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Synthesis and reactivity of gold(III) complexes containing cycloaurated iminophosphorane ligands

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Abstract

Transmetallation reactions of *ortho*-mercurated iminophosphoranes (2-ClHgC₆H₄)Ph₂P=NR with [AuCl₄]⁻ gives new cycloaurated iminophosphorane complexes of gold(III) (2-Cl₂AuC₆H₄)Ph₂P=NR [R = (*R,S*)- or (*S*)-CHMePh, *p*-C₆H₄F, ^tBu], characterised by NMR and IR spectroscopies, ESI mass spectrometry and an X-ray structure determination on the chiral derivative R = (*S*)-CHMePh. The chloride ligands of these complexes can be readily replaced by the chelating ligands thiosalicylate and catecholate; the resulting derivatives show markedly higher

antitumour activity versus P388 murine leukemia cells compared to the parent chloride complexes. Reaction of $(2\text{-Cl}_2\text{AuC}_6\text{H}_4)\text{Ph}_2\text{P}=\text{NPh}$ with PPh_3 results in displacement of a chloride ligand giving the cationic complex $[(2\text{-Cl}(\text{PPh}_3)\text{AuC}_6\text{H}_4)\text{Ph}_2\text{P}=\text{NPh}]^+$, indicating that the P=N donor is strongly bonded to the gold centre.

Keywords: Gold complexes; Iminophosphorane complexes; Ligand substitution; X-ray crystal structures

Introduction

Gold complexes are well-known to show interesting biological¹⁻³ and catalytic⁴⁻⁵ behaviour. Complexes containing cycloaurated ligands are of interest for the stabilisation of the gold(III) centre that they impart. However, the number of ligands that form cycloaurated gold(III) complexes with C,N donor atoms are relatively few compared with other platinum group metals. The syntheses and reactivity of such Au(III) complexes is the subject of a recent review.⁶

Iminophosphoranes (of the general formula $\text{R}_3\text{P}=\text{NR}'$) are attractive candidates as ligands not only because the phosphorus atom introduces a powerful (³¹P NMR) spectroscopic probe, but also due to their facile synthesis. Using either the Staudinger reaction between an organic azide and a tertiary phosphine ($\text{R}_3\text{P} + \text{N}_3\text{R}' \rightarrow \text{R}_3\text{P}=\text{NR}'$), or the Kirsanov reaction between a phosphine dibromide and a primary amine ($\text{R}_3\text{PBr}_2 + \text{H}_2\text{NR}' \rightarrow \text{R}_3\text{P}=\text{NR}'$), the organic moieties of the iminophosphorane can easily be modified to give ligands with different steric and electronic properties.⁷

Transition metal iminophosphorane complexes are well known in the literature. Bielsa *et al.* have recently published a paper which thoroughly summarises the different coordination modes of iminophosphorane ligands, commenting however that examples of *ortho*-metallated complexes are scarce.⁸ The first *ortho*-metallated complexes, formed directly by the reaction of the iminophosphorane ligands ($\text{Ar}_3\text{P}=\text{NR}$; Ar = Ph, *p*- $\text{CH}_3\text{C}_6\text{H}_5$; R = *m*- $\text{CH}_3\text{C}_6\text{H}_5$, *p*- $\text{CH}_3\text{C}_6\text{H}_5$, *p*- $\text{CH}_3\text{OC}_6\text{H}_5$) with Na_2PdCl_4 , were reported by Alper in 1977.⁹ Later, examples of the *ortho*-manganated and -rheniated iminophosphorane $\text{Ph}_3\text{P}=\text{NPh}$ were reported,¹⁰ and *ortho*-metallated palladium(II),^{8,11-13} iridium, rhodium¹⁴ and main group complexes¹⁵ are also known. Recently, we have reported the synthesis of cycloaurated $\text{Ph}_3\text{P}=\text{NPh}$ **1** from the *ortho*-mercurated compound **2**.¹⁶ Following this, a report on a 'greener' synthetic route to **1** from the corresponding gold(I) complex **3** was published along with evidence that **1** and related compounds are effective at catalysing the addition of electron rich arenes and 2-methylfuran to methyl vinyl ketone.¹⁷ In addition there are a number of *ortho*-metallated derivatives of related silyl-iminophosphoranes.^{15,18-20} This paper gives new examples of both cycloaurated and *ortho*-mercurated N-alkyl and -aryl iminophosphoranes; the reactivity and a preliminary assessment of the biological activity of these compounds is also reported.

Results and discussion

Scheme 1 summarises the syntheses of both *ortho*-mercurated and cycloaurated iminophosphoranes. The Kirsanov reaction between primary alkylamines and Ph_3PBr_2 yields the alkylaminophosphonium salts $[\text{R}_3\text{P}-\text{NH}-\text{R}']\text{Br}$

almost quantitatively. Subsequent deprotonation of these salts by addition of a base yields the neutral iminophosphorane ligands. The use of arylamines in the synthesis gives the iminophosphorane ligands directly.⁷ Lee and Singer have reported that the deprotonation of aminophosphonium salts takes place readily and in high yields using KOH as the base.²¹ However, our experience showed that yields were often lower than reported and the resulting iminophosphoranes were unstable towards hydrolysis, especially when the N-bonded substituent was -CHMePh.

Boubekeur *et al.* have recently shown that isolation of the iminophosphorane is not necessary - reaction of alkylaminophosphonium salts with two equivalents of *n*-butyllithium leads to deprotonation of the phosphonium salt and *ortho*-lithiation of the resulting iminophosphorane in one step.²² We have adapted this methodology to synthesize *ortho*-mercurated iminophosphoranes in a one-pot reaction. Thus, when the alkylaminophosphonium salts were reacted with two equivalents of *n*-butyllithium followed by HgCl₂, the *ortho*-mercurated bromide compounds were isolated in good yields. In contrast, the aryliminophosphorane ligands are appreciably more stable. They can be isolated in good yields and reacted with PhLi followed by HgCl₂, as previously described,^{16,17} to give the *ortho*-mercurated compounds, also in good yields.

Vicente *et al.*²³ have demonstrated that direct mercuration of Ph₃P=NC₆H₄Me gives the *ortho*-mercurated compound with the mercury bound to the *p*-tolyl ring, the wrong isomer for subsequent cycloauration. The use of Ph₃P=NBu' eliminates the possibility of metallation on the N-substituent and when reacted directly with Hg(OAc)₂ in THF it appears that mercuration takes place in the

desired position – on the *ortho* position of a P-bonded phenyl ring. However, yields were low compared with the synthetic route that proceeds *via* the *ortho*-lithiated intermediate, and appreciable decomposition of the ligand to $[\text{Ph}_3\text{P-NH-Bu}^t]^+$ and $\text{Ph}_3\text{P=O}$ is observed by $^{31}\text{P}\{^1\text{H}\}$ NMR during the reaction.

Transmetallation of either the *ortho*-mercurated chloride or bromide species with $\text{NMe}_4[\text{AuCl}_4]$ produced the cycloaurated complexes in good yields. In all cases the gold(III) dichloride is formed and no evidence of mono- or di-brominated compounds are seen, even when the bromo-mercury iminophosphoranes are used.

Using the above methodology, the *ortho*-mercurated compounds **9-12** and the cycloaurated complexes **13-16** were successfully synthesised. With the exception of **14** which decomposed slowly over time, all the compounds (including the racemic mixture **13**) appear to be stable towards air and light. The compounds were analysed by mass spectrometry, IR and NMR spectroscopy and microelemental analysis. In addition, an X-ray structure determination of the chiral complex **14** was carried out.

X-ray crystal structure of (2-Cl₂AuC₆H₄)Ph₂P=N-(S)-CHMePh **14**

In order to fully characterise (2-Cl₂AuC₆H₄)Ph₂P=N-(S)-CHMePh **14** and compare it with the N-aryl complex **1**, an X-ray crystal structure determination was carried out. Figure 1 shows the structure of the complex with the atom labelling scheme, while Table 1 gives important bond parameters. The crystal is a rare example of a P1, Z = 1 structure. The gold atom is essentially square planar with C(12) showing the greatest deviation from the coordination plane [defined by C(12), N(1), Au(1), Cl(1) and Cl(2)]. Because of the greater *trans* influence of the aryl carbon, the

Au-Cl(1) bond length is greater than the Au-Cl(2) bond length *trans* to the nitrogen. The metallacyclic ring made up of Au(1), N(1), P(1), C(11) and C(12) is significantly puckered, as in the previously characterised cycloaurated iminophosphorane **1**.¹⁶ Again, the nitrogen atom shows the greatest deviation [0.288(5) Å above the plane]. The bond lengths and angles in **14** are generally similar to those in the N-phenyl complex **1**.¹⁶ However, compared to **1**, the Au(1)-N(1) bond of **14** is longer [2.072(10) versus 2.034(4) Å] and the *trans* chloride Au(1)-Cl(2) of **14** is slightly shorter [2.297(3) versus 2.289(1) Å]. This indicates that the N(alkyl) group has a slightly lower *trans* influence than the NPh group, which may have implications in the catalytic activity of such complexes.¹⁷

Spectroscopic and mass spectrometric characterisation

Because of the presence of multiple inequivalent phenyl rings and coupling to phosphorus in the *ortho*-mercurated and cycloaurated complexes, both the ¹H and ¹³C{¹H} NMR spectra are complex and difficult to fully interpret. ³¹P{¹H} NMR remains the most useful experiment. The *ortho*-mercurated complexes have chemical shifts ranging from 2.2 ppm (**12**) to 14.8 ppm (**9/10**), with ³J(¹⁹⁹Hg-P) coupling averaging 330 Hz. Upon transmetallation to the cycloaurated complexes, there is a significant downfield shift in the signal of approximately 50 ppm, consistent with the formation and inclusion of the phosphorus in a 5-membered ring.²⁴

The ESI-MS of the *ortho*-mercurated complexes **9-12** all show strong [M+H]⁺ ions which can easily be identified by the characteristic isotope pattern of

mercury. Complex **12** also indicated the presence of the diarylmercury complex $2\text{-Hg}(\{\text{C}_6\text{H}_4\}\text{Ph}_2\text{P}=\text{N}^t\text{Bu})_2$ however there was no evidence of this compound in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum or microelemental analysis. This form of ionisation is consistent with little N-Hg interaction in these species, leaving the N available for protonation.

In contrast, the primary route of ionisation for the cycloaurated complexes appears to be loss of a chloride ligand to give the ions $[\text{M}-\text{Cl}]^+$, protonation to give $[\text{M}+\text{H}]^+$ being precluded by the strong N-Au bond. As previously observed, addition of a small amount of highly coordinating pyridine produces the species $[\text{M}-\text{Cl}+\text{py}]^+$.²⁵ Interestingly, the complex **16** also shows the ion $[\text{M}+\text{Me}_4\text{N}]^+$ with traces of the cation carried over from $\text{Me}_4\text{N}[\text{AuCl}_4]$ and Me_4NCl in the synthesis. The Me_4N^+ cation would be expected to have very high ionisation efficiency in ESI MS when compared to a neutral gold complex; no evidence of Me_4N^+ is observed in NMR spectra. This type of adduct is the predominant gold species when monitoring the progression of the transmetallation reaction by ESI-MS.

Reactivity of cycloaurated iminophosphorane complexes with dianionic ligands

The chloride ligands on C,N cyclometallated Au(III) compounds can be readily replaced by dianionic ligands such as catecholate²⁶ and thiosalicylate,²⁷⁻²⁹ forming new five- and six-membered chelate rings respectively. Such complexes are of interest because other analogues containing these anionic ligands have shown good anti-tumour activity. The iminophosphorane complexes **1** and **16** show analogous behaviour and when reacted with either catechol or thiosalicylic acid in methanol

with excess trimethylamine, the cycloaurated complexes **17-20** can easily be isolated in high yields by addition of water to the reaction mixture. NMR spectroscopy, ESI mass spectrometry and microanalysis confirm the formulation. Compound **18** appears to crystallise with one molecule of water as microanalysis of two independent samples gave a composition which is in agreement with the proposed formula.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the new cycloaurated derivatives show only a slight difference in chemical shift from the original dichloride species. The chemical shift of **1** is 65.5 ppm¹⁶ whereas **17** and **19** have shifts of 60.9 and 54.1 ppm respectively. Likewise, the dichloride **16** has a shift of 46.1 ppm, which moves slightly to 55.7 and 43.2 ppm in **18** and **20** respectively. Such data indicate that the original cycloaurated iminophosphorane ring remains intact upon derivatisation; if the ring was opened an upfield shift in the $^{31}\text{P}\{^1\text{H}\}$ spectrum would be expected.²⁴

Both the catechol and thiosalicylate derivatives show clean mass spectra and, with the exception of **19**, have strong parent ions of the type $[\text{M}+\text{H}]^+$ or $[\text{M}+\text{Na}]^+$ when the sample is doped with NaCl. However for the complex **19**, the parent ion is $[\text{2-Au}(\{\text{C}_6\text{H}_4\}\text{Ph}_2\text{P}=\text{NPh})_2]^+$, even when the sample is doped with NaCl. The presence of this type of diarylgold species in ESI-MS spectra of thiosalicylate complexes has been seen previously.²⁹

To confirm the geometry of the thiosalicylate complexes, an X-ray crystal structure of **20** was carried out. Figure 2 shows the molecular structure with the atom labelling scheme, and Table 2 gives selected bond lengths and angles. As with other gold(III) thiosalicylate complexes²⁷⁻²⁹ the ligand is coordinated to the gold with the two highest *trans* influence donors (aryl C and thiolate S) mutually *cis* to each other.

The geometry around the gold is square planar with the largest deviation from the N(1), C(12), Au(1), S(1) and O(2) plane being for C(12), which sits 0.1620(7) Å below the plane. The fold angle between the Au coordination plane [defined by Au(1), S(1) and O(2)] and the plane of the thiosalicylate ligand (excluding the oxygen atoms) is 43.34(4)°, which falls in the range of 30.1(8)° (**21**) and 59.6° (**22**) previously seen in gold(III) thiosalicylate systems.²⁷⁻²⁹ The bite angle of the thiosalicylate ligand is 91.46(4)°, comparable to those seen in (**22**) and (**23**) [89.82(8)° and 90.1(2)° respectively]. The five-membered ring created by the cycloaurated iminophosphorane is also puckered with the greatest deviations for N(1) (0.3226(7) Å above the plane) and P(1) (0.2788(7) Å below the plane). The puckering of the thiosalicylate and the iminophosphorane rings can clearly be seen in Figure 3. The fold angle between the Au coordination plane and that of the thiosalicylate ring is 43.3°, towards the lower end of the range found for a series of Pt(II) thiosalicylate complexes.³⁰

Reactivity with phosphines

Previously, reaction of C,N cyclometallated Au(III) dichloride complexes with PPh₃ has given an indication of the strength of the N-Au bond.⁶ If the bond is strong, then a chloride ion will be displaced to give a cationic complex. Alternatively, if the N-Au bond is relatively weak, it will be cleaved and coordination of the phosphine will give a neutral phosphine complex. The behaviour is dependent on the ligand. For example, when the damp complex (Scheme 2a) is reacted with one equivalent of PPh₃ substitution of the chloride takes place.³¹ In contrast, when

papAuCl₂ (Scheme 2b) is reacted in the same manner the nitrogen is displaced and the neutral phosphine complex is obtained.^{32,33}

To assess the strength of the Au-N bond in Au(III) iminophosphoranes, **1** was reacted with one molar equivalent of PPh₃ together with NH₄PF₆ in dichloromethane, producing the compound **24** where the PPh₃ has displaced the chloride ligand. The products were initially characterised by ESI-MS and ³¹P{¹H} NMR. The ³¹P{¹H} NMR shows the expected two signals at 60.6 and 41.0 ppm in a 1:1 ratio. The first arises from the iminophosphorane, and is only slightly shifted from that of the parent dichloride (65.5 ppm) indicating that the phosphorus is still present in a ring. This was unambiguously confirmed by an X-ray crystal structure determination.

The molecular structure of the cation of **24** is shown in Figure 4, and important bond parameters are presented in Table 3. The geometry around the gold atom is essentially square planar and N(1) shows the greatest deviation [0.113(3) Å] from the coordination plane. The X-ray crystal structure shows that the phosphine is coordinated *trans* to the nitrogen, thus placing the two softest ligands (the phosphine and aryl groups) mutually *cis* to each other, giving the most thermodynamically stable configuration (*antisymbiosis*).³⁴ This is also observed in other phosphine substituted Au(III) cationic complexes, and the Au-P bond lengths are comparable with those previously seen.³⁵⁻³⁸ Upon substitution of the chloride with the bulky phosphine group the bond angle between the two monodentate ligands has increased [from 90.70(4)° in **1** to 92.88(17)° in **24**] which in turn has decreased the bite angle of the iminophosphorane ligand [from 84.86(17) to 84.0(2)°]. However, the ligand

remains significantly puckered, with N(1) and P(1) showing the greatest deviation from the mean plane of the ring [defined by N(1), P(1), Au(1), C(11) and C(12)].

Attempted displacement of the N-donor ligand

In order to evaluate our hypothesis that displacement of the N-donor would result in a significant upfield shift in the ^{31}P spectra from a monodentate iminophosphorane ligand we attempted to synthesise complexes of this type. Previously this has been achieved with gold(III) complexes by replacement of the relatively weakly bound chloride ligands with stronger cyanide³⁹ or dithiocarbamate^{40,41} groups.

Cyanide complexes of the damp system have been spectroscopically characterised. Reaction of dampAuCl₂ (see scheme 2) with two equivalents of KCN gave the neutral complex dampAu(CN)₂, whereas excess cyanide gave the anionic [Au(damp)(CN)₃]⁻ complex as the potassium salt.²⁸ When **1** was reacted with excess KCN the corresponding anion could be seen in the ESI mass spectrum, and an unexpected new peak at 69.5 ppm in the $^{31}\text{P}\{^1\text{H}\}$ is observed. However, isolation and microanalysis of this complex as a white solid produced microelemental data completely inconsistent with the expected formulation.

Reaction of dampAuCl₂ with one equivalent of NaS₂CNMe₂ produced the cationic complex **25**. However, if two equivalents of dithiocarbamate were used a neutral complex was obtained where one dithiocarbamate ligand was coordinated in a bidentate fashion, the other as a monodentate ligand, as shown by an X-ray crystal

structure analysis, **26**. Rapid interchange between the ligands occurs on the NMR timescale.³⁹ Analogous results are seen with oxazoline gold(III) complexes.⁴⁰

When **1** is reacted with a molar equivalent of NaS₂CNEt₂ and NH₄PF₆ in dichloromethane the complex **27** is obtained as a yellow solid. The analogous reaction with two equivalents of NaS₂CNEt₂ also gives a yellow complex which is identical to **27** (on the basis of ¹H and ¹³P{¹H} NMR experiments). No evidence of the complex analogous to **26** is observed. These observations indicate that the iminophosphorane complexes contain a robust cyclometallated ring.

Biological activity

A number of gold(III) complexes have previously been found to show anti-tumour activity.^{6,41,42} The biological activity of **1** has been reported, and showed low anti-cancer activity against the P388 murine leukemia cell line.¹⁶ In order to determine if this is characteristic of cycloaurated iminophosphoranes, the activity of the alkyl compound **16** was evaluated. The bicyclic catecholate (**17** and **18**) and thiosalicylate (**19** and **20**) derivatives were also evaluated, since related derivatives have been previously been found to exhibit high anti-tumour activity.²⁹

Results of the biological assays are presented in Table 4. In contrast to the dichloride complexes **1** and **16** which show low anti-tumour activity, the catecholate and thiosalicylate complexes show a ten-fold increase in the level of activity. In particular the complexes **17** and **19**, originating from complex **1**, show a high level of activity. These observations confirm that the presence of catecholate or thiosalicylate

ligands tends to lead to complexes with good activity, and warrants further detailed studies on these systems.

Conclusions

A range of new *ortho*-mercurated and cycloaurated iminophosphorane complexes and their derivatives have been synthesised and fully characterised by NMR spectroscopy and ESI mass spectrometry. X-ray crystal structures of three of these compounds have been carried out. The Au–N coordinate bond is relatively strong because when **1** is reacted with PPh₃ the Au–N bond remains intact and a chloride ligand is substituted by PPh₃. Attempts at cleaving this bond by reacting **1** with ligands such as CN[−] and dithiocarbamates were unsuccessful. Both chloride ligands can be replaced by chelating dianionic ligands to give bi-metallacyclic compounds with enhanced anti-tumour activity, possibly due to the reduced reactivity of the complexes.

Experimental

General procedures

The known aminophosponium salts **4** and **5** and the iminophosphoranes **7** and **8** were prepared by literature procedures; **6** was prepared by a completely analogous method to **5**.^{7,21} Complex **1** was prepared by the literature procedure.¹⁶ *n*-Butyllithium (either 1.6 M in hexanes or 2.0 M in cyclohexane, Aldrich), PhBr (AJAX Chemicals), HgCl₂, catechol, sodium diethyldithiocarbamate trihydrate

(BDH), Hg(OAc)₂ (Riedel de Haën) and thiosalicylic acid (Sigma) were used as received. Me₄N[AuCl₄] was prepared by reaction of H[AuCl₄].4H₂O with Me₄NCl. Dry de-oxygenated diethyl ether and THF were obtained from a Pure Solv™ solvent purification system, and metallation reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques, with light also being excluded in the case of cycloauration reactions.

Positive ion ESI mass spectra were acquired on a VG Platform II instrument using methanol as the solvent after the compound had first been dissolved in a small amount of dichloromethane. IR spectra were acquired as KBr disks on a Digilab Scimitar FT-IR spectrometer. ³¹P{¹H} and ¹H NMR spectra (solvent CDCl₃) were recorded on a Bruker DRX 300 FT NMR spectrometer at 121.5 and 300.1 MHz respectively. Microelemental analysis was carried out at the Campbell Microanalytical Laboratory at the University of Otago. Anti-tumour assays were carried out using previously described methods;⁴³ samples were tested in a 2:1 dichloromethane:methanol solvent system.

Preparation of (2-BrHgC₆H₄)Ph₂P=N-(*R,S*)-CHMePh 9

[Ph₃P-NH-(*R,S*)-CHMePh]⁺Br⁻ **5** (1.000 g, 2.16 mmol) was suspended in diethyl ether (30 mL) and cooled to -84 °C in an ethyl acetate slush bath. ⁿBuLi (1.6 M, 2.7 mL, 4.32 mmol) was added dropwise with stirring. The solution was allowed to warm to room temperature to give a clear orange solution that was stirred for an additional 30 min. HgCl₂ (0.586 g, 2.16 mmol) was added in one portion and after stirring for 1 h the solvent was removed and the solid extracted into dichloromethane (2 × 10 mL),

filtered and diethyl ether (20 mL) was added to the filtrate. Storage at -20 °C gave white crystals of (2-BrHgC₆H₄)Ph₂P=N-(*R,S*)-CHMePh (0.606 g, 42%). Found: C 47.7, H 3.6, N 2.2; C₂₆H₂₃NPBrHg requires C 47.3, H 3.5, N 2.1%. NMR: ¹H: δ (ppm) 1.64 (d, CH₃), 4.68 (m, CH), 7.00-7.69 (m, Ar-H); ³¹P{¹H}: δ (ppm) 14.8, ³J(¹⁹⁹Hg-P) = 317 Hz. ESI-MS: *m/z*: 662 (100%, [M+H]⁺). IR: ν(P=N) = 1163 cm⁻¹ (vs).

Preparation of (2-BrHgC₆H₄)Ph₂P=N-(*S*)-CHMePh 10

As for the preparation of **9** above, [Ph₃P-NH-(*S*)-CHMePh]⁺Br⁻ **6** (2.000 g, 4.34 mmol) was suspended in diethyl ether (30 mL) and ⁿBuLi (1.6 M, 5.4 mL, 8.68 mmol) added. After addition of HgCl₂ (1.178 g, 4.34 mmol), work-up as above gave 1.780 g, (62%) of (2-BrHgC₆H₄)Ph₂P=N-(*S*)-CHMePh. The product was identified by ¹H and ³¹P{¹H} NMR spectroscopy.

Preparation of (2-ClHgC₆H₄)Ph₂P=NC₆H₄F 11

A solution of ⁿBuLi (2 mL, 2.69 mmol) was added to a solution of PhBr (0.28 mL, 2.69 mmol) in diethyl ether (20 mL) and stirred for 15 min. Ph₃P=NC₆H₄F **7** (1.000 g, 2.69 mmol) was added to immediately give a dark orange solution. After stirring for 1.5 h a white precipitate had formed. HgCl₂ (0.730 g, 2.69 mmol) was added and the mixture stirred for an additional hour. Workup as for **9** gave crystals of (2-ClHgC₆H₄)Ph₂P=NC₆H₄F (0.927 g, 57%). Found: C 47.5, H 2.9, N 2.4; C₂₄H₁₈NFPClHg requires C 47.5, H 3.0, N 2.3%. NMR: ¹H: δ (ppm) 6.69-6.75, 6.80-6.85, 7.27-7.34, 7.40-7.70 (all m, Ar-H); ³¹P{¹H}: δ (ppm) 9.0 (br), ³J(¹⁹⁹Hg-P) = 320

Hz. ESI-MS: m/z : 607 (100%, $[M+H]^+$), 942 (35%, $[2\text{-Hg}(\{\text{C}_6\text{H}_4\})\text{Ph}_2\text{P}=\text{NC}_6\text{H}_4\text{F})_2+\text{H}]^+$). IR: $\nu(\text{P}=\text{N}) = 1309 \text{ cm}^{-1}$ (vs).

Preparation of (2-ClHgC₆H₄)Ph₂P=N^tBu **12**

As for **11** above, Ph₃P=N^tBu **8** (1.199 g, 3.60 mmol) was added to a solution of PhBr (0.38 mL, 3.60 mmol) and ⁿBuLi (1.6 M, 2.25 mL, 3.60 mmol) in diethyl ether (20 mL). Addition of HgCl₂ (0.977 g, 3.60 mmol) followed by workup gave (2-ClHgC₆H₄)Ph₂P=N^tBu (0.909 g, 44%). Found: C 46.0, H 4.1, N 2.5; C₂₂H₂₃NPClHg requires C 46.4, H 4.1, N 2.5%. NMR: ¹H: δ (ppm) 1.29 (s, CH₃), 7.13-7.19, 7.31-7.64, 7.74-7.81 (all m, Ar-H); ³¹P{¹H}: δ (ppm) 2.2, ³J(¹⁹⁹Hg-P) = 341 Hz. ESI-MS: m/z : 569 (100%, $[M+H]^+$). IR: $\nu(\text{P}=\text{N}) = 1223 \text{ cm}^{-1}$ (vs).

Alternative synthesis:

Ph₃P=N^tBu **8** (0.300 g, 0.90 mmol) and Hg(OAc)₂ (0.288 g, 0.90 mmol) were refluxed under nitrogen in dry degassed THF (20 mL) for 16 h. The solution was allowed to cool, LiCl (0.076 g, 1.79 mmol) was added and stirred for an additional 4 h. The solution was then filtered and evaporated to dryness. The filtrate was redissolved in dichloromethane (2 × 10 mL) and diethyl ether (20 mL) was added. Storage at -20 °C gave crystals of (2-ClHgC₆H₄)Ph₂P=N^tBu (0.128 g, 25%), identified by ¹H and ³¹P{¹H} NMR spectroscopy.

Preparation of (2-Cl₂AuC₆H₄)Ph₂P=N-(*R,S*)-CHMePh **13**

The complex (2-BrHgC₆H₄)Ph₂P=N-(*R,S*)-CHMePh **9** (0.100 g, 0.15 mmol), Me₄N[AuCl₄] (0.062 g, 0.15 mmol) and Me₄NCl (0.016 g, 0.15 mmol) were added to degassed acetonitrile (15 mL) and stirred in a foil-covered flask for 48 h. The solvent was removed and the yellow solid extracted into dichloromethane (2 × 10 mL), filtered and diethyl ether was added to the filtrate. Storage at -20 °C gave yellow crystals of (2-Cl₂AuC₆H₄)Ph₂P=N-(*R,S*)-CHMePh (0.062 g, 64%). Found: C 47.2, H 3.5, N 2.1; C₂₆H₂₃NPCl₂Au requires C 48.2, H 3.6, N 2.2%. NMR: ¹H: δ (ppm) 1.62 (d, CH₃), 5.85 (m, CH), 6.92-7.01, 7.05-7.08, 7.18-7.23, 7.32-7.53, 7.58-7.67, 8.17-8.21 (all m, Ar-H); ³¹P{¹H}: δ (ppm) 59.0. ESI-MS: pyridine doped *m/z*: 654 (100%, [M-Cl+MeCN]⁺), 692 (85%, [M-Cl+py]⁺), 613 (53%, [M-Cl]⁺). IR: ν(P=N) = 1138 cm⁻¹ (s).

Preparation of (2-Cl₂AuC₆H₄)Ph₂P=N-(*S*)-CHMePh **14**

Analogous to **13**, (2-BrHgC₆H₄)Ph₂P=N-(*S*)-CHMePh **10** (1.000 g, 1.51 mmol), Me₄N[AuCl₄] (0.623 g, 1.51 mmol) and Me₄NCl (0.166 g, 1.51 mmol) were reacted in acetonitrile (30 mL) for 48 h. Workup gave (2-Cl₂AuC₆H₄)Ph₂P=N-(*S*)-CHMePh as pale yellow crystals (0.139 g, 14%). The product was identified by ¹H and ³¹P{¹H} NMR spectroscopy.

Preparation of (2-Cl₂AuC₆H₄)Ph₂P=NC₆H₄F **15**

As for **13**, (2-ClHgC₆H₄)Ph₂P=NC₆H₄F **11** (0.174 g, 0.29 mmol), Me₄N[AuCl₄] (0.119 g, 0.29 mmol) and Me₄NCl (0.032 g, 0.29 mmol) in acetonitrile (20 mL) for

24 h. Work-up gave (2-Cl₂AuC₆H₄)Ph₂P=NC₆H₄F as bright yellow crystals (0.074 g, 40%). Found: C 45.2, H 3.1, N 2.2; C₂₄H₁₈NFPCl₂Au requires C 45.2, H 2.8, N 2.2%. NMR: ¹H: δ (ppm) 6.73-6.80, 6.92-6.97, 7.10-7.17, 7.33-7.38, 7.49-7.62, 7.71-7.78, 8.41-8.46 (all m, Ar-H); ³¹P{¹H}: δ (ppm) 66.9. ESI-MS: *m/z*: 603 (100%, [M-Cl]⁺), 1241 (80%, [2M-Cl]⁺); pyridine doped *m/z*: 682 (100%, [M-Cl+py]⁺). IR: ν(P=N) = 1219 cm⁻¹ (s).

Preparation of (2-Cl₂AuC₆H₄)Ph₂P=N^tBu 16

As for **13**, (2-ClHgC₆H₄)Ph₂P=N^tBu **12** (0.400 g, 0.70 mmol), Me₄N[AuCl₄] (0.291 g, 0.70 mmol) and Me₄NCl (0.077 g, 0.70 mmol) were reacted in acetonitrile (20 mL) for 24 h. Workup gave yellow crystals of (2-Cl₂AuC₆H₄)Ph₂P=N^tBu (0.312 g, 74%). Found: C 44.2, H 3.9, N 2.4; C₂₂H₂₃NPCl₂Au requires C 44.0, H 3.9, N 2.3%. NMR: ¹H: δ (ppm) 1.34 (s, CH₃), 7.31-7.40, 7.55-7.62, 7.67-7.72, 7.85-7.91, 8.04-8.07 (all m, Ar-H); ³¹P{¹H}: δ (ppm) 46.1. ESI-MS: *m/z*: 565 (100%, [M-Cl]⁺), 673 (35%, [M+Me₄N]⁺), 1165 (30%, [2M-Cl]⁺); pyridine doped *m/z*: 644 (100%, [M-Cl+py]⁺), 565 (60%, [M-Cl]⁺). IR: ν(P=N) = 1183 cm⁻¹ (m).

Synthesis of 17

The complex (2-Cl₂AuC₆H₄)Ph₂P=NPh **1** (0.100 g, 0.16 mmol) and catechol (0.018 g, 0.16 mmol) were refluxed in methanol (20 mL). With stirring, Me₃N (1 mL, excess) was added resulting in the yellow solution immediately turning dark orange. After refluxing for a further 20 min. the solution was allowed to cool, water (20 mL) was added and stirring continued overnight. The precipitate that had formed was filtered,

washed with water (2×10 mL) and diethyl ether (10 mL) and dried under vacuum to give **17** (0.085 g, 81%) as a rose-coloured solid. Found: C 54.8, H 3.6, N 2.2; $C_{30}H_{23}NO_2PAu$ requires C 54.8, H 3.5, N 2.1%. NMR: 1H : δ (ppm) 6.42-6.47, 6.73-6.76, 7.01-7.15, 7.29-7.36, 7.49-7.57, 7.66-7.79, 8.19-8.22 (all m, Ar-H); $^{31}P\{^1H\}$: δ (ppm) 60.9. ESI-MS: m/z : 658 (100%, $[M+H]^+$), 1315 (60%, $[2M+H]^+$); NaCl doped m/z : 680 (100%, $[M+Na]^+$), 1337 (34%, $[2M+Na]^+$), 658 (28%, $[M+H]^+$), 1315 (12%, $[2M+H]^+$). IR: $\nu(P=N) = 1254\text{ cm}^{-1}$ (m).

Synthesis of **18**

The complex $(2-Cl_2AuC_6H_4)Ph_2P=N^tBu$ (0.100 g, 0.17 mmol) and catechol (0.019 g, 0.17 mmol) were brought to reflux in methanol (15 mL). With stirring, Me_3N (1 mL, excess) was added resulting in the yellow solution turning dark orange. After refluxing for a further 15 min. the now purple solution was allowed to cool, water (20 mL) was added, and stirring continued overnight. The precipitate that had formed was filtered, washed with water (3×10 mL) and diethyl ether (20 mL) and dried under vacuum to give **18** (0.067 g, 62%) as a rose-coloured solid. A sample for microanalysis was recrystallised from dichloromethane/diethyl ether. Found: C 51.3, H 4.2, N 2.2; $C_{28}H_{27}NO_2PAu$ requires C 52.8, H 4.3, 2.2; $C_{28}H_{27}AuNO_2P \cdot H_2O$ requires C 51.3, H 4.5, N 2.1%. NMR: 1H : δ (ppm) 1.52 (s, CH_3), 6.45-6.50, 6.53-6.58, 6.67-6.79, 7.13-7.20, 7.34-7.39, 7.56-7.62, 7.66-7.71, 7.91-7.98, 8.11-8.14 (all m, Ar-H) $^{31}P\{^1H\}$: δ (ppm) 55.7. ESI-MS: m/z : 638 (100%, $[M+H]^+$), 1275 (30%,

[2M+H]⁺); NaCl doped *m/z*: 660 (100%, [M+Na]⁺), 1297 (60%, [2M+Na]⁺), 638 (40% [M+H]⁺). IR: $\nu(\text{P}=\text{N}) = 1254 \text{ cm}^{-1}$ (m).

Synthesis of **19**

To a stirred methanolic solution (15 mL) of (2-Cl₂AuC₆H₄)Ph₂P=NPh **1** (0.100 g, 0.16 mmol) and thiosalicylic acid (0.025 g, 0.16 mmol), Me₃N (1 mL, excess) was added, resulting in the pale yellow solution immediately becoming darker. Stirring was continued in the dark for a further 90 min. before water (20 mL) was added. The fine yellow precipitate that had formed was filtered and washed with water (3 × 10 mL) and diethyl ether (1 × 10 mL) and dried under vacuum to give **19** (0.099 g, 88%). Found: C 53.1, H 3.4, N 2.0; C₃₁H₂₃NO₂PSAu requires C 53.1, H 3.3, N 2.0%. NMR: ¹H: δ (ppm) 6.88-6.92, 7.01-7.21, 7.28-7.35, 7.46-7.57, 7.64-7.75, 8.00-8.04, 8.15-8.20 (all m, Ar-H); ³¹P{¹H}: δ (ppm) 54.1. ESI-MS: *m/z*: 902 (100%, [2-Au({C₆H₄)Ph₂P=NPh)₂]⁺), 703 (30%, [M+H]⁺), 1404 (25%, [2M+H]⁺); NaCl doped *m/z*: 901 (100%, [2-Au({C₆H₄)Ph₂P=NPh)₂]⁺), 1426 (85%, [2M+Na]⁺), 725 (40%, [M+Na]⁺), 703 (10%, [M+H]⁺), 1404 (7%, [2M+H]⁺). IR: $\nu(\text{P}=\text{N}) = 1316 \text{ cm}^{-1}$ (m), $\nu(\text{C}=\text{O}) = 1626 \text{ cm}^{-1}$ (vs).

Synthesis of **20**

As for **19**, (2-Cl₂AuC₆H₄)Ph₂P=N^tBu **16** (0.101 g, 0.17 mmol) and thiosalicylic acid (0.026 g, 0.17 mmol) were reacted in methanol (15 mL). Addition of Me₃N (1 mL, excess) and water (20 mL) followed by workup gave 0.085 g (73%) of **20** as a yellow solid. Found: C 51.0, H 4.0, N 2.0; C₂₉H₂₇NO₂PSAu requires C 51.1, H 4.0, N 2.1%.

NMR: ^1H : δ 1.40 (s, CH_3), 7.01-7.05, 7.15-7.25, 7.32-7.38, 7.43-7.47, 7.53-7.59, 7.63-7.69, 7.86-7.99, 8.14-8.19 (all m, Ar-H); $^{31}\text{P}\{^1\text{H}\}$: δ 43.2 ppm. ESI-MS: m/z : 683 (100%, $[\text{M}+\text{H}]^+$), 1212 (52%, unidentified), 1364 (30%, $[2\text{M}+\text{H}]^+$); NaCl doped m/z : 705 (100%, $[\text{M}+\text{Na}]^+$), 1386 (87%, $[2\text{M}+\text{Na}]^+$). IR: $\nu(\text{P}=\text{N}) = 1310 \text{ cm}^{-1}$ (m), $\nu(\text{C}=\text{O}) = 1626 \text{ cm}^{-1}$ (vs).

Synthesis of [(2-Cl(PPh_3) AuC_6H_4) $\text{Ph}_2\text{P}=\text{NPh}$] PF_6 **24**

The complex (2- $\text{Cl}_2\text{AuC}_6\text{H}_4$) $\text{Ph}_2\text{P}=\text{NPh}$ **1** (0.104 g, 0.17 mmol), PPh_3 (0.045 g, 0.17 mmol) and NH_4PF_6 (0.111 g, 0.68 mmol) were stirred in dichloromethane (10 mL) for 4 h. The solution was filtered and the dark orange filtrate reduced in volume (~2 mL). Diethyl ether was added until the solution went cloudy. Storage at $-20 \text{ }^\circ\text{C}$ gave yellow crystals of [(2-Cl(PPh_3) AuC_6H_4) $\text{Ph}_2\text{P}=\text{NPh}$] PF_6 (0.088 g, 52%). Found: C 50.2, H 3.5, N 1.5; $\text{C}_{42}\text{H}_{34}\text{NF}_6\text{P}_3\text{ClAu}$ requires C 50.9, H 3.5, N 1.4%. NMR: ^1H : δ (ppm) 6.90-7.03, 7.09-7.14, 7.30-7.34, 7.51-7.57, 7.61-7.71, 7.78-7.87 (all m, Ar-H); $^{31}\text{P}\{^1\text{H}\}$: δ (ppm) 60.6 ($\underline{\text{P}}=\text{N}$), 41.0 ($\underline{\text{P}}\text{Ph}_3$), 1:1 ratio. ESI-MS: m/z : 847 (100%, [(2-Cl(PPh_3) AuC_6H_4) $\text{Ph}_2\text{P}=\text{NPh}$] $^+$). IR: $\nu(\text{P}=\text{N}) = 1253 \text{ cm}^{-1}$ (w).

Synthesis of **27**

The complex (2- $\text{Cl}_2\text{AuC}_6\text{H}_4$) $\text{Ph}_2\text{P}=\text{NPh}$ **1** (0.100 g, 0.16 mmol) and $\text{NaS}_2\text{CNet}_2 \cdot 3\text{H}_2\text{O}$ (0.036 g, 0.16 mmol) were stirred in dichloromethane (10 mL) for 2.5 h. NH_4PF_6 (0.065 g, 0.40 mmol) was added and the solution stirred for an additional 18 h. The insoluble material was removed by filtration and the yellow solution reduced in volume (~2 mL). Diethyl ether was added until the solution went cloudy. Storage

at -20 °C gave yellow microcrystals (0.099 g, 73%) of **27**. Found: C 41.8, H 3.6, N 3.2; C₂₉H₂₉N₂F₆P₂S₂Au requires C 41.3, H 3.5, N 3.3%. NMR: ¹H: δ (ppm) 1.30 (t, CH₃), 1.43 (t, CH₃), 3.71 (q, CH₂), 3.82 (q, CH₂), 6.83-6.86, 7.06-7.12, 7.17-7.23, 7.28-7.35, 7.39-7.43, 7.47-7.54, 7.57-7.80 (all m, Ar-H); ³¹P{¹H}: δ (ppm) 65.9. ESI-MS: *m/z*: 843 (100%, [M]⁺). IR: ν(P=N) = 1232 cm⁻¹ (w).

Crystal structure determinations of **14**, **20** and **24**

Single crystals of X-ray quality were grown by vapour diffusion of either diethyl ether (**14** and **24**) or pentane (**20**) into a dichloromethane solution of the compound at room temperature. Both **14** and **24** crystallised as yellow blocks, **20** as orange plates.

Data Collection

Unit cell dimensions and intensity data (Table 5) were collected at the University of Canterbury on a Bruker Nonius Apex II CCD Diffractometer. Absorption was corrected for by semi-empirical methods (SADABS⁴⁴).

Solution and Refinement

Structures were solved by either the direct methods (**24**) or Patterson (**14** and **20**) options of SHELXS-97.⁴⁵ In all cases the gold atom was initially located, and all other atoms by a series of difference maps. Full-matrix least-squares refinement (SHELXL-97⁴⁶) was based upon F_0^2 , with all non-hydrogen atoms refined anisotropically (with the exception of the cases mentioned below) and hydrogen atoms in calculated positions.

Complex **24** crystallised with the phosphorus of one PF_6^- falling on an inversion centre. The other half anion was in a hole which contained both a PF_6^- and a diethyl ether molecule (50:50 occupancy). Both the PF_6^- and the diethyl ether showed considerable disorder and as a result were not refined anisotropically and the hydrogen atoms were excluded from the diethyl ether. Bond lengths in these species were constrained.

Complex **14** showed significant ripples around the gold after the final refinement. As a result, the anisotropic displacement parameters for C(12) and C(13) were unrealistic and thus were refined isotropically.

Supplementary material

Crystallographic data (excluding structure factors) for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 699890 (**14**), 699891 (**20**) and 699892 (**24**). Copies of the 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](http://www.ccdc.cam.ac.uk)).

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Table 1 Important structural parameters for (2-Cl₂AuC₆H₄)Ph₂P=N-(*S*)-CHMePh **14**, with esds in parentheses

Atoms	Lengths (Å)	Atoms	Angles (°)
Au(1)-Cl(1)	2.371(2)	Cl(1)-Au(1)-Cl(2)	89.70(9)
Au(1)-Cl(2)	2.297(3)	N(1)-Au(1)-C(12)	85.1(4)
Au(1)-N(1)	2.072(10)	C(12)-Au(1)-Cl(2)	92.4(3)
Au(1)-C(12)	2.045(8)	N(1)-Au(1)-Cl(1)	93.0(3)
P(1)-N(1)	1.615(10)	N(1)-P(1)-C(11)	101.9(4)
P(1)-C(11)	1.790(6)	P(1)-N(1)-C(41)	131.4(8)
N(1)-C(41)	1.473(12)		

Table 2 Selected bond parameters for **20**, with esds in parentheses

Atoms	Lengths (Å)	Atoms	Angles (°)
N(1)–Au(1)	2.1196(13)	N(1)–Au(1)–C(12)	85.90(6)
C(12)–Au(1)	2.0194(16)	O(2)–Au(1)–S(1)	91.46(4)
O(2)–Au(1)	2.0676(13)	C(3)–S(1)–Au(1)	103.08(6)
S(1)–Au(1)	2.2760(4)	O(1)–C(1)–O(2)	121.52(17)
S(1)–C(3)	1.7618(17)	C(1)–O(2)–Au(1)	130.92(11)
O(1)–C(1)	1.226(2)	O(1)–C(1)–C(2)	119.45(15)
O(2)–C(1)	1.306(2)		

Table 3 Selected bond parameters for [(2-Cl(PPh₃)AuC₆H₄)Ph₂P=NPh]PF₆ · 0.5Et₂O,
with esds in parentheses

Atoms	Lengths (Å)	Atoms	Angles (°)
Au(1)–Cl(1)	2.3463(11)	N(1)–Au(1)–C(12)	84.0(2)
Au(1)–P(2)	2.3030(12)	C(12)–Au(1)–P(2)	92.88(17)
Au(1)–C(12)	2.057(5)	P(2)–Au(1)–Cl(1)	91.11(4)
Au(1)–N(1)	2.079(5)	Cl(1)–Au(1)–N(1)	92.26(13)
P(1)–N(1)	1.620(6)	Au(1)–N(1)–P(1)	108.3(3)
N(1)–C(41)	1.419(7)	P(1)–N(1)–C(41)	124.9(4)
C(11)–C(12)	1.401(9)	N(1)–P(1)–C(11)	100.6(3)

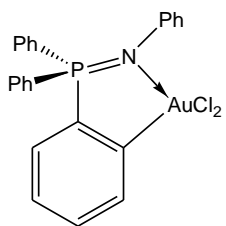
Table 4 Anti-tumour (P388 murine leukaemia) activities for selected gold(III) iminophosphoranes and related systems

Complex	IC ₅₀ ^a	
	ng mL ⁻¹	μM
1	7546	10.7
16	20021	33.4
17	<487	<0.74
18	655	1.03
19	<487	<0.69
20	658	0.97

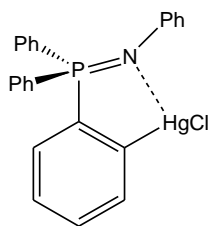
^a Concentration of sample required to reduce the cell growth of the P388 murine leukaemia cell line by 50%

Table 5 Crystallographic details for **14**, **20** and **24**

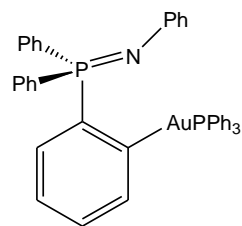
	14	20	24·0.5Et₂O
Formula	C ₂₆ H ₂₃ NPCl ₂ Au	C ₂₉ H ₂₇ NO ₂ PSAu	C ₄₄ H ₃₉ NO _{0.5} F ₆ PClAu
Molecular Weight	648.29	681.51	1029.09
<i>T</i> /K	93	93	93
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.0297(4)	9.0966(2)	50.109(2)
<i>b</i> (Å)	9.2152(4)	17.4390(4)	9.8843(5)
<i>c</i> (Å)	9.3699(4)	15.6240(4)	18.3601(8)
<i>α</i> (°)	61.462(2)	90	90
<i>β</i> (°)	63.334(2)	93.998(1)	111.043(2)
<i>γ</i> (°)	61.134(2)	90	90
<i>V</i> (Å ³)	575.22(4)	2472.49(1)	8487.2(7)
<i>Z</i>	1	4	8
<i>D</i> _{calc} (g cm ⁻³)	1.871	1.831	1.611
<i>T</i> _{max,min}	0.5534, 0.0508	0.5267, 0.2164	0.530, 0.327
Total reflections (<i>R</i> _{int})	7298 (0.0358)	44421 (0.0302)	64794 (0.0376)
Number of unique reflections	5778	10185	13986
Number of observed reflections	5273	8940	11379
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0319	0.0198	0.0536
<i>wR</i> ₂ (all data)	0.077	0.0454	0.1385
Goodness of Fit	1.062	1.016	1.142
Flack <i>x</i> parameter	0.005(7)	-	-



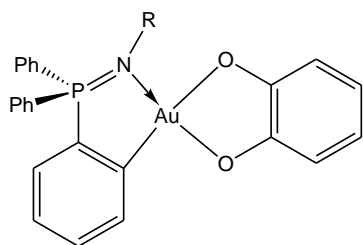
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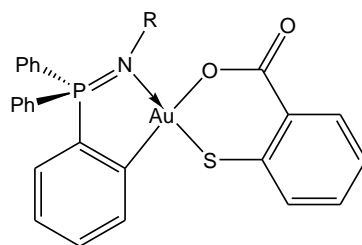


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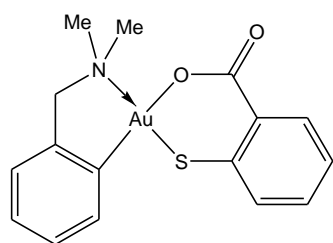
17 R = Ph

18 R = Bu^t

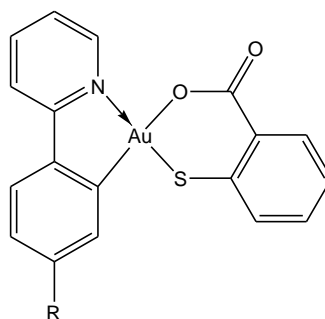


19 R = Ph

20 R = Bu^t

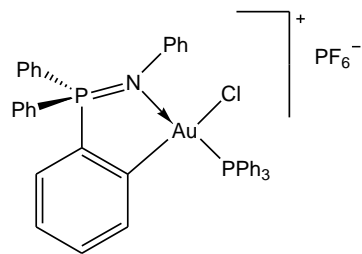


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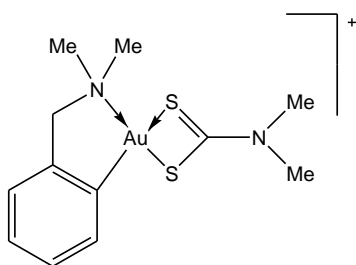


22 R = Me

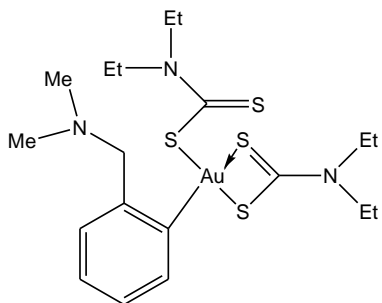
23 R = H



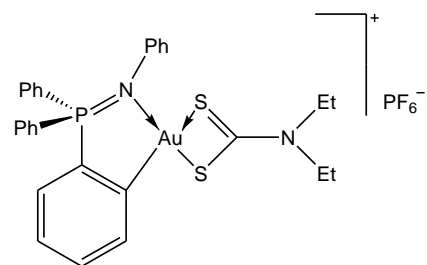
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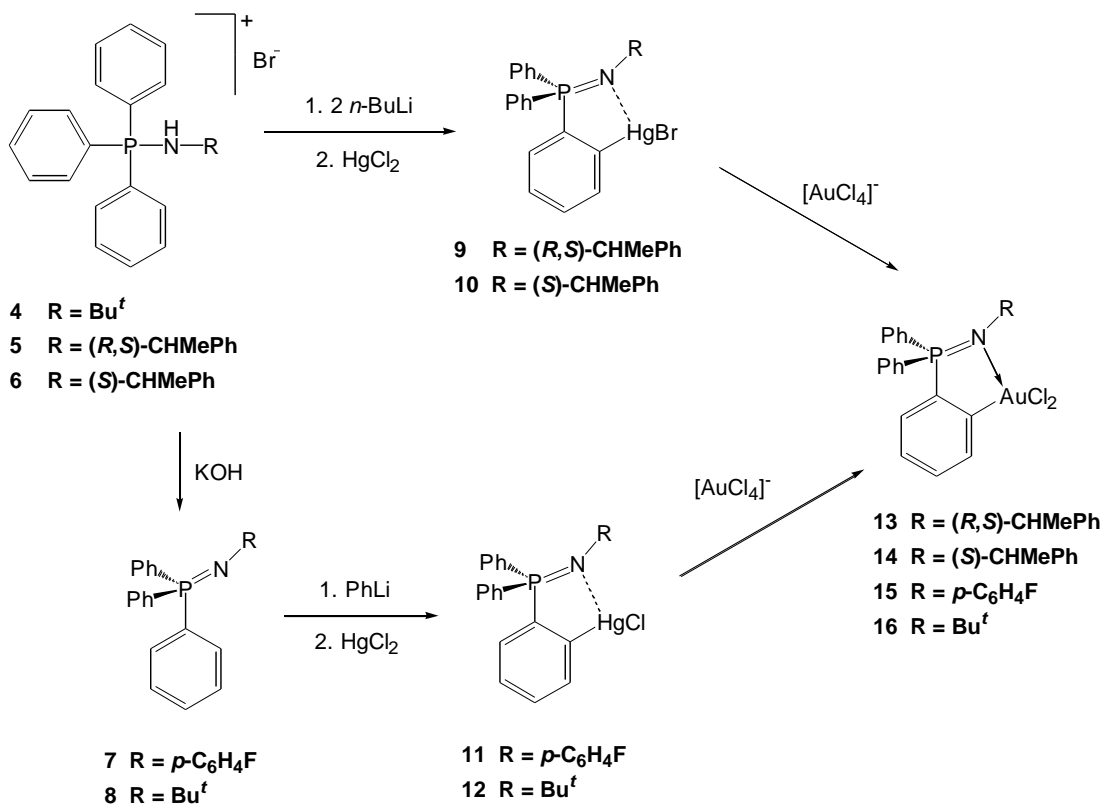
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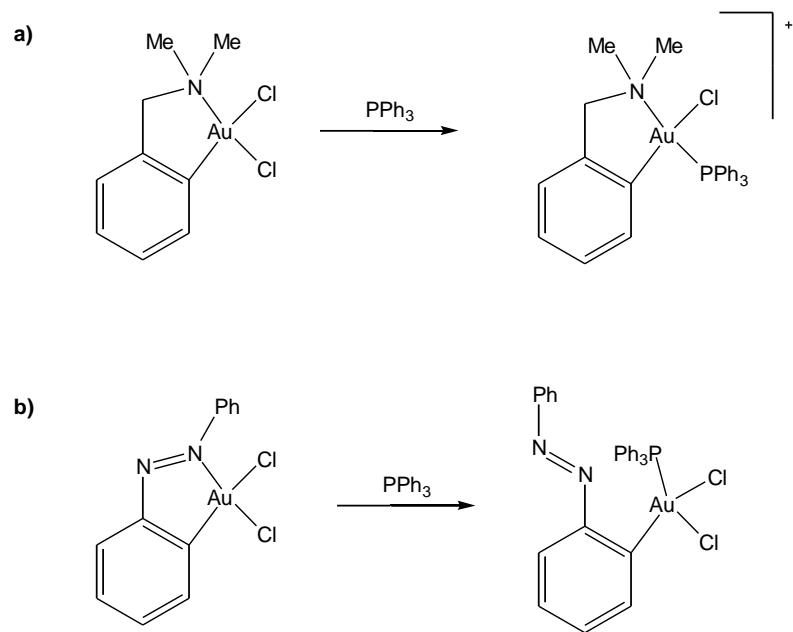
26



27



Scheme 1 Synthetic routes used for *ortho*-mercurated and cycloaurated iminophosphoranes



Scheme 2 Reaction of a) dampAuCl₂ and b) papAuCl₂ with PPh₃

Captions for Figures

Figure 1 ORTEP view of (2-Cl₂AuC₆H₄)Ph₂P=N-(*S*)-CHMePh **14**, showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level.

Figure 2 ORTEP diagram of **20**, showing atom numbering scheme with ellipsoids shown at 50% probability.

Figure 3 ORTEP diagram of **20**, showing the fold angle of the thiosalicylate ligand and puckering of the iminophosphorane ring. For clarity, only the *ipso* carbons of the uncoordinated phenyl rings and the tertiary carbon of the Bu^{*t*} group are shown.

Ellipsoids are shown at 50% probability.

Figure 4 ORTEP diagram of [(2-Cl(PPh₃)AuC₆H₄)Ph₂P=NPh]⁺. Ellipsoids are shown at 30% probability.

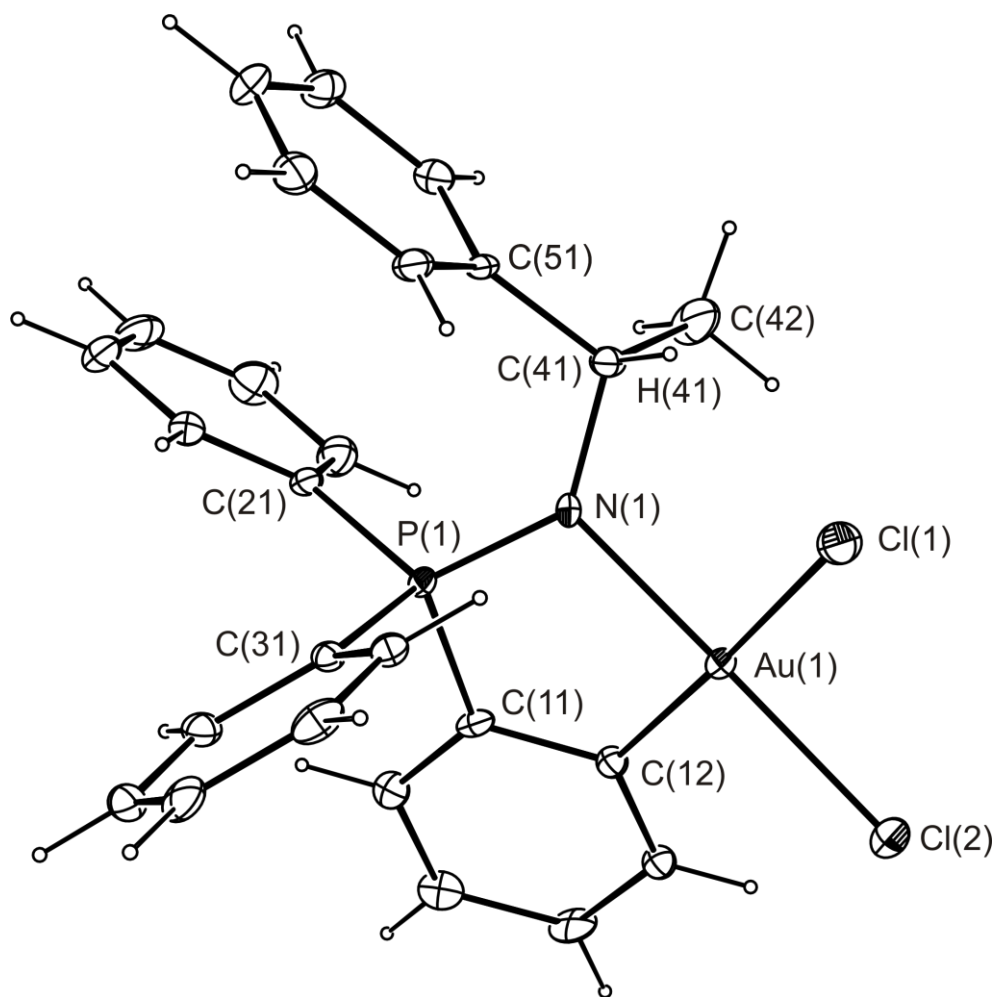


Figure 1

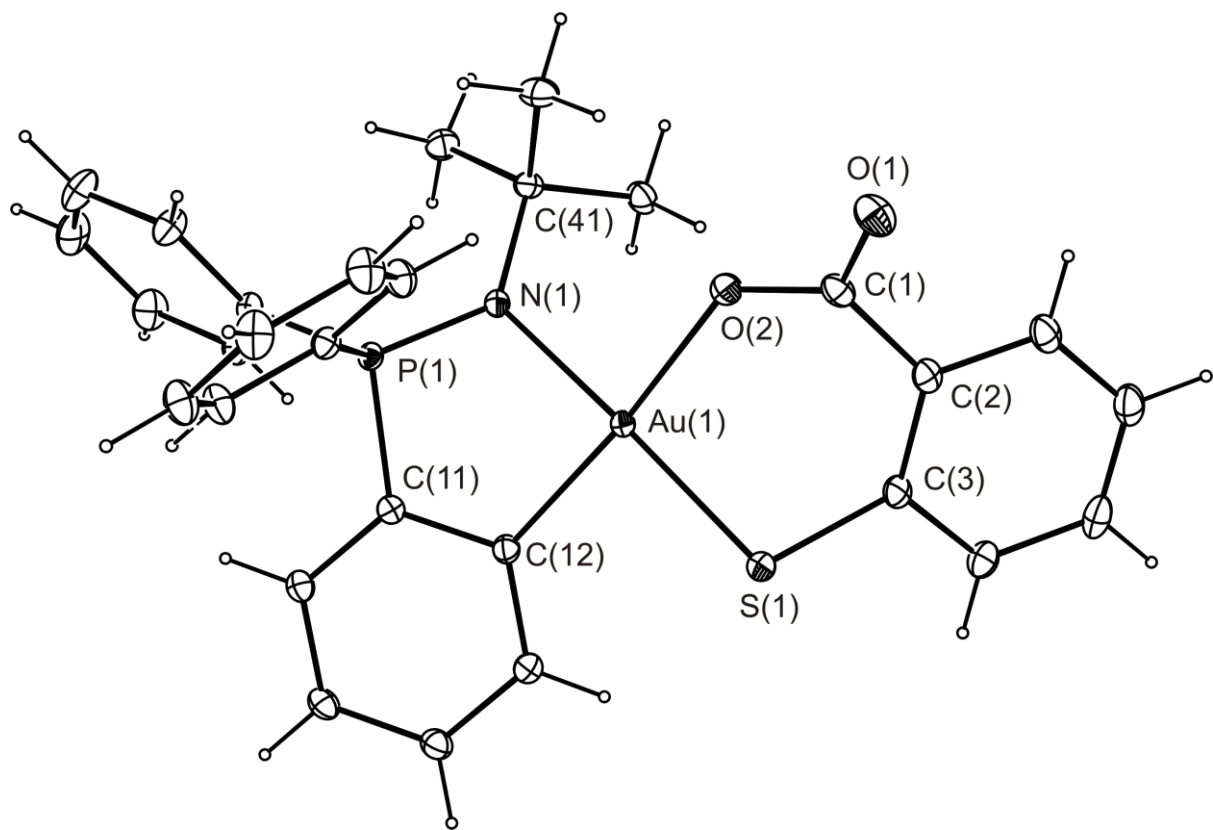


Figure 2

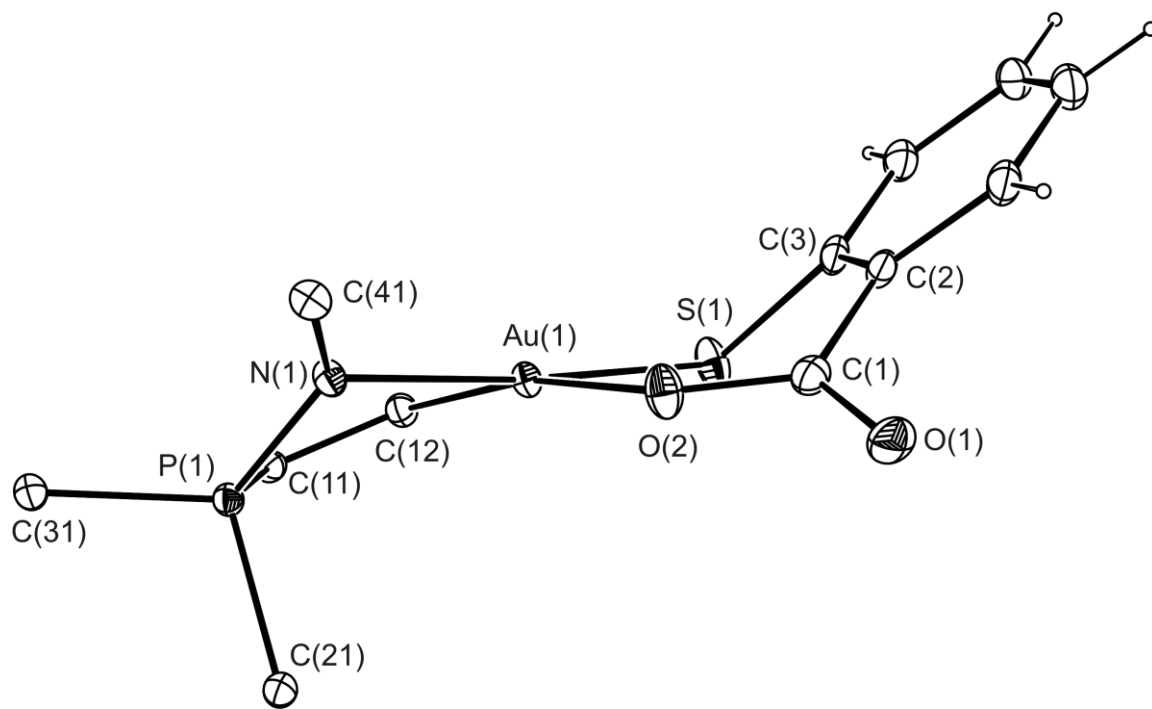


Figure 3

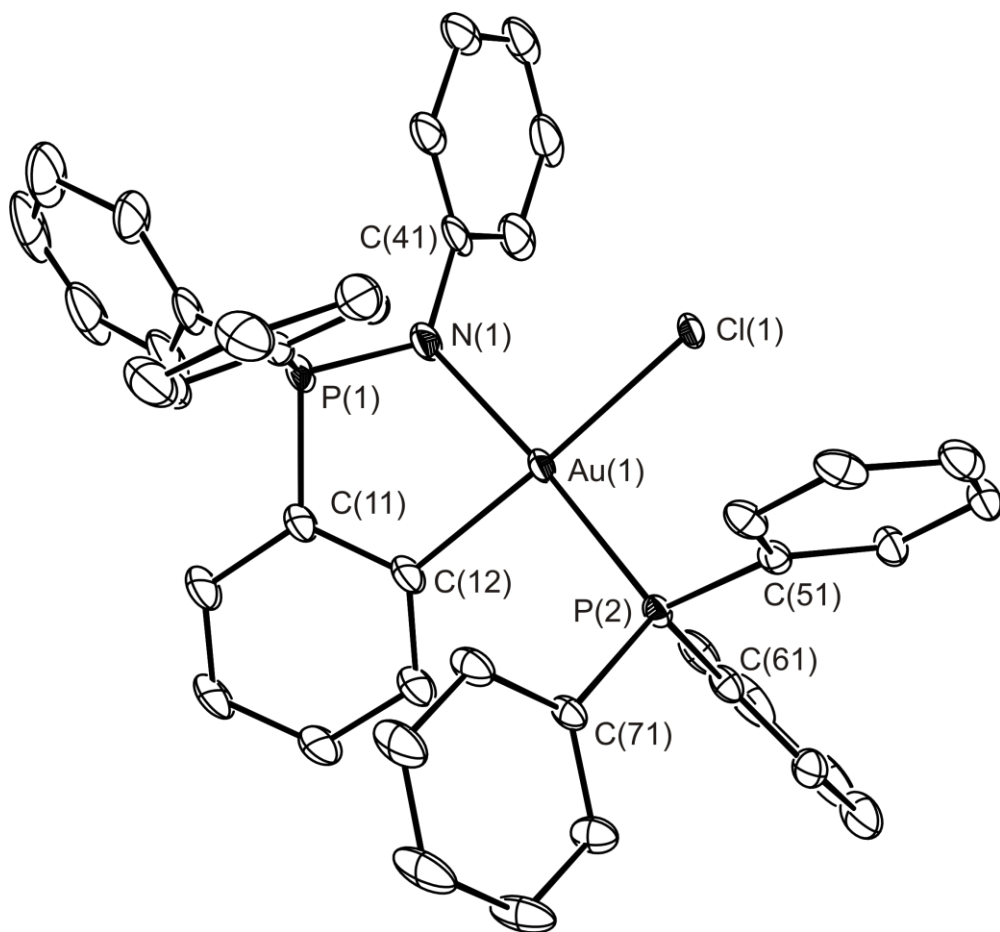


Figure 4

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