, 1.0 Hz, 1H), 5.11 (d, *J* 15.2 Hz, 1H), 4.84 (q, *J* 7.0 Hz, 1H), 4.51 (d, *J* 15.2 Hz, 1H), 3.79 (d, *J* 4.6 Hz, 1H), 2.46 (m, 1H), 2.08 (m, 2H), 1.88 (m, 1H), 1.62 (d, *J* 7.0 Hz, 3H), 1.01 (s, 3H), 0.94 (s, 3H), 0.55 (s, 3H), ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 125.8 MHz) δ 155.2 (C), 153.3 (CH), 148.9 (CH), 137.1 (CH), 134.0 (d, *J* 14.1 Hz, C), 133.7 (d, *J* 14.0 Hz, C), 133.4 (d, *J* 7.2 Hz, C), 132.1 (br, C), 131.9 (d, *J* 2.0 Hz, CH), 129.3 (d, *J* 12.4 Hz, CH), 129.1 (d, *J* 12.1 Hz, CH), 128.5 (d, *J* 9.2 Hz, CH), 126.4 (d, *J* 33.9 Hz, CH), 125.9 (d, *J* 34.0 Hz, CH), 125.4 (d, *J* 57.4 Hz, CH), 123.4 (CH), 122.2 (CH), 72.1 (C), 63.8 (CH), 63.3 (CH), 49.7 (d, *J* 14.6 Hz, $CH_2$), 40.5 (C), 39.1 ($CH_2$), 31.6 ($CH_2$), 20.6 ($CH_3$), 16.9 ($CH_3$), 15.9 ($CH_3$), 14.3 ($CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.7 MHz, $CD_2Cl_2$) δ 25.0 ppm. HRMS (ES+): *m/z* 764.2230 (calc. 764.2236) [LH + Au + Cl]$^+$, 100%. Anal. Calcd for $C_{35}H_{39}N_3P_2F_6ClAu$: C, 46.19; H, 4.32; N, 4.62%. Found: C, 46.1; H, 4.3; N, 4.5%.

**[Au(κ-*P*-N$^{Me}$CHP)$_2$]Cl.(PF$_6$)$_2$, 6**

A solution of *S*-[N$^{Me}$CHP]$PF_6$ (100 mg, 0.15 mmol) and Au(THT)Cl (24 mg, 0.075 mmol) in THF (5 mL) was stirred overnight at RT and the volatiles removed in *vacuo* to give a white solid that was dissolved in a 1:1 mixture of $Et_2O$ and $CH_2Cl_2$ and set aside at -20° C. The microcrystalline solid that formed was isolated by filtration and dried at the pump. Yield: 105 mg, 64%. $^1H$ NMR (400 MHz, $d_6$-acetone) δ (major isomer) 8.66 (d, *J* 4.8 Hz, 2H), 8.40 (s, 2H), 7.90 (dt, *J* 7.6, 1.8 Hz, 2H), 7.73 (m, 4H), 7.65 – 7.38 (m, 26H), 6.99 (t, *J* 8.7, 2H), 5.13 (m, 4H), 5.07 (q, *J* 7.0 Hz, 2H), 3.88 (d, *J* 5.0 Hz, 2H), 2.57 (m, 2H), 2.17 (m, 2H), 2.08 (m, 2H), 1.93 (m, 1H), 1.74 (d, *J* 7.0 Hz, 3H), 1.19 (s, 3H), 1.06 (s, 3H), 0.77 (s, 3H), ppm. $^{13}C\{^1H\}$ NMR ($d_6$-acetone, 125.8 MHz) δ 157.7 (C), 155.4 (CH), 150.6 (CH), 139.6 (d, *J* 16.0 Hz, C), 138.6 (CH), 136.0 - 130.0 (3 x C, 13 x CH), 124.9 (CH), 123.6 (CH), 73.4 (C), 66.5 (CH), 64.8 (CH), 51.8 ($CH_2$, d, *J* 21.0 Hz), 42.0 (C), 40.5 ($CH_2$), 32.6 ($CH_2$), 21.7 ($CH_3$), 18.3 ($CH_3$), 17.4 ($CH_3$), 15.5 ($CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.7 MHz, $CD_2Cl_2$) δ 9.6 (br) ppm. HRMS (ES+): *m/z* 1441.4806 (calc. 1441.4759) [2LH + Au + $PF_6$ + Cl]$^+$, 100%. Anal. Calcd for $C_{70}H_{78}N_6P_4F_{12}ClAu$: C, 52.95; H, 4.95; N, 5.29%. Found: C, 52.8; H, 5.0; N, 5.3%.

***H,T*-[Au$_2$(μ-*C,P*-N$^{Me}$CP)$_2$](PF$_6$)$_2$, 7**

*S*-[N$^{Me}$CHP][$PF_6$] (100 mg, 0.15 mmol) and Au(THT)Cl (48 mg,

0.15 mmol) were dissolved in THF (10 mL) and the solution stirred for 20 mins at RT before adding solid KHMDS (33 mg, 0.16 mmol) in one portion. The solution was left to stir for a further 24 hrs at RT, filtered and the solvent removed *in vacuo* to yield an off-white solid that was washed with diethyl ether (2 x 10 mL) and dried at the pump. Recrystallization was achieved via the slow diffusion of diethyl ether into a saturated solution of acetone. Yield: 101 mg, 77%. $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 8.06 (d, *J* 5.0, 2H), 7.61 (dt, *J* 7.5, 1.7 Hz, 2H), 7.58 – 7.41 (m, 18H), 7.37 (dt, *J* 7.7, 1.8 Hz, 2H), 7.31 (d, *J* 7.1 Hz, 2H), 7.28 (d, *J* 7.4 Hz, 2H), 7.16 (d, *J* 7.8 Hz, 2H), 7.07 (dd, *J* 7.6, 4.8 Hz, 2H), 7.02 (t, *J* 7.4 Hz, 2H), 6.45 (dd, *J* 13.2, 7.6 Hz, 2H), 5.98 (q, *J* 7.2 Hz, 2H), 5.64 (d, *J* 18.3 Hz, 2H), 4.04 (d, *J* 18.3 Hz, 2H), 3.59 (d, *J* 4.0 Hz, 2H), 2.06 (m, 6H), 1.79 (d, *J* 7.2 Hz, 6H), 1.44 (m, 2H), 0.76 (s, 6H), 0.31 (s, 6H), 0.25 (s, 6H) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $CD_2Cl_2$) δ 206.4 (d, $J_{C\text{-}P}$ 119.0 Hz, C), 157.6 (C), 149.4 (CH), 141.9 (d, *J* 10.7 Hz, C), 137.1 (CH), 134.9 (d, *J* 13.3 Hz, C), 134.7 (br, C), 133.4 (CH), 132.8 (d, *J* 7.2 Hz, C), 132.6 (CH), 131.5 (CH), 130.3 (d, *J* 11.6 Hz, CH), 129.7 (d, *J* 11.6 Hz, CH), 127.7 (d, *J* 8.9 Hz, CH), 126.6 (d, *J* 9.0 Hz, CH), 126.5 (d, *J* 10.0 Hz, CH), 126.2 (d, *J* 11.0 Hz, CH), 125.5 (CH), 123.7 (CH), 121.4 (CH), 71.8 (C), 67.2 (CH), 62.8 (d, *J* 3.3 Hz, $CH_2$), 41.0 (C), 38.9 ($CH_2$), 31.8 ($CH_2$), 22.0 ($CH_3$), 17.8 ($CH_3$), 15.8 ($CH_3$), 14.1 ($CH_3$) ppm. $^{31}$P{$^{1}$H} NMR (121.7 MHz, $CD_2Cl_2$) δ 30.4 ppm. HRMS (ES+): *m/z* 1601.4553 (calc. 1601.4580) [2L + 2Au + $PF_6$]$^+$, 40%; 728.2456 (calc. 728.2463) [2L + 2Au]$^+$, 100%. Anal. Calcd for $C_{70}H_{76}N_6P_4F_{12}Au_2$.THF: C, 48.85; H, 4.65; N, 4.62%. Found: C, 48.9; H, 4.5; N, 4.6%.

**[Au(κ-*C*-N$^{Me}$CP)$_2$]PF$_6$, 8**

*S*-[N$^{Me}$CHP][$PF_6$] (100 mg, 0.15 mmol) and Au(THT)Cl (24 mg, 0.075 mmol) were added to THF (10 mL) and left to stir for 24 h at RT whereupon KHMDS (33 mg, 0.16 mmol) was added as a solid. The reaction mixture was left to stir for 24 h, the solution filtered and the volatiles removed *in vacuo* to give a light yellow solid. The solid was washed with diethyl ether (2 x 10 mL) and subsequently recrystallized via slow diffusion of diethyl ether into a saturated acetone solution of the complex. Yield: 93 mg, 81%. $^{1}$H NMR (500 MHz, $d_6$-acetone) δ 8.68 (d, *J* 4.1 Hz, 2H), 7.87 (br, 2H), 7.63 (br, 2H), 7.58 (br, 2H), 7.40 (m, 12H), 7.26 (m, 8H), 7.13 (t, *J* 5.3 Hz, 2H), 7.00 (br, 2H), 6.84 (dd, *J* 7.1, 4.7 Hz, 2H), 5.75 (q br, *J* 7.2 Hz, 2H), 5.20 (br, 4H), 3.64 (d, *J* 5.4 Hz, 2H), 2.35 (br, 2H), 2.21 (br, 2H), 1.85 (br, 2H), 0.81 (s, 12H), 0.33 (s, 6H) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $d_6$-acetone) δ 202.8 (C), 158.6 (C), 150.2 (CH), 143.4 (d, *J* 21.3 Hz, C), 138.0 (CH), 135.0 (d, *J*, 19.7 Hz, C), 134.6 (d, *J* 19.7 Hz, C), 134.2 (s, CH), 130.3 (d, *J* 12.6 Hz, CH), 129.8 (d, *J* 3.8 Hz, CH), 129.8 (d, *J* 3.6 Hz, CH), 128.5 (CH), 126.6 (br, C), 124.5 (CH), 123.9 (CH), 72.9 (C), 67.0 (CH), 62.7 ($CH_2$), 41.1 (C), 39.9 ($CH_2$), 33.1 ($CH_2$), 22.1 ($CH_3$), 18.4 ($CH_3$), 16.9 ($CH_3$), 16.0 ($CH_3$) ppm. $^{31}$P{$^{1}$H} NMR (121.7 MHz, $d_6$-acetone) δ -17.0 (br) ppm. HRMS (ES+): *m/z* 1291.5125 (calc. 1291.5171) [2L + Au + 2O]$^+$, 100%; 1275.5201 (calc. 1275.5222) [2L + Au + O]$^+$, 70%; 1259.5305 (calc. 1259.5272) [2L + Au]$^+$, 25%. Anal. Calcd for $C_{70}H_{76}N_6P_3F_6Au$: C, 59.83; H, 5.45; N, 5.98%. Found: C, 59.5; H, 5.4; N, 5.9%.

**[Ni(κ$^3$-*N,C,P*-N$^{Me}$CP)(η$^3$-C$_8$H$_{13}$)]PF$_6$, 9**

A solution of *S*-[N$^{Me}$CHP][$PF_6$] (100 mg, 0.15 mmol) and [Ni(1,5-COD)$_2$] (41 mg, 0.075 mmol) in THF (10 mL) was left to stir for 24 h at RT before removing all volatiles at the pump. The resulting yellow solid was washed with diethyl ether (2 x 10 mL) and dried at the pump. Yield: 115 mg, 91%. $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 8.45 (d, *J* 4.7 Hz, 1H), 7.57 (m, 6H), 7.45 (m, 1H), 7.41 (t, *J* 7.6 Hz, 1H), 7.25 (m, 5H), 7.15 (m, 3H), 6.98 (d, *J* 8.0 Hz, 1H), 6.78 (d, *J* 15.2 Hz, 1H), 5.09 (t, *J* 8.4 Hz, 1H), 4.79 (d, *J* 15.0 Hz, 1H), 4.54 (q, *J* 7.2 Hz, 1H), 4.44 (q, *J* 8.8 Hz, 1H), 3.89 (m, 1H), 3.59 (d, *J* 5.3 Hz, 1H), 2.09 (m, 1H), 1.80 (m, 1H), 1.73-0.94 (m, 12H), 1.44 (s, 3H), 0.87 (s, 3H), 0.75 (s, 3H), 0.20 (d, *J* 7.0 Hz, 3H) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $d_8$-THF) δ 202.1 (d, *J* 16.6 Hz, C), 159.3 (C), 146.7 (CH), 143.9 (d, *J* 15.2 Hz, C), 137.0 (CH), 135.6 (d, *J* 41.7 Hz, C), 135.2 (CH), 131.4 (d, *J* 11.0 Hz, C), 130.2 (CH), 129.5 (d, *J* 8.5 Hz, CH), 129.4 (d, *J* 11.0 Hz, CH), 129.0 (CH), 128.3 (C), 128.0 (d, *J* 9.7 Hz, CH), 127.5 (CH), 127.0 (d, *J* 6.3 Hz, CH), 120.7 (CH), 119.7 (CH), 109.5 (CH), 87.5 (CH), 75.9 (C), 68.7 (CH), 62.8 ($CH_2$), 61.8 ($CH_2$), 54.8 (d, *J* 9.5 Hz, $CH_2$), 40.1 (C), 37.1 ($CH_2$), 30.7 ($CH_2$), 30.3 ($CH_2$), 29.2 ($CH_2$), 28.4 ($CH_2$), 21.2 ($CH_3$), 19.5 ($CH_3$), 17.3 ($CH_3$), 16.4 ($CH_3$), 14.0 ($CH_3$) ppm. $^{31}$P{$^{1}$H} NMR (121.7 MHz, $CD_2Cl_2$) δ 13.1 ppm. HRMS (ES+): *m/z* 698.3165 (calc. 698.3174) [L + Ni + $C_8H_{13}$]$^+$, 100%. Unfortunately, despite multiple attempts, acceptable analytical data could not be obtained for this complex.

**[Ni(κ$^3$-*N,C,P*-N$^{Me}$CP)(Cl)]PF$_6$, 10**

A solution of **9** (40 mg, 0.47 x 10$^{-4}$ mol) was stirred in $CHCl_3$ (3 mL) under air for 24 h, filtered and the yellow solution taken to dryness. The residual solid was recrystallized from MeOH to give small orange crystals of **10**. Yield: 9 mg, 22%. $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ (major isomer) 8.83 (d, *J* 5.8 Hz, 1H), 8.0-7.0 (m, 17H), 6.25 (q, *J* 7.0 Hz, 1H), 4.81 (d, *J* 15.4 Hz, 1H), 2.92 (d, *J* 4.9 Hz, 1H), 1.80-0.74 (m, 4H), 1.47 (s, 3H), 1.35 (d, *J* 7.0 Hz, 3H), 0.74 (s, 3H), -0.30 (s, 3H) ppm. Due to the small scale of the reaction and the fact that the complex appeared unstable in solution over time (see main text) we were unable to get satisfactory $^{13}$C{$^{1}$H} NMR data for **10**. $^{31}$P{$^{1}$H} NMR (121.7 MHz, $CD_2Cl_2$) δ 8.0 (minor), 5.2 (major) ppm. HRMS (ES+): *m/z* 624.1868 (calc. 624.1845) [L + Ni + Cl]$^+$, 100%. Anal. Calcd for $C_{35}H_{38}N_3P_2F_6ClNi$: C, 54.54; H, 4.97; N, 5.45%. Found: C, 54.5; H, 5.1; N, 5.5%.

**[Pt(κ-*P*-N$^{Me}$CHP)$_2$Cl$_2$](PF$_6$)$_2$, 11**

A mixture of *S*-[N$^{Me}$CHP]$PF_6$ (100 mg, 0.15 mmol) and $K_2[PtCl_4]$ (31 mg, 0.075 mmol) was heated near reflux in EtOH (10 mL) for 18 hrs. After cooling, the white solid was isolated by filtration and recrystallized from MeCN. Yield: 65 mg, 53%. A second crop was obtained upon leaving the filtrate to slowly evaporate. Yield = 25%. $^{1}$H NMR (400 MHz, $CD_3CN$) δ (major isomer) 8.48 (d, *J* 4.8 Hz, 2H), 7.95 (m, 8H), 7.76 (dt, *J* 7.5, 1.3 Hz, 2H), 7.61 (m, 14H), 7.44 (t, *J* 7.5 Hz, 2H), 7.31 (m, 6H), 7.20 (m, 2H), 4.76 (d, *J* 16.0 Hz, 2H), 4.65 (d, J 16.0 Hz, 2H), 4.64 (obs, 2H), 3.57 (d, *J* 5.1 Hz, 2H), 2.05 (m, 4H), 1.78 (m, 4H), 1.45 (d, *J* 7.4 Hz, 6H), 1.00 (s, 6H), 0.95 (s, 6H), 0.57 (s, 6H), ppm. $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 75.6 MHz) δ 156.1 (C), 152.0 (d, J 2.9 Hz, CH), 149.7 (d, J 2.3 Hz, CH), 137.7 (C), 137.3 (C), 135.4 (br), 134.0 (br), 131.9 (br), 129.2 (br), 128.7 (CH), 124.0 (CH), 122.4 (CH), 72.2 (C), 65.6 (CH), 63.5 (CH), 50.4 (br, $CH_2$), 40.7 (C), 39.2 ($CH_2$), 31.8 ($CH_2$), 20.7 ($CH_3$), 17.5 ($CH_3$), 16.3 ($CH_3$), 13.8 ($CH_3$) ppm. $^{31}$P{$^{1}$H} NMR (121.7 MHz, $CD_3CN$) δ 17.1 ($^{1}J_{Pt}$ 2570 Hz) ppm. HRMS (ES+): *m/z* 664.7383 (calc. 664.7394) ([2LH + Pt + 2Cl]$^{2+}$, 100%. Anal. Calcd for $C_{70}H_{78}N_6P_4F_{12}Cl_2Pt$:

C, 51.86; H, 4.85; N, 5.18%. Found: C, 51.9; H, 5.0; N, 5.2%.

**[Pt(κ$^3$-*N,C,P*-N$^{Me}$CP)Cl]PF$_6$, 12**

A solution of **11** (100 mg, 6.2 x $10^{-5}$ mol) in THF (20 mL) was cooled to -78 $^0$C whereupon KHMDS (30 mg, 1.5 x $10^{-4}$ mol) was added as a solid. The solution was stirred for 20 mins at this temperature before being allowed to warm to RT and stirring continued overnight. On return the mixture was exposed to air and allowed to slowly evaporate on the bench. Initial powdery precipitates were filtered off and discarded before the desired complex was formed, after evaporation of most of the solvent, as large colourless crystals. Yield: 41 mg, 73%. $^1$H NMR (500 MHz, d$_6$-acetone) δ 9.04 (br, 1H), 8.20 (t, *J* 7.8 Hz, 1H), 7.80 (m, 3H), 7.63 (m, 6H), 7.35 (m, 6H), 7.21 (dd, *J* 11.0, 8.1 Hz, 1H), 6.82 (d, *J* 15.9 Hz, 1H), 4.99 (d, J 15.9 Hz, 1H), 4.95 (q, *J* 7.2 Hz, 1H), 3.46 (d, *J* 4.1 Hz, 1H), 2.28 (m, 1H), 1.88 (m obs, 1H), 1.88 (d, J 7.2 Hz, 3H), 1.53 (m, 1H), 1.27 (s, 3H), 0.90 (s, 3H), 0.44 (s, 3H) ppm. $^{13}$C{$^1$H} NMR (150 MHz, d$_6$-acetone) δ 170.6 (d, $^2J_{C\text{-}P}$ 6.7 Hz, C), 157.7 (C), 152.9 (CH), 143.2 (d, *J* 10.9 Hz, C), 141.5 (CH), 137.2 (d, *J* 3.2 Hz, CH), 134.2 (d, *J* 10.5 Hz, C), 132.7 (d, *J* 10.0 Hz, C), 131.8 (3 x CH), 131.5 (CH), 130.3 (d, *J* 2.4 Hz, CH), 129.0 (d, *J* 11.0 Hz, CH), 128.6 (d, *J* 8.6 Hz, CH), 127.8 (d, *J* 11.9 Hz, CH), 125.4 (d, *J* 2.8 Hz, CH), 123.7 (d, *J* 2.8 Hz, CH), 73.2 (C), 73.2 (CH), 68.2 (CH), 55.1 (d, *J* 8.9 Hz, CH$_2$), 41.3 (C), 38.8 (CH$_2$), 31.2 (CH$_2$), 22.3 (CH$_3$), 21.1 (CH$_3$), 17.3 (CH$_3$), 16.5 (CH$_3$) ppm. $^{31}$P{$^1$H} NMR (121.7 MHz, d$_6$-acetone) δ -7.8 ($^1J_{P\text{-}Pt}$ 3661 Hz) ppm. HRMS (ES+): *m/z* 761.2125 (calc. 761.2140) [L + Pt + Cl]$^+$, 100%. Anal. Calcd for $C_{35}H_{38}N_3P_2F_6ClPt.THF$: C, 47.83; H, 4.74; N, 4.29%. Found: C, 47.5; H, 4.6; N, 4.4%.

**[Rh(κ-*P*-N$^{Me}$CHP)(acac)CO]PF$_6$, 13**

To a solution of [Rh(acac)CO]$_2$ (35 mg, 0.075 mmol) in THF (10 mL) was added solid *S*-[N$^{Me}$CHP]PF$_6$ (100 mg, 0.15 mmol). The addition gave an immediate effervescence and after stirring for 10 mins the volatiles were removed in *vacuo* to give the desired compound as a yellow solid. Yield = 130 mg (96%). $^1$H NMR (400 MHz, CDCl$_3$) δ (major isomer) 8.46 (d, *J* 4.0 Hz, 1H), 7.88 (s, 1H), 7.71 (dt, *J* 7.9, 1.8 Hz, 1H), 7.63-7.31 (m, 14H), 7.22 (m, 1H), 6.82 (dd, *J* 11.1, 7.7 Hz, 1H), 4.76 (d, *J* 16.0 Hz, 2H), 5.74 (d, *J* 16.0 Hz, 1H), 4.88 (q, *J* 7.2 Hz, 1H), 4.82 (d, *J* 16.0 Hz, 1H), 3.88 (d, *J* 5.3 Hz, 1H), 2.26 (m, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.87 (m, 1H), 1.68 (m, 2H), 1.60 (d, *J* 7.2 Hz, 3H), 1.10 (s, 3H), 0.92 (s, 3H), 0.48 (s, 3H), ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75.6 MHz) δ 189.1 (dd, $^1J_{C\text{-}Rh}$ 75.4 Hz, $^2J_{C\text{-}P}$ 24.2 Hz, CO), 188.1 (C=O), 185.4 (C=O), 156.2 (C), 153.1 (CH), 149.6 (CH), 138.1 (CH), 137.1 (d, *J* 10.8 Hz, C), 135.2 (d, *J* 11.4 Hz, CH), 134.3 (d, *J* 11.4 Hz, C), 132.9 (d, *J* 6.0 Hz, C), 131.4 (CH), 131.1 (CH), 129.5 (d, *J* 6.6 Hz, C), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 124.1 (CH), 123.1 (CH), 101.0 (CH), 72.5 (C), 64.1 (CH), 63.9 (CH), 50.9 (d, *J* 13.2 Hz, CH$_2$), 41.1 (C), 39.3 (CH$_2$), 32.3 (CH$_2$), 27.7 (CH$_3$), 27.6 (CH$_3$), 21.6 (CH$_3$), 17.8 (CH$_3$), 16.7 (CH$_3$), 14.7 (CH$_3$) ppm. $^{31}$P{$^1$H} NMR (121.7 MHz, CD$_3$CN) δ 42.8 ($^1J_{P\text{-}Rh}$ 169 Hz) ppm. HRMS (ES+): *m/z* 762.2358 (calc. 762.2332) [LH + Rh + acac + CO]$^+$, 100%. Anal. Calcd for $C_{41}H_{46}N_3P_2O_3F_6Rh$: C, 54.25; H, 5.11; N, 4.63%. Found: C, 53.9; H, 5.4; N, 4.8%.

**[Rh(κ$^3$-*N,C,P*-N$^{Me}$CP)(CO)]PF$_6$, 14**

A solution of **13** (70 mg, 7.7 x $10^{-5}$ mol) in $C_6H_5Cl$ (1 mL) in a Young's type NMR tube was heated to 140 $^0$C (oil bath temperature) for two hours. Inspection of the yellow solution at this stage by $^{31}$P{$^1$H} NMR showed complete disappearance of the signal for **13** and the presence of two new doublets at 27.2 (minor, $^1J_{P\text{-}Rh}$ 162 Hz) and 25.4 (major, $^1J_{P\text{-}Rh}$ 165 Hz) ppm. The mixture was filtered and the volatiles removed in *vacuo* to yield an orange solid which was washed quickly with cold $CHCl_3$ (1 ml) to leave a microcrystalline solid. Yield: 25 mg, 40%. The compound could be recrystallized from MeOH in very low yield, sufficient for $^1$H and $^{31}$P{$^1$H} NMR spectroscopy and microanalysis only. $^1$H NMR (500 MHz, d$_6$-acetone, ~1:1 isomeric mixture) δ 9.13 (br, 1H), 9.05 (br, 1H), 8.16 (m, 2H), 7.87 – 7.36 (m, 30H), 7.16 (m, 2H), 7.05 (d, *J* 15.4 Hz, 1H), 6.90 (d, *J* 15.4 Hz, 1H), 5.92 (q, *J* 7.5 Hz, 1H), 4.92 (d, *J* 15.4 Hz, 1H), 4.85 (q, *J* 7.1 Hz, 1H), 4.69 (d, *J* 15.4 Hz), 3.29 (d, *J* 4.7 Hz, 1H), 3.26 (d, *J* 4.5 Hz, 1H), 2.20 (m, 1H), 1.82 (m, 4H), 1.59 (d, *J* 7.4 Hz, 3H), 1.46 (m, 3H), 1.46 (s, 3H), 1.23 (s, 3H), 0.88 (s, 3H), 0.85 (s, 3H), 0.29 (s, 3H), 0.01 (s, 3H) ppm. $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$, ~3:1 isomeric mixture: major isomer unless stated otherwise) δ 203.9 (dd, $^1J_{C\text{-}Rh}$ 40.4 Hz, $^2J_{C\text{-}P}$ 11.3 Hz, CO), 202.1 (dd, $^1J_{C\text{-}Rh}$ 38.2 Hz, $^2J_{C\text{-}P}$ 13.5 Hz, CO, minor), 192.4 (dd, $^1J_{C\text{-}Rh}$ 61.2 Hz, $^2J_{C\text{-}P}$ 13.9 Hz, C, minor), 191.4 (dd, $^1J_{C\text{-}Rh}$ 60.4 Hz, $^2J_{C\text{-}P}$ 16.6 Hz, C), 160.7 (C), 154.9 (CH), 143.9 (d, *J* 13.3 Hz, C), 140.1 (CH), 137.0 (CH), 135.0 – 128.0 (aromatics), 126.5 (CH), 71.8 (C), 71.3 (CH), 68.0 (CH), 56.8 (d, *J* 10.0 Hz, CH$_2$), 41.5 (C), 39.0 (CH$_2$), 31.4 (CH$_2$), 26.2 (CH$_3$), 21.9 (CH$_3$), 17.4 (CH$_3$), 16.9 (CH$_3$) ppm. $^{31}$P{$^1$H} NMR (121.7 MHz, d$_6$-acetone, ~1:1 isomeric mixture) δ 28.7 ($^1J_{P\text{-}Rh}$ 166 Hz), 27.2 ($^1J_{P\text{-}Rh}$ 165 Hz) ppm. HRMS (ES+): *m/z* 662.1829 (calc. 662.1808) [L + Rh + CO]$^+$, 100%. Anal. Calcd for $C_{36}H_{38}N_3P_2F_6ORh$: C, 53.54; H, 4.74; N, 5.20%. Found: C, 53.1; H, 4.6; N, 5.3%. It is of interest to note that if the reaction is performed in $C_6H_5Cl$ that has not been predried, the $PF_6^-$ anion is hydrolysed to $PO_2F_2^-$.

## 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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Graphical Abstract

Mono- and dimeric complexes of an asymmetric heterotopic P,CNHC,pyr ligand

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An asymmetric tridentate ligand with three different donors coordinates to Ag(I) and Au(I) to give discreet ligand-bridged dimers or $\kappa^1$-*C* species whilst full $\kappa^3$-binding occurs with Ni(II), Pt(II) and Rh(I).