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Synthesis and characterisation of isomeric cycloaurated complexes derived from the iminophosphorane Ph_3P=NC(O)Ph

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Abstract

Using different organomercury substrates, two isomeric cycloaurated complexes derived from the stabilised iminophosphorane Ph_3P=NC(O)Ph were prepared. Reaction of Ph_3P=NC(O)Ph with $PhCH_2Mn(CO)_5$ gave the manganated precursor $(CO)_4Mn(2\text{-}C_6H_4C(O)N{=}PPh_3)$, metallated on the C(O)Ph substituent, which yielded the organomercury complex $ClHg(2\text{-}C_6H_4C(O)N{=}PPh_3)$ by reaction with $HgCl_2$ in methanol. Transmetallation of the mercurated derivative with $Me_4N[AuCl_4]$ gave the cycloaurated iminophosphorane $AuCl_2(2\text{-}C_6H_4C(O)N{=}PPh_3)$ with an *exo* PPh_3 substituent. The *endo*-isomer $AuCl_2(2\text{-}C_6H_4Ph_2P{=}NC(O)Ph)$ [aurated on a PPh_3 ring] was obtained by an independent reaction sequence, involving reaction of the diarylmercury precursor $Hg(2\text{-}C_6H_4P(=NC(O)Ph)Ph_2)_2$

[prepared from the known compound $Hg(2\text{-}C_6H_4PPh_2)_2$ and $PhC(O)N_3$] with $Me_4N[AuCl_4]$. Both of the isomeric iminophosphorane derivatives were structurally characterised, together with the precursors $(2\text{-}HgClC_6H_4)C(O)N{=}PPh_3$ and $(CO)_4Mn(2\text{-}C_6H_4C(O)N{=}PPh_3)$. The utility of ^{31}P NMR spectroscopy in monitoring reaction chemistry in this system is described.

Keywords: Gold complexes; Cyclometallated ligands; Iminophosphoranes; X-ray crystal structure; Organomercury compounds

Introduction

Iminophosphoranes[1,2] $R_3P{=}NR'$ are attractive substrates for cyclometallation reactions;[3] the synthesis of the ligands is simple, and the chemical and physical properties of the resulting complexes can be tailored through appropriate choice of substituents R and R'. Furthermore, the presence of phosphorus confers a powerful NMR spectroscopic 'handle' that facilitates analysis of cyclometallation and ligand substitution reactions. We have been investigating the chemistry of cycloaurated complexes, where the presence of the cyclometallated ligand confers stability of the gold(III) centre towards reduction.[4] The majority of ligands in cycloaurated complexes bond through C and N donor atoms, though we have recently described syntheses of related cycloaurated complexes of phosphine-sulfides **1** and triphenylphosphine selenide **2**,[5] and a related cycloaurated phosphine oxide **3** has been reported.[6] Previously, we[7,8] and others[9] have reported routes to *N*,*C*-cycloaurated derivatives of 'simple' iminophosphoranes $Ph_3P{=}NR$ **4**, where R is an alkyl or aryl group. Subsequently, the biological activity of derivatives of the cycloaurated iminophosphorane **4** (R = Ph), formed by displacement of the chloride ligands, has recently been investigated in detail.[10] Related cationic *N*,*N*-bonded complexes (**5** and **6**) of pyridyl-functionalised

iminophosphoranes have also recently been synthesised, and their catalytic activity in C-O and C-C bond forming reactions evaluated.[11]

In this paper we report studies on the *N*-acyl substituted iminophosphorane $Ph_3P{=}NC(O)Ph$, which is stabilised towards hydrolysis (iminophosphoranes can hydrolyse to form phosphine oxide and amine). While there have been a number of studies on the coordination chemistry and cyclometallation (especially cyclopalladation) reactions of stabilised iminophosphoranes[12,13,14,15] little has been done on gold. Aguilar *et al*. demonstrated that when the stabilised iminophosphoranes $Ph_3P{=}NC(O)C_6H_4R$ (R = 2-Me, 4-MeO or 2-Br) were reacted with $K[AuCl_4]$ only the *N*-coordinated adducts **7** could be obtained, and heating did not result in cycloauration.[9] Here we describe how the use of two different organomercury derivatives of the stabilised iminophosphorane $Ph_3P{=}NC(O)Ph$ can be utilised in the synthesis of isomeric *exo* and *endo* cycloaurated derivatives, with the P atom respectively outside and inside the cycloaurated ring.

Results and discussion

Synthesis of stabilised *ortho*-mercurated and cycloaurated iminophosphoranes

The synthesis of stabilised iminophosphoranes is summarised in Scheme 1. $Ph_3P{=}NC(O)Ph$[16] was synthesised from Ph_3P and $PhC(O)N_3$ using the conventional Staudinger reaction, while $Ph_3P{=}NC(O)Bu^t$ was synthesised by a modified version of the same reaction. Frøyen had previously demonstrated that iminophosphoranes could conveniently be synthesised by the one-pot reaction between an acid chloride, sodium azide and triphenylphosphine.[17] We have found that exchanging the acid chloride for an anhydride

gives the same product, though the reaction times are longer because the anhydride is less reactive. $Ph_3P{=}NC(O)Bu^t$ has been recently synthesised for the first time through imido transfer reaction between the *N*-phenacyl iminodibenzothiophene **8** and PPh_3.[18] $Ph_3P{=}NC(O)Bu^t$ is an air stable crystalline solid with ^1H NMR and IR spectroscopic data consistent with the literature.

The cycloauration of stabilised iminophosphoranes (to give either the *exo* product metallated on the C(O)Ph group, or the *endo* compound metallated on a PPh_3 ring) is an interesting synthetic problem. Aguilar *et al.* have shown that the reaction of $Ph_3P{=}NC(O)C_6H_4R$ with $K[AuCl_4]$ gave the coordination compounds **7** where the nitrogen of the iminophosphorane acts as a simple two electron donor to the gold centre.[9] In cyclopalladation reactions of $Ph_3P{=}NC(O)R$ (R = Ph or substituted aryl), a strong preference for *exo* palladation was found, *i.e.* metallation of the *NC(O)*-bonded aryl ring.[12,13]

We considered that transmetallation from the corresponding *ortho*-mercurated complex would be a viable option for the synthesis of cycloaurated derivatives of $Ph_3P{=}NC(O)Ph$. However, the presence of the carbonyl group on the ligand means that synthesis of the *ortho*-mercurated compound *via* the *ortho*-lithiated compound (*i.e.* the method we previously used for the synthesis of simple *ortho*-mercurated iminophosphoranes)[7,8] is no longer viable. Unfortunately, attempts at direct mercuration of $Ph_3P{=}NC(O)Ph$ with $Hg(OAc)_2$ in refluxing THF, analogous to the successful direct mercuration of $Ph_3P{=}NPh$ on the *N*-phenyl ring,[19] were also unsuccessful. It is possible that the use of a stronger mercurating agent [*e.g.* $Hg(ClO_4)_2$ or $Hg(OTf)_2$] could produce the organomercury complex, however this was not attempted.

Organomanganese chemistry was therefore utilised. Cooney *et al.* have previously demonstrated that reaction of *ortho*-manganated acetophenone with $HgCl_2$ gave *ortho*-mercurated acetophenone **9** in good yields.[20] This compound cannot be synthesised by

conventional methods – again, the presence of a carbonyl group excludes the use of organolithium reagents and direct mercuration occurs at the methyl carbon due to keto-enol tautomerisation. We have recently extended this methodology to the synthesis of *ortho*-mercurated triphenylphosphine sulfide **10**, which was used in the synthesis of the cycloaurated phosphine sulfide **1a**.[5] Therefore *ortho*-manganation of Ph_3P=NC(O)Ph was investigated as a route to the *ortho*-mercurated derivative.

The simple iminophosphorane Ph_3P=NPh is known to undergo *ortho*-metallation with $PhCH_2Mn(CO)_5$ in refluxing heptane to give the manganated compound **11**.[21] However, the stabilised iminophosphorane Ph_3P=NC(O)Ph underwent manganation at the *ortho*-position of the *NC(O)*-bonded phenyl ring to give the *exo* isomer **12**, Scheme 2. The geometry was initially assigned by NMR and IR spectroscopies; the $^{31}P\{^1H\}$ NMR spectrum showed a single peak at 23.5 ppm, only slightly shifted from the free ligand (21.3 ppm), strongly suggesting *ortho*-metallation on the N-C(O)Ph group. The ^{31}P chemical shift of the *endo* isomer would be expected to be much further downfield because the phosphorus would be incorporated into a five-membered ring.[22] The $^{13}C\{^1H\}$ spectrum showed the correct number of signals for metallation of the *NC(O)*-bonded substituent. The carbonyl carbon of **12** appears at 189.0 ppm, shifted from the free ligand (δ 176.4 ppm), suggesting that the oxygen atom is coordinated to manganese. The C=O stretch in the IR spectrum of **12** occurs at 1488 cm^{-1}, (compared to 1595 cm^{-1} in the uncoordinated ligand), which suggests that the oxygen atom is coordinated. The mechanism of *ortho*-manganation is not well understood so it is unclear why metallation occurs on the *N*-acyl ring with the oxygen atom acting as the neutral donor. However the reaction of *N,N*-dialkylbenzamides with $PhCH_2Mn(CO)_5$ also gave the isomer with the oxygen coordinated to the manganese, though in this case the nitrogen would be expected to have poor donor ability.[23]

Unambiguous characterisation of **12** was achieved by an X-ray crystal structure determination. As suggested by spectroscopic investigations, the manganese is attached in the *ortho* position of the phenacyl ring with the carbonyl oxygen acting as a neutral donor. The molecular structure is shown in Figure 1, and selected bond lengths and angles are in Table 1. The five-membered manganacyclic ring is planar to within ±0.04 Å, with the adjacent C(11)-C(16) ring bent only 3.4° from the plane. The Mn(1)-C(1) and Mn(1)-O(1) distances of 2.0513(14) and 2.0458(10) Å respectively are in the range found for other cyclomanganated acyl-arenes[24] although usually the Mn-C bond is slightly shorter than the Mn-O one. The C(1)-O(1) bond of 1.277(2) Å is 0.032 Å longer than in the free ligand, consistent with the drop in the ν(CO) stretching frequency seen in the infrared spectrum of **12**. The P(1)-N(1) and C(1)-N(1) bond lengths are essentially unchanged from the free ligand,[25] as expected given their largely spectator role in the cyclometallation. The bite angle of the ligand acting as a *C*,*O*-donor is 80.17(5)°, very similar to that for the cycloaurated example **14** where there is *C*,*N*-coordination (see below); for the latter example the Au-C and Au-N distances are essentially the same as the Mn-C and Mn-O ones in **12**, so the puckering of the ring in **14** cannot be attributed to different sizes of the metal atoms. Rather it appears that the puckering arises from a twist to minimise the interactions between the adjacent C=O and N=P bonds in **14**. In **12** the CO ligand *trans* to the O donor has a noticeably shorter Mn-C and a longer C-O distance than the other three COs.

As anticipated, reaction of **12** with $HgCl_2$ in refluxing methanol gave the *ortho*-mercurated complex **13** in good yield, Scheme 2. Transmetallation with $Me_4N[AuCl_4]/Me_4NCl$, analogous to the method used for the synthesis of a range of other organo-gold compounds,[26,27] including simple cycloaurated iminophosphoranes,[7,8] gave the *exo*-cycloaurated complex **14**, also in good yield. Me_4NCl was added to transmetallation reaction mixtures to promote cycloauration by the formation of sparingly soluble

$(Me_4N)_2[Hg_2Cl_6]$.[26,27,28] Interestingly, the transmetallation reaction from **13** to **14** took two days – much slower than the corresponding reactions for simple iminophosphoranes,[7,8] presumably because the neighbouring carbonyl group pulls electron density away from the nitrogen atom.

To synthesise the *endo* isomer, containing a cycloaurated PPh_3 group, a different organomercury precursor was used; the synthetic procedure is depicted in Scheme 3. Bennett *et al*. have previously synthesised the diaryl-mercury compound **15**, which reacted with H_2O_2 or sulfur to give the phosphine oxide or sulfide respectively, and with $BH_3.SMe_2$ to give the borane complex.[29,30] When **15** was reacted with two equivalents of $PhC(O)N_3$, as per the Staudinger reaction, the new iminophosphorane derivative **16** was obtained. The reaction however took longer than expected - typically when a phosphine is added to the azide rapid evolution of nitrogen occurs. When the mechanism of the Staudinger reaction is considered,[2] it is not surprising that the reaction was sluggish – sterically bulky groups hinder the formation of the four-membered transition state. Again, transmetallation with $Me_4N[AuCl_4]$/$[Me_4N]Cl$ gave the *endo*-cycloaurated compound **17**, by a slower reaction than for the simple iminophosphoranes **4**.

In contrast, when $Ph_3P{=}NC(O)Bu^t$ was reacted with $PhCH_2Mn(CO)_5$ in refluxing heptane no reaction occurred, even after 8 hours. In addition, reaction of $Ph_3P{=}NC(O)Ph$ with two equivalents of $PhCH_2Mn(CO)_5$, in an attempt to make a di-cyclomanganated complex, only gave the mononuclear compound **12**. It appears that the P-bonded phenyl rings of stabilised iminophosphoranes are inert towards manganation.

X-ray crystal structures of ClHg(2-$C_6H_4C(O)N=PPh_3$) 13, $AuCl_2$(2-$C_6H_4C(O)N=PPh_3$) 14 and $AuCl_2$(2-$C_6H_4Ph_2P=NC(O)Ph$) 17

The molecular structures of **13**, **14** and **17** are shown in Figures 2, 3 and 4 respectively and important structural parameters are presented in Tables 2, 3 and 4.

ClHg(2-$C_6H_4C(O)N=PPh_3$) **13**

Interestingly, as with the manganese complex **12**, it is the oxygen that is interacting with the metal centre. In this example, the somewhat surprising preference for the hard oxygen donor may be because of steric reasons. The molecules of the mercury complex are packed together so that there are weak intermolecular interactions (3.143 Å) between the metal and a chlorine atom of a neighbouring molecule – in essence a dimeric structure is present in the solid state. If however there was an interaction between the nitrogen and the mercury the bulky triphenylphosphine group would twist around and sit over the metal centre and "clash" with the phenacyl phenyl ring on the adjacent molecule.

As expected, the coordination around the mercury shows only a slight deviation from linearity [the C(2)–Hg(1)–C(1) angle is 176.24(6)°]. Although the mercury–oxygen interaction is weak [Hg(1)···O(1) 2.6281(16) Å] it is significantly shorter than in mercurated ethyl benzoate **18** [2.734 Å][31] and the mercurated acetophenone **9** [2.712 Å][20] and is sufficient to keep the core of the molecule co-planar. Indeed the greatest deviations from the metallacyclic ring are C(1) and C(2) [which sit 0.0254(15) Å and 0.0338(13) Å above and below the plane of the ring respectively]. The PNCO network is also essentially planar but tilted upward at an angle of 6.84(17)° to the metallacyclic ring meaning that the molecule has a slight bow in it. This differs from the free ligand[25] where the phenyl ring is twisted 11.49° from the planar PNCO moiety. As in the uncoordinated ligand, the triphenylphosphine groups have a propeller-like arrangement.

$AuCl_2(2\text{-}C_6H_4C(O)N{=}PPh_3)$ **14**

In this complex, the nitrogen of the iminophosphorane is now coordinated to the gold centre. This preference for coordination of the softer nitrogen to the metal centre was also observed in the analogous cyclopalladated complex of the same ligand.[12] As for the palladium complex, the metallacyclic ring is not planar; instead it has an envelope conformation with the gold atom sitting 0.528(5) Å above the ring, resulting in a twisted (19.11°) PNCO network, as discussed above. The dangling triphenylphosphine moiety has phenyl groups which are arranged in a propeller-like fashion. Upon coordination to the gold there is an increase in both the P=N and N-C bond lengths when compared to the uncoordinated ligand[25] [P=N: 1.626(3) Å in ligand, 1.655(3) Å in **14**; N-C: 1.353(5) Å in ligand, 1.401(4) Å in **14**]. In addition the C=O bond length has decreased [from 1.245(5) Å in the ligand to 1.218(4) Å in the cycloaurated complex] – a similar change in bond lengths was observed in cyclopalladated complexes of such ligands.[12,13]

The coordination around the gold atom is square-planar, as expected; the bite angle of the ligand is 80.90(11)°. The greatest deviation from the mean coordination plane is C(2) which is 0.0906(15) Å below the plane. As with other crystallographically characterised gold(III) complexes containing *C,N* donor ligands[4] the Au-Cl(1) bond *trans* to the carbon (which has a higher *trans* influence) is longer [2.3694(8) Å] than the Au-Cl(2) bond *trans* to the nitrogen [2.2798(8) Å]. These compare favourably with Au-Cl bond distances of 2.368(1) and 2.289(1) Å in the phenyl-substituted iminophosphorane **4** (R = Ph).[7]

The compound crystallises with a molecule of dichloromethane held in the lattice by interaction of a hydrogen on the dichloromethane with the two chloride ligands on the gold complex (*i.e.* a bifurcated hydrogen bond).

$AuCl_2(2\text{-}C_6H_4Ph_2P{=}NC(O)Ph)$ **17**

The X-ray crystal structure of **17** confirms the formation of the *endo* isomer with the P=N bond contained in the metallacyclic ring. The environment around the gold is again essentially square planar, as expected. Like the simple iminophosphorane complexes **4**, the metallacyclic ring is severely puckered with the phosphorus and the nitrogen atoms showing the greatest deviations from the plane [P(1) sits 0.2369(9) Å below the plane, N(1) 0.2880(9) Å above the plane]. As a result of the puckering, the PNCO moiety is no longer planar and has a twist of 24.97°. The bite angle of the ligand [84.38(9)°] is similar to what is seen in the simple iminophosphorane complexes **4**.[7,8]

As with the *exo* isomer, the C=O bond length is shorter in the cycloaurated species [1.222(3) Å] than in the free ligand [1.245(5) Å].[25] This coincides with the P=N and N(1)-C(7) bonds becoming longer and is a result of loss of conjugation as the electron density is pulled onto the gold atom. The Au-Cl bond *trans* to C is again the longer of the two Au-Cl bond distances, 2.3578(6) Å *versus* 2.2721(6) Å. Furthermore, the Au-Cl bond *trans* to the nitrogen is slightly shorter in **17** than it is in **14** [2.2798(8) Å] and **4** (R = Ph) [2.289(1) Å], indicating than an acyl group on the nitrogen results in the nitrogen having a lower *trans* influence. The Au-N bond length of the *endo* complex [2.0321(18) Å] is significantly shorter than in the *exo* complex [2.048(3) Å] and is comparable to that in the cationic pyridyl analogue **6b** [2.030(3) Å].[11] The Au-Cl bond *trans* to the NC(O)Ph group of **6b** [bond length 2.2636 Å] is shorter than that in **14**, presumably reflecting the cationic nature of **6b**, and the lower *cis*-influence of a nitrogen-donor pyridyl ring in **6b** compared to a carbon-donor phenyl in **12**.

Spectroscopic and mass spectrometric characterisation of *ortho*-mercurated and cycloaurated stabilised iminophosphoranes

Spectroscopy of *exo* complexes

As observed previously,[7,8] $^{31}P\{^{1}H\}$ NMR spectroscopy is very indicative of the ligand coordination mode in iminophosphorane complexes. Figure 5 shows the $^{31}P\{^{1}H\}$ NMR spectra of the series of complexes *en route* to the *exo* cyclometallated complex **14**. The parent ligand Ph_3P=NC(O)Ph has a chemical shift of 21.3 ppm and the *ortho*-manganated complex **12** has a shift of 23.5 ppm – there is essentially no change between the two. This indicates that the phosphorus atom is not part of the metallacyclic ring.[22] There is little change on transmetallation to the *ortho*-mercurated complex – the chemical shift of **13** is 26.6 ppm. There are no satellite lines due to ^{199}Hg coupling, because the mercury atom is separated from the phosphorus by five bonds. The cycloaurated complex **14** has a chemical shift of 35.8 ppm which is slightly shifted from the manganese and mercury precursors. This is most probably because the nitrogen is now coordinated to gold so the phosphorus (which is directly bonded to the nitrogen) is slightly more deshielded than in the other examples where the oxygen is coordinated to the metal. The chemical shift in **14** is significantly further upfield than in the simple cycloaurated iminophosphorane **4** (R = Ph) (65.5 ppm)[7] where the phosphorus is in the five-membered ring.

Infrared spectroscopy can also be used to determine the binding mode of iminophosphoranes; IR data are summarised in Table 5. It has previously been reported that when stabilised iminophosphoranes form cyclometallated complexes with a nitrogen-metal bond the P=N stretch moves to lower energies and the C=O stretch moves to slightly higher energies.[12,14] In Ph_3P=NC(O)Ph the P=N stretch occurs at 1341 cm^{-1} and the C=O stretch at 1595 cm^{-1}. The *ortho*-mercurated *exo* complex **13** (in which the nitrogen is not involved in

any interactions with the mercury) has a P=N stretch at 1340 cm^{-1} and a C=O stretch at 1532 cm^{-1}. The P=N shift remains relatively unchanged, but the C=O shift has moved to lower wavenumbers because of a slight interaction with the mercury. In contrast, the cycloaurated *exo* complex **14** has a P=N stretch at 1285 cm^{-1}; the significant shift to lower wavenumbers is consistent with the ligand coordinating through the nitrogen atom. The C=O stretch occurs at 1684 cm^{-1}, the higher energy stretch associated with the loss of conjugation that is present in the ligand.

Spectroscopy of *endo* complexes

The diarylmercury complex **15** has a $^{31}P\{^{1}H\}$ NMR chemical shift of 0.4 ppm and the di-iminophosphorane **16** undergoes a significant shift to 27.4 ppm upon conversion of P(III) to P(V). The chemical shift is very close to the *exo* isomer **13** but now ^{199}Hg satellite peaks can also be seen – the $^{3}J_{HgP}$ coupling constant (171 Hz) indicates that the mercury is attached at the *ortho* position of one of the *P*-bonded phenyl rings [compare **4** (R = Ph) where $^{3}J_{HgP}$ = 326 Hz]. Upon transmetallation to gold in **17** there is a significant downfield shift (of approximately 30 ppm) as the phosphorus is now in a five-membered ring. The chemical shift of 60.5 ppm is now comparable with the cycloaurated iminophosphorane **4** (R = Ph) (65.6 ppm).[7] Figure 6 shows the $^{31}P\{^{1}H\}$ chemical shifts associated with the *endo* complexes.

The *endo* series of complexes show different IR spectroscopic behaviour (Table 5) to that of the *exo* isomers. The P=N stretch of **16** occurs at 1323 cm^{-1}, approximately 20 cm^{-1} lower than in the free ligand, which suggests an interaction between the nitrogen and the mercury. Upon transmetallation to gold, there is a further decrease to 1282 cm^{-1}. This pattern is analogous to that seen in the simple iminophosphorane complexes **4**.[7,8] There is little change between the C=O stretches in Ph_3P=NC(O)Ph and the *ortho*-mercurated complex **16**,

however in the cycloaurated complex **17** the C=O stretch occurs at higher wavenumbers, again because of loss of conjugation in the metallacycle.

Conclusion

By appropriate choice of organomercury precursor we have synthesised two isomeric cycloaurated complexes of the iminophosphorane $Ph_3P{=}NC(O)Ph$. Specifically, by controlling the order of metallation with respect to phosphine → iminophosphorane conversion, the site of metallation can be controlled. Organomanganese chemistry has been successfully used in the synthesis of organo-mercury and –gold complexes, extending the synthetic utility of these reagents.

Experimental

Safety note: CAUTION! Azides are hazardous materials that should be handled with caution, using appropriate procedures.[32]

Materials and methods

The compounds $PhCH_2Mn(CO)_5$[24] and $Hg(2\text{-}C_6H_4PPh_2)_2$[29,30] were prepared by literature methods. $Ph_3P{=}NC(O)Ph$ was prepared from PPh_3 and $PhC(O)N_3$ by the Staudinger reaction.[15] Pivalic anhydride (Aldrich), tetramethylammmonium chloride (BDH) and sodium azide (BDH) were used as supplied; other reagents were at least of LR grade.

General experimental techniques were as previously described.[33] Metallation reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques,[34] with light also being excluded in the case of cycloauration reactions. High resolution ESI mass spectra were recorded on a Bruker Daltonics MicrOTOF instrument, calibrated using a

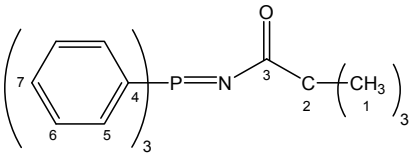
solution of sodium formate. Samples were dissolved in a few drops of CH_2Cl_2 prior to dilution with methanol, and infused by a syringe pump.

Synthesis of $[Me_4N][AuCl_4]$

To an aqueous (50 mL) solution of $H[AuCl_4].4H_2O$ (2.00 g, 4.85 mmol) excess $[Me_4N]Cl$ (0.65 g) was added. A yellow precipitate formed immediately and the resulting suspension was stirred for a further 30 min. The mixture was filtered and the bright yellow solid washed with copious amounts of water followed by ethanol and diethyl ether. Drying under vacuum gave $[Me_4N][AuCl_4]$ in near quantitative yields.

Synthesis of $Ph_3P{=}NC(O)Bu^t$

Pivalic anhydride (2.0 mL, 9.9 mmol) and sodium azide (0.769 g, 11.8 mmol) were stirred in dry, degassed acetone (100 mL) for 10 min. PPh_3 (2.59 g, 9.9 mmol) was added in one portion and the resulting solution was stirred at room temperature for 72 h. The solvent was removed under reduced pressure and the solid extracted into dichloromethane (40 mL) and filtered. Diethyl ether (60 mL) was added and the solution was stored at -25°C. $Ph_3P{=}NC(O)Bu^t$ crystallised as white crystals (2.20 g, 62%). Found: C 76.3, H 6.8, N 3.8; $C_{23}H_{24}NOP$ requires C 76.4, H 6.7, N 3.9%. NMR: ^{1}H δ 1.29 (s, 9H, H-1), 7.44 (m, 6H, H-5), 7.53 (m, 3H, H-7), 7.74 (m, 6H, H-6); $^{13}C\{^1H\}$ δ 28.8 (s, C-1), 41.4 (d, $^3J_{PC}$ 17.2 Hz, C-2), 128.6 (d, $^3J_{PC}$ 12.0 Hz, C-6), 129.2 (d, $^1J_{PC}$ 98.8 Hz, C-4), 131.9 (d, $^4J_{PC}$ 2.9 Hz, C-7), 133.1 (d, $^2J_{PC}$ 9.8 Hz, C-5), 190.6 (d, $^2J_{PC}$ 11.0 Hz, C-3); $^{31}P\{^1H\}$ δ 18.3 ppm. ESI-MS: *m/z*: 362.167 (100%, $[M+H]^+$, calc 362.169), 384.148 (47%, $[M+Na]^+$, calc 384.149), 745.308 (21%, $[2M+Na]^+$, calc 745.308). IR: ν(P=N) 1322 (vs), ν(C=O) 1580 (s) cm^{-1}.



NMR labelling scheme for $Ph_3P{=}NC(O)Bu^t$

Synthesis of $(CO)_4Mn(2\text{-}C_6H_4C(O)N{=}PPh_3)$ 12

$PhCH_2Mn(CO)_5$ (0.200 g, 0.70 mmol) and $Ph_3P{=}NC(O)Ph$ (0.268 g, 0.70 mmol) were refluxed in *n*-heptane (30 mL) for 2 h. While hot, the solution was filtered and the yellow filtrate reduced in volume until signs of crystallisation. Storage at -20 °C gave yellow crystals of $(CO)_4Mn(2\text{-}C_6H_4C(O)N{=}PPh_3)$ (0.246 g, 65%). Found: C 64.8, H 3.8, N 2.6; $C_{29}H_{19}NO_5PMn$ requires C 63.6, H 3.5, N 2.6%. NMR (see Scheme 4 for the labelling system): ^{1}H δ 7.13 (t, 1H, H-5), 7.33 (t, 1H, H-4), 7.51 (m, 6H, H-10), 7.62 (m, 3H, H-11), 7.75 (m, 6H, H-9), 7.90 (d, 1H, H-3), 8.09 (d, 1H, H-6); $^{13}C\{^1H\}$ δ 123.1 (C-5), 127.2 (d, $^1J_{PC}$ 100.1 Hz, C-8), 128.9 (d, $^3J_{PC}$ 12.6 Hz, C-10), 129.3 (C-6), 131.8 (C-4), 132.9 (d, $^4J_{PC}$ 3.1 Hz, C-11), 133.2 (d, $^2J_{PC}$ 10.1 Hz, C-9), 140.9 (C-3), 143.3 (d, $^3J_{PC}$ 16.6 Hz, C-1), 181.2 (d, $^4J_{PC}$ 2.8 Hz, C-2), 189.0 (d, $^2J_{PC}$ 10.7 Hz, C-7), 213.4 (C=O), 214.8 (C=O), 221.8 (C=O); $^{31}P\{^1H\}$ δ 23.5 ppm. ESI-MS (-ve): *m/z*: 553.958 (100%, $[M\text{-}CO+Cl]^-$, calc 554.012), 581.949 (90%, $[M+Cl]^-$, calc 582.007), 525.968 (25%, $[M\text{-}2CO+Cl]^-$, calc 526.017). IR: ν(P=N) 1341 (vs), ν(C=O) 1488 (s) cm^{-1}.

Synthesis of $ClHg(2\text{-}C_6H_4C(O)N{=}PPh_3)$ 13

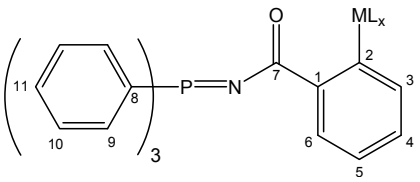
$(CO)_4Mn(2\text{-}C_6H_4C(O)N{=}PPh_3)$ **12** (0.200 g, 0.37 mmol) and $HgCl_2$ (0.199 g, 0.73 mmol) were refluxed in methanol (20 mL) for 5 h during which time the yellow solution became colourless and a white solid formed. The mixture was cooled in ice then filtered and the white solid washed well with cold methanol. The solid was redissolved in dichloromethane (50 mL) and filtered through a column of celite. The resulting clear solution was reduced in volume

(~5 mL) and diethyl ether was added dropwise until the solution went cloudy. Storage at -20 °C gave white crystals of ClHg(2-$C_6H_4C(O)N{=}PPh_3$) (0.129 g, 57%). Found: C 48.9, H 3.1, N 2.3; $C_{25}H_{19}NOPClHg$ requires C 48.7, H 3.1, N 2.3%. NMR (see Scheme 4 for the labelling system): ^{1}H δ 7.36 (m, 1H, H-5), 7.38 (m, 1H, H-3), 7.48 (m, 1H, H-4), 7.51 (m, 6H, H-10), 7.60 (m, 3H, H-11), 7.79 (m, 6H, H-9), 8.49 (m, 1H, H-6); ^{13}C{^{1}H} δ 127.5 (d, $^1J_{PC}$ 99.9 Hz, C-8), 128.3 (C-5), 129.0 (d, $^3J_{PC}$ 12.3 Hz, C-10), 130.8 (C-6), 131.5 (C-4), 132.7 (d, $^4J_{PC}$ 2.5 Hz, C-11), 133.5 (d, $^2J_{PC}$ 10.5 Hz, C-9), 136.2 (C-3), 142.9 (d, $^3J_{PC}$ 18.5 Hz, C-1), 150.1 (d, $^4J_{PC}$ 3.7 Hz, C-2), 177.6 (d, $^2J_{PC}$ 7.7 Hz, C-7); ^{31}P{^{1}H} δ 26.6 ppm. ESI-MS: *m/z*: 640.044 (100%, $[M+Na]^+$, calc 640.049), 656.018 (60%, $[M+K]^+$, calc 656.022), 618.062 (20%, $[M+H]^+$, calc 618.067), 1255.097 (8%, $[2M+Na]^+$, calc 1255.106), 1197.140 (4%, $[2M-Cl]^+$, calc 1197.149). IR: ν(P=N) 1340 (vs), ν(C=O) 1532 (s) cm^{-1}.

Preparation of $AuCl_2$(2-$C_6H_4C(O)N{=}PPh_3$) 14

ClHg(2-$C_6H_4C(O)N{=}PPh_3$) **13** (0.100 g, 0.16 mmol), [Me_4N][$AuCl_4$] (0.067 g, 0.16 mmol) and [Me_4N]Cl (0.018 g, 0.17 mmol) were stirred in acetonitrile (10 mL) for 2 d in a foil-covered flask. The solvent was removed under reduced pressure and the yellow solid extracted into dichloromethane (3 × 10 mL) and filtered. The yellow solution was reduced in volume (~5 mL) and subsequent addition of diethyl ether and storage at -20 °C gave pale yellow crystals of $AuCl_2$(2-$C_6H_4C(O)N{=}PPh_3$) as the dichloromethane solvate (0.065 g, 62%). Found: C 42.7, H 2.9, N 1.9, $C_{25}H_{19}NOPCl_2Au \cdot CH_2Cl_2$ requires C 42.6, H 2.9, N 1.9%. NMR (see Scheme 4 for the labelling system): ^{1}H δ 7.29 (d, 1H, H-6), 7.37 (m, 1H, H-4), 7.40 (m, 1H, H-5), 7.58 (m, 6H, H-10), 7.69 (m, 3H, H-11), 7.95 (m, 6H, H-9), 8.10 (d, 1H, H-3); ^{13}C{^{1}H} δ 124.0 (d, $^1J_{PC}$ 103.3 Hz, C-8), 128.5 (C-6), 129.2 (d, $^3J_{PC}$ 13.6 Hz, C-10), 130.1 (C-3), 130.3 (C-5 and C-2), 133.6 (C-4), 133.8 (d, $^4J_{PC}$ 2.6 Hz, C-11), 133.9 (d,

$^{2}J_{PC}$ 10.6 Hz, C-9), 144.9 (C-1), 179,5 (d, $^{2}J_{PC}$ 3.9 Hz, C-7); $^{31}P\{^{1}H\}$ δ 35.8 ppm. ESI-MS: *m/z*: 612.059 (100%, $[M\text{-}Cl]^{+}$, calc 612.055). IR: ν(P=N) 1285 (vs), ν(C=O) 1684 (s) cm^{-1}.



Scheme 4 NMR labelling scheme for the *exo*-series complexes **12** (ML_x = $Mn(CO)_4$), **13** (ML_x = HgCl) and **14** (ML_x = $AuCl_2$).

Preparation of $Hg(2\text{-}C_6H_4P(=NC(O)Ph)Ph_2)_2$ 16

To a degassed solution of $PhC(O)N_3$ (0.081 g, 0.55 mmol) in dry dichloromethane (10 mL), $Hg(2\text{-}C_6H_4PPh_2)_2$ **15** (0.200 g, 0.28 mmol) was added and the resulting mixture was stirred at room temperature under nitrogen for 24 h. The solution was reduced in volume and diethyl ether was added until signs of crystallisation. Storage at -20 °C gave white microcrystals of $Hg(2\text{-}C_6H_4P(=NC(O)Ph)Ph_2)_2$ (0.207 g, 77%). Found: C 62.2, H 4.1, N 2.8; $C_{50}H_{38}P_2N_2O_2Hg$ requires C 62.5, H 4.0, N 2.9%. NMR: ^{1}H δ 7.09 (m, 3H), 7.22 (m, 4H), 7.40 (m, 4H), 7.51 (m, 2H), 7.72 (m, 4H), 8.12 (d, 2H); $^{31}P\{^{1}H\}$ δ 27.4 ($^{3}J_{HgP}$ 171 Hz) ppm. ESI-MS: *m/z*: 985.205 (100%, $[M+Na]^{+}$, calc 985.202), 963.224 (21%, $[M+H]^{+}$, calc 963.220). IR: ν(P=N) 1323 (vs), ν(C=O) 1598 (s) cm^{-1}.

Preparation of $AuCl_2(2\text{-}C_6H_4Ph_2P=NC(O)Ph)$ 17

$Hg(2\text{-}C_6H_4P(=NC(O)Ph)Ph_2)_2$ **16** (0.100 g, 0.10 mmol), $[Me_4N][AuCl_4]$ (0.086 g, 0.21 mmol) and $[Me_4N]Cl$ (0.011g, 0.10 mmol) were stirred in acetonitrile (10 mL) for 7 d in a foil-covered flask. Work-up as for **14** gave yellow microcrystals (0.091 g, 68%). NMR: ^{1}H δ 7.18 (m, 1H), 7.41 (m, 3H), 7.51 (m, 2H), 7.60 (m, 4H), 7.72 (m, 2H), 7.88 (m, 4H), 8.01 (d, 2H),

8.26 (d, 1H); $^{31}P\{^{1}H\}$ δ 60.5 ppm. ESI-MS: *m/z*: 612.052 (100%, $[M-Cl]^+$, calc 612.055), 1319 (36%, $[2M+Na]^+$, calc 1319.037), 670.013 (16%, $[M+Na]^+$, calc 670.020). IR: ν(P=N) 1282 (vs), ν(C=O) 1641 (vs) cm^{-1}.

Attempted cyclomanganation of $Ph_3P=NC(O)Bu^t$

Following a similar procedure for the synthesis of **12**, the attempted reaction of $Ph_3P=NC(O)Bu^t$ and $PhCH_2Mn(CO)_5$ was monitored by IR spectroscopy and thin layer chromatography; after refluxing for 8 h only unreacted $PhCH_2Mn(CO)_5$ was observed, together with some brown insoluble matter that is typically associated with slow thermal decomposition of refluxing solutions of $PhCH_2Mn(CO)_5$.

X-ray crystal structure determinations

Crystals of **13** and **14** were grown by adding diethyl ether to a dichloromethane solution of the compound and storing at -20 °C, while single crystals of **12** and **17** were grown by vapour diffusion of diethyl ether into a dichloromethane solution of the compound at room temperature. Crystallographic details are presented in Table 6.

Data collection

Unit cell dimensions and intensity data were collected at either the University of Canterbury on a Bruker Nonius Apex II CCD diffractometer (**17**) or the University of Auckland on a Bruker Smart CCD diffractometer (**12**, **13** and **14**). Absorption correction of the data was carried out by semi-empirical methods (SADABS).[35]

Solution and refinement

Structures were solved by either the direct methods (**12**) or the Patterson options of SHELXS-97[36] and were developed routinely. Full-matrix least-squares refinement (SHELXL-97)[37] was based upon F_o^2 with all non-hydrogen atoms refined anisotropically and hydrogen atoms in calculated positions.

Supplementary material

Crystallographic data for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. (746296) **12**, (746299) **13**, (746297) **14** and (746298) **17**. Copies of these data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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Table 1 Selected bond lengths (Å) and angles (°) for the complex $(CO)_4Mn(2\text{-}C_6H_4C(O)N{=}PPh_3)$ **12** with esds in parentheses

Atoms	Lengths (Å)	Atoms	Angles (°)
Mn(1) – C(11)	2.0513(14)	O(1) – Mn(1) – C(11)	80.17(5)
Mn(1) – O(1)	2.0458(10)	Mn(1) – O(1) – C(1)	115.92(8)
P(1) – N(1)	1.6213(12)	Mn(1) – C(11) – C(16)	111.82(10)
C(1) – N(1)	1.333(2)	N(1) – C(1) – O(1)	123.84(12)
C(1) – O(1)	1.277(2)	P(1) – N(1) – C(1)	118.88(9)

Table 2 Selected bond lengths (Å) and angles (°) for the complex ClHg(2-$C_6H_4C(O)N{=}PPh_3$) **13** with esds in parentheses

Atoms	Lengths (Å)	Atoms	Angles (°)
P(1) – N(1)	1.620(2)	C(2) – Hg(1) – Cl(1)	176.24(6)
N(1) – C(7)	1.346(3)	Hg(1) – C(2) – C(1)	118.83(17)
C(7) – O(1)	1.250(3)	C(2) – C(1) – C(7)	120.9(2)
C(7) – C(1)	1.515(3)	C(1) – C(7) – O(1)	119.80(19)
C(1) – C(2)	1.398(3)	C(7) – O(1) – Hg(1)	106.40(14)
C(2) – Hg(1)	2.063(2)	C(1) – C(7) – N(1)	114.86(19)
Hg(1) – Cl(1)	2.3293(6)	C(7) – N(1) – P(1)	118.37(16)
Hg(1) --- O(1)	2.6281(16)	N(1) – C(7) – O(1)	125.3(2)

Table 3 Selected bond lengths (Å) and angles (°) for the complex $AuCl_2(2\text{-}C_6H_4C(O)N{=}PPh_3)$ **14**, with esds in parentheses

Atoms	Lengths (Å)	Atoms	Angles (°)
P(1) – N(1)	1.655(3)	Cl(1) – Au(1) – Cl(2)	90.18(3)
N(1) – C(7)	1.401(4)	Cl(2) – Au(1) – C(2)	93.24(9)
C(7) – O(1)	1.218(4)	C(2) – Au(1) – N(1)	80.90(11)
C(7) – C(1)	1.481(4)	N(1) – Au(1) – Cl(1)	95.55(7)
C(1) – C(2)	1.395(4)	Au(1) – C(2) – C(1)	111.7(2)
C(2) – Au(1)	2.025(3)	C(2) – C(1) – C(7)	117.0(3)
Au(1) – Cl(1)	2.3694(8)	C(1) – C(7) – N(1)	112.0(3)
Au(1) – Cl(2)	2.2798(8)	C(1) – C(7) – O(1)	125.7(3)
Au(1) – N(1)	2.048(3)	O(1) – C(7) – N(1)	122.3(3)
		C(7) – N(1) – Au(1)	112.8(2)
		C(7) – N(1) – P(1)	119.5(2)
		P(1) – N(1) – Au(1)	127.68(16)

Table 4 Selected bond lengths (Å) and angles (°) for the complex $AuCl_2(2\text{-}C_6H_4Ph_2P{=}NC(O)Ph)$ **17**, with esds in parentheses

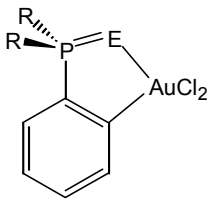
Atoms	Lengths (Å)	Atoms	Angles (°)
Au(1) – Cl(1)	2.3578(6)	Cl(1) – Au(1) – Cl(2)	90.89(2)
Au(1) – Cl(2)	2.2721(6)	Cl(2) – Au(1) – C(12)	92.59(7)
Au(1) – C(12)	2.039(3)	C(12) – Au(1) – N(1)	84.38(9)
Au(1) – N(1)	2.0321(18)	N(1) – Au(1) – Cl(1)	91.97(6)
P(1) – N(1)	1.645(2)	C(12) – C(11) – P(1)	115.72(17)
N(1) – C(7)	1.401(3)	C(11) – P(1) – N(1)	99.18(10)
C(7) – O(1)	1.222(3)	P(1) – N(1) – Au(1)	111.98(9)
C(12) – C(11)	1.412(3)	P(1) – N(1) – C(7)	116.59(15)
C(11) – P(1)	1.777(2)	N(1) – C(7) – O(1)	119.1(2)
		N(1) – C(7) – C(1)	118.96(19)

Table 5 Selected IR absorbances (KBr disk) for the iminophosphorane Ph_3P=NC(O)Ph and derivatives thereof, including *endo* and *exo* isomers

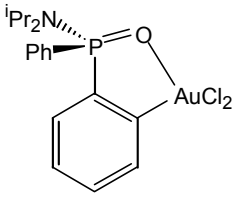
	IR absorbances (cm^{-1})	
Complex	υ(P=N)	υ(C=O)
Ph_3P=NC(O)Ph	1341	1595
12	1341	1488
13	1340	1532
14	1285	1684
16	1323	1598
17	1282	1641

Table 6 Crystallographic data for the complexes **12**, **13**, **14** and **17**

Complex	**12**	**13**	**14**·CH_2Cl_2	**17**
Formula	$C_{29}H_{19}MnNO_5P$	$C_{25}H_{19}NOPClHg$	$C_{26}H_{21}NOPCl_4Au$	$C_{25}H_{19}NOPCl_2Au$
Molecular Weight	547.36	616.42	733.17	648.25
T/K	89	89	89	93
Crystal system	Monoclinic	Triclinic	Monoclinic	Tetragonal
Space group	$P2_1/n$	*P*-1	$P2_1/n$	*I*-4
a (Å)	14.2665(1)	8.7828(3)	10.4176(3)	21.4348(6)
b (Å)	10.7250(1)	10.6870(3)	17.6738(4)	21.4348(6)
c (Å)	16.7856(2)	12.5133(4)	15.0557(5)	9.7613(3)
α (°)	90	105.335(1)	90	90
β (°)	98.732(1)	104.864(1)	110.231(2)	90
γ (°)	90	90.765(2)	90	90
V (Å^3)	2538.57(4)	1090.64(6)	2601.02(13)	4484.8(2)
Z	4	2	4	8
D_{calc} (g cm^{-3})	1.432	1.877	1.872	1.920
$T_{max,min}$	0.9014, 0.8160	0.5301, 0.3545	0.6390, 0.5257	0.3396, 0.1159
Number of unique reflections	6186	5239	6087	8411
Number of observed reflections [I>2σ(I)]	5427	4927	4985	8021
R[I>2σ(I)]	0.0302	0.0171	0.0252	0.0193
wR_2 (all data)	0.0822	0.0422	0.0503	0.0401
Goodness of Fit	1.038	1.077	0.996	1.011
Flack *x* parameter	-	-	-	0.017(3)



1a E = S, R = Ph
1b E = S, R = NEt_2
2 E = Se, R = Ph



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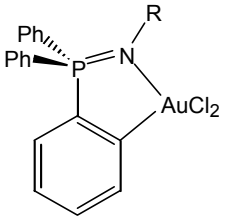

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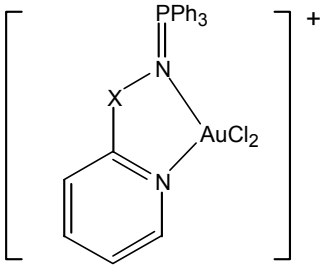
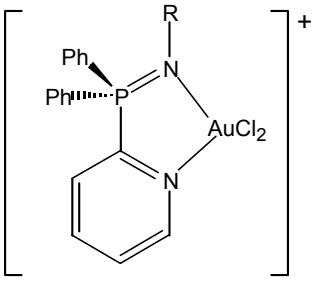
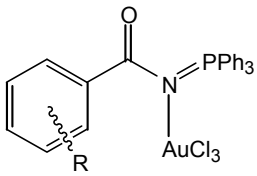


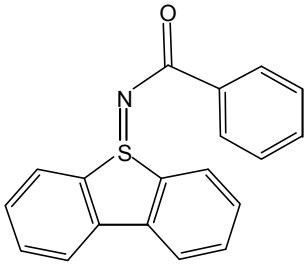
5a, X = CH_2
5b, X = CO



6a, R = Ph
6b, R = COPh



7 R = 2-Me, 4-OMe, 2-Br).



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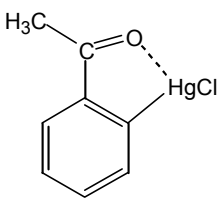

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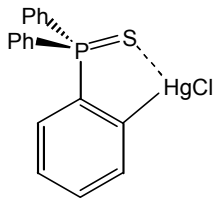

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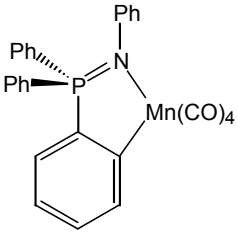

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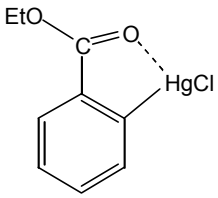

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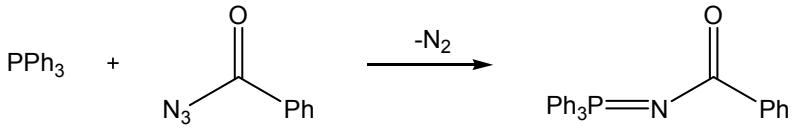

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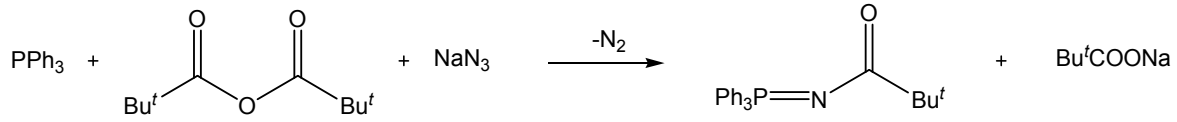
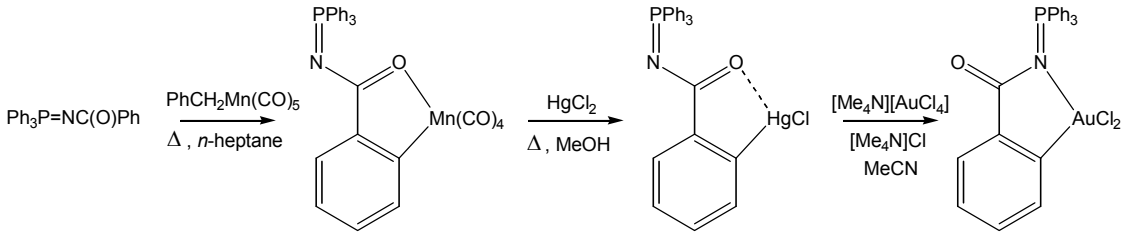
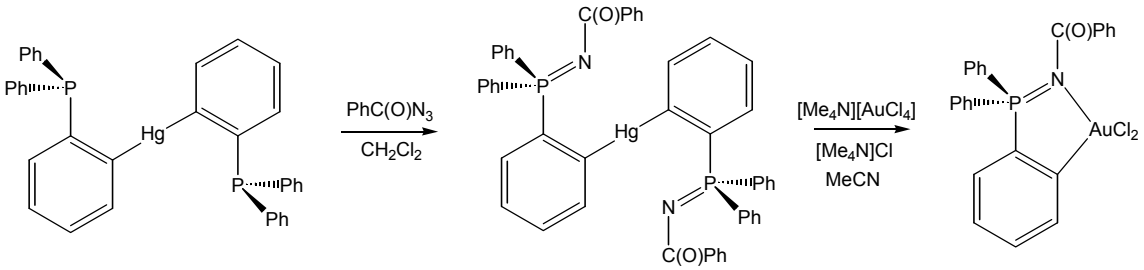


Scheme 1 Synthesis of the stabilised iminophosphoranes a) $Ph_3P{=}NC(O)Ph$ and b) $Ph_3P{=}NC(O)Bu^t$



12 **13** **14**

Scheme 2 Synthesis of *exo*-cyclometallated complexes from the stabilised iminophosphorane $Ph_3P{=}NC(O)Ph$



15 **16** **17**

Scheme 3 Synthesis of *endo*-cyclometallated complexes

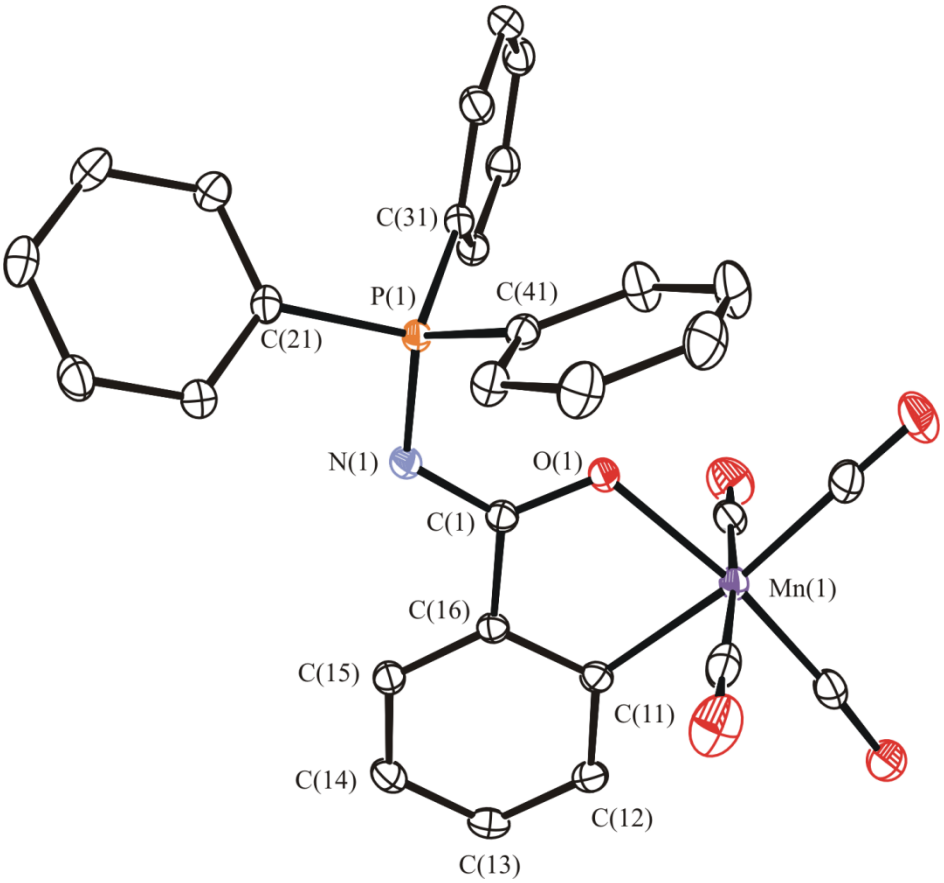


Figure 1 Molecular structure of $(CO)_4Mn(2\text{-}C_6H_4C(O)N{=}PPh_3)$, **12**. Hydrogen atoms have been excluded for clarity. Thermal ellipsoids are shown at the 50% probability level.

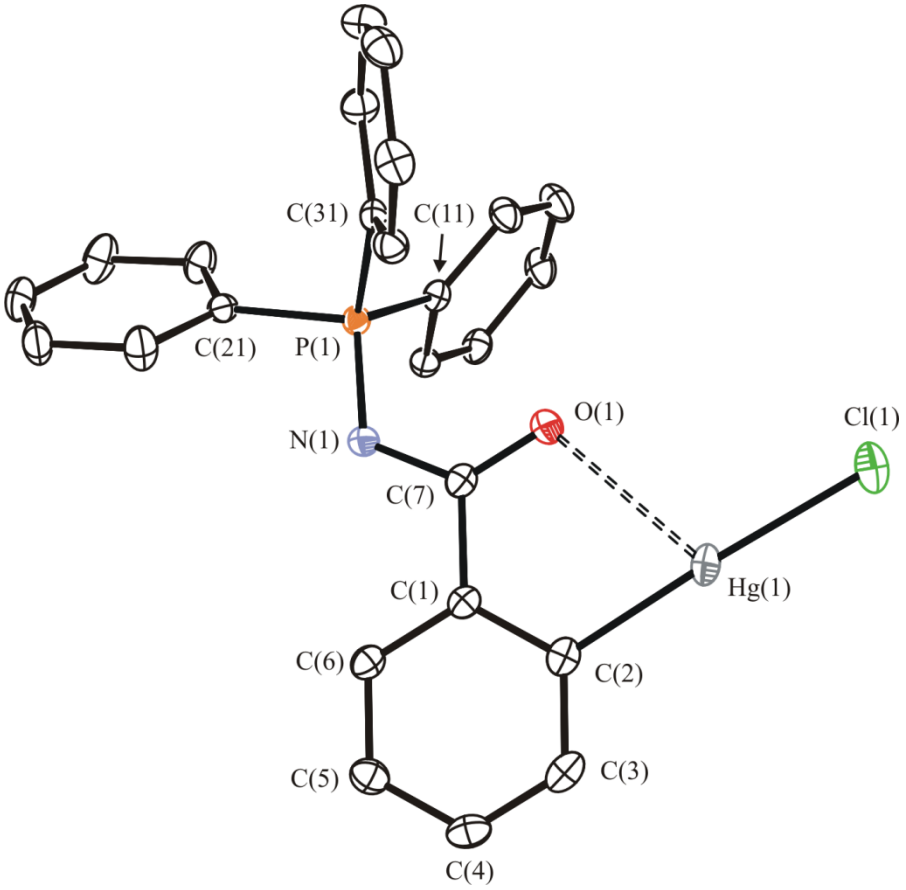


Figure 2 Molecular structure of ClHg(2-$C_6H_4C(O)N{=}PPh_3$) **13** showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown at the 50% probability level

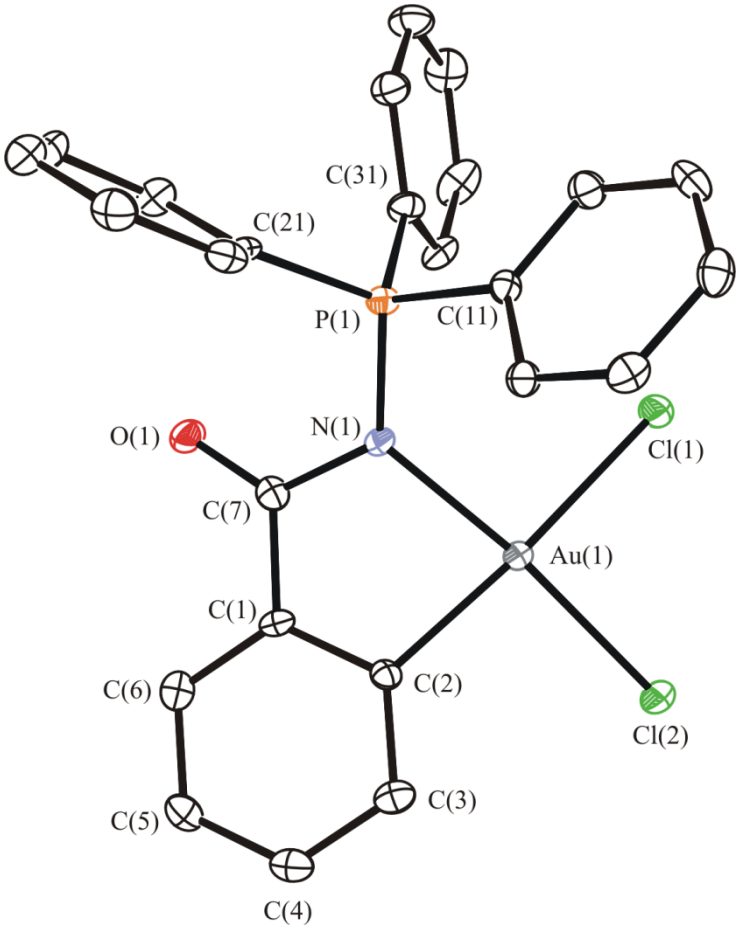


Figure 3 Molecular structure of the *exo* isomer $AuCl_2(2\text{-}C_6H_4C(O)N{=}PPh_3)$ **14** showing the atom numbering scheme. The dichloromethane solvent and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

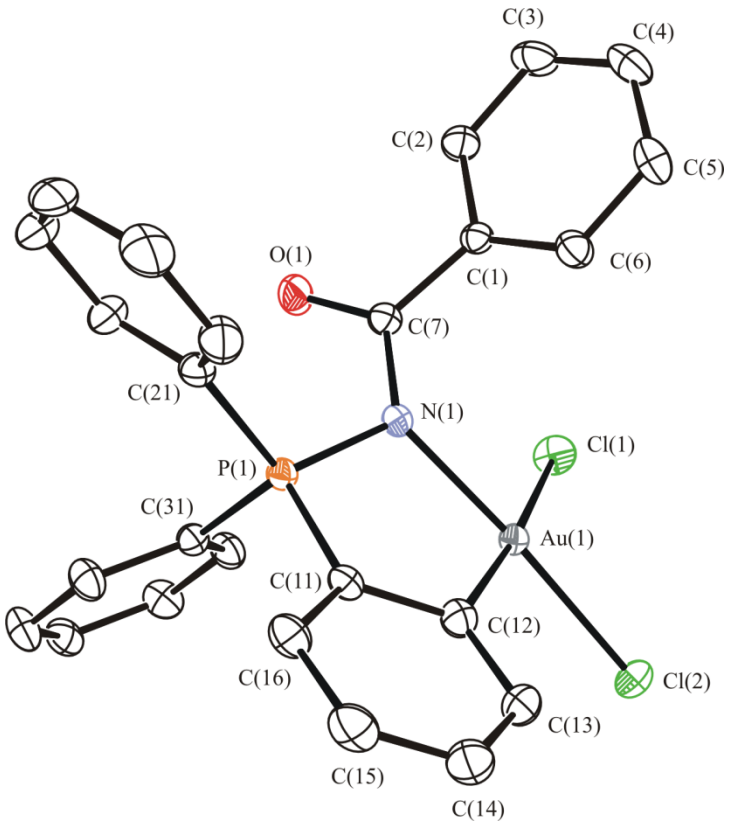


Figure 4 Molecular structure of the *endo* isomer $AuCl_2(2\text{-}C_6H_4Ph_2P{=}NC(O)Ph)$ **17** showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown at the 50% probability level.

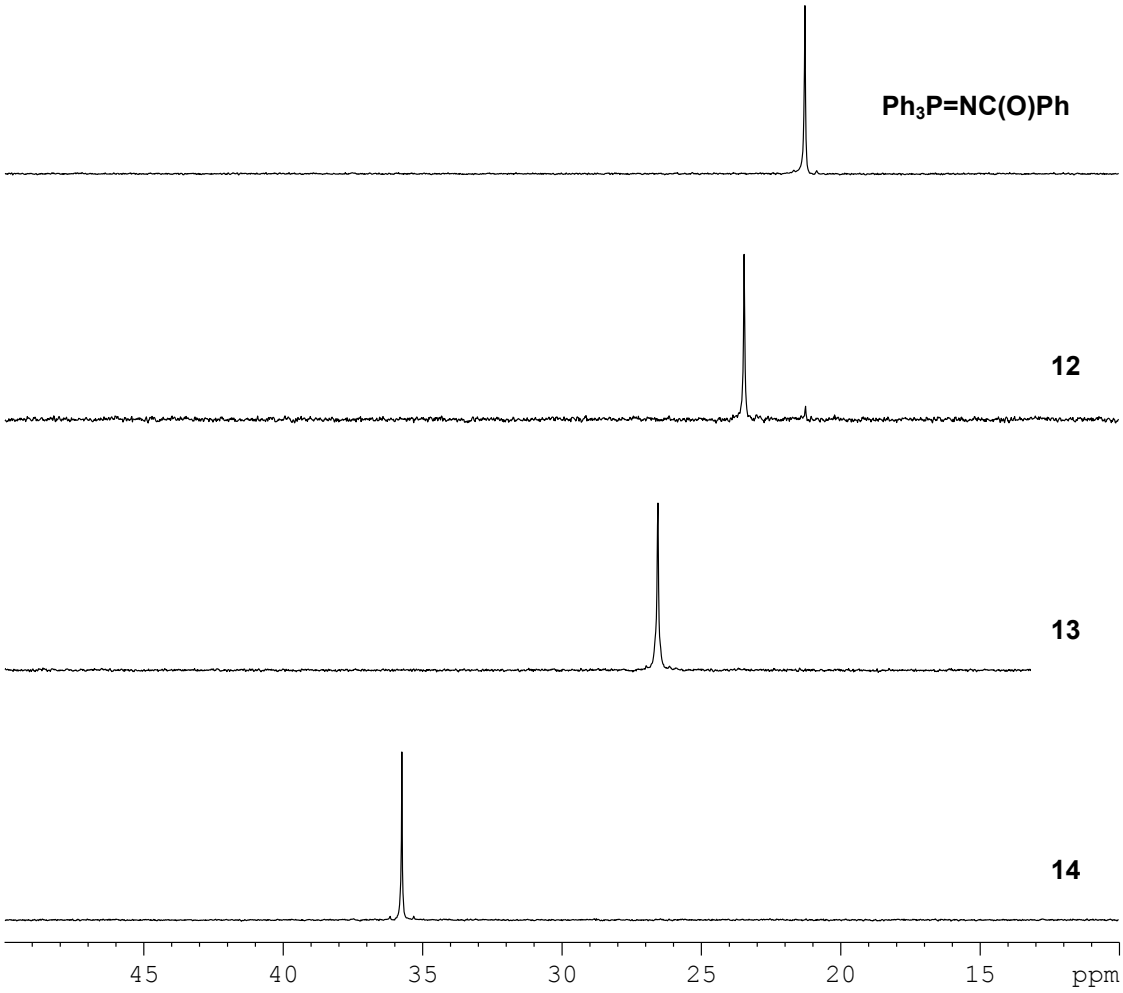


Figure 5 $^{31}P\{^{1}H\}$ NMR spectra of the series of *exo* cyclometallated complexes and $Ph_3P=NC(O)Ph$.

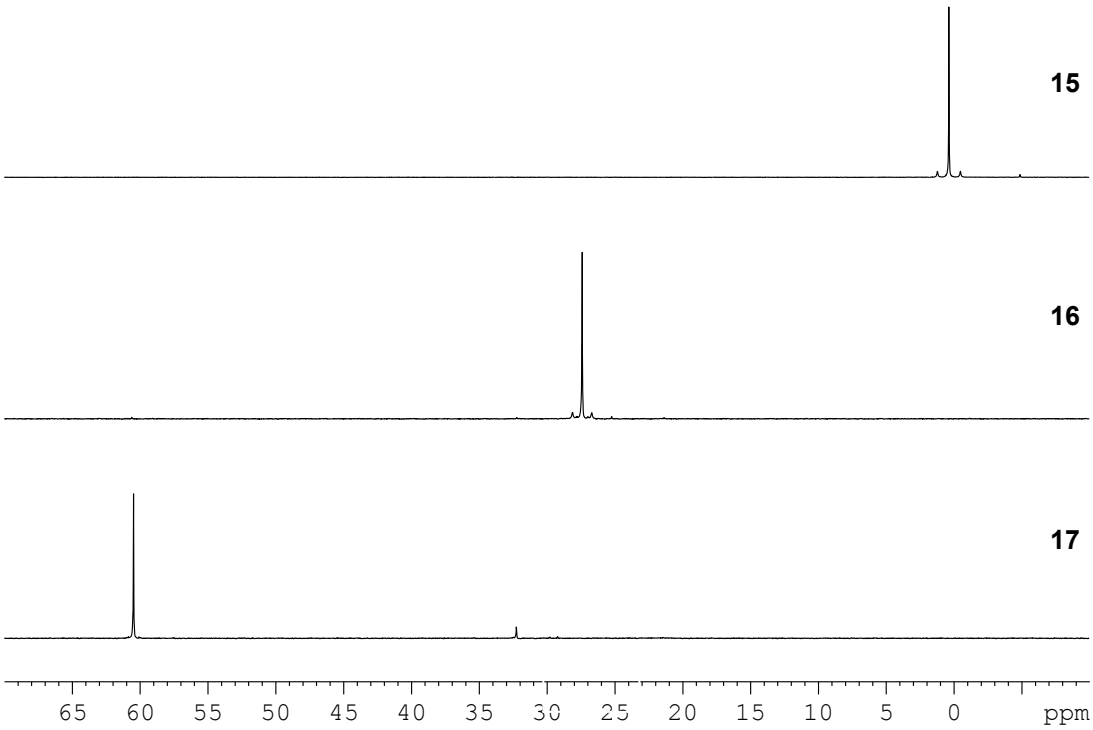


Figure 6 $^{31}P\{^{1}H\}$ NMR spectra of the series of *endo* cyclometallated complexes. The presence of $^{3}J_{HgP}$ coupling can be observed for complexes **15** and **16** as weak satellite peaks

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