

Synthesis and Reactions of Mixed N,P Ligands

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The gold complexes $[\text{RN}=\text{C}(\text{R}')\text{CH}(\text{R})\text{PPh}_2(\text{AuCl})]$ (**6a**, $\text{R}' = t\text{Bu}$; **6b**, $\text{R}' = \text{Ad}$; $\text{R} = \text{SiMe}_3$) were synthesised from the ketimines $\text{RN}=\text{C}(\text{R}')\text{CH}(\text{R})\text{PPh}_2$ (**2a**, $\text{R}' = t\text{Bu}$; **2b**, $\text{R}' = \text{Ad}$; $\text{R} = \text{SiMe}_3$) and Me_2SAuCl . The hydrolysis of the complexes to $[\text{H}_2\text{NC}(\text{R}')=\text{CHPPH}_2(\text{AuCl})]$ (**8a**, $\text{R}' = t\text{Bu}$; **8b**, $\text{R}' = \text{Ad}$) in protic solvents was studied and the reaction intermediate $[\text{H}(\text{R})\text{NC}(t\text{Bu})=\text{CHPPH}_2(\text{AuCl})]$ (**7a**) was isolated. The ketimines were further reacted with PhPCl_2 to the cyclic phosphonium

salts $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(\text{R}')=\text{CH}]\text{X}$ (**3a**, $\text{R}' = t\text{Bu}$, $\text{X} = \text{Cl}$; **3c**, $\text{R}' = \text{Ad}$, $\text{X} = \text{Cl}$; **3d**, $\text{R}' = \text{Ad}$, $\text{X} = \text{BPh}_4$) and in the case of **3a** oxidised with sulfur to give the ring-opened β -keto thiophosphane oxide $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{C}(\text{O})t\text{Bu}$ (**9**). All compounds were fully characterised by NMR spectroscopy and in the case of **6b**, **8a** and **9** by X-ray crystallography.

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Introduction

While the use of 1-azaallyllithium complexes as ligand transfer agents has received considerable attention,^[1] the development of their utility in the context of phosphorus chemistry is in its infancy. In two recent papers,^[2,3] it was shown that treatment of the ketimine $\text{Me}_3\text{SiN}=\text{C}(t\text{Bu})\text{CH}(\text{SiMe}_3)\text{PPh}_2$ (**2a**) with $\text{R}'''\text{PCl}_2$ or PCl_3 gave the cyclic phosphonium salts $[\text{Ph}_2\text{PP}(\text{R}''')\text{N}(\text{H})\text{C}(t\text{Bu})=\text{CH}]\text{Cl}$ **3** (**3a**, $\text{R}''' = \text{Ph}$; **3b**, $\text{R}''' = \text{Et}$) and $[\text{Ph}_2\text{PP}(\text{Cl})\text{N}(\text{R})\text{C}(t\text{Bu})=\text{CH}]\text{Cl}$ ($\text{R} = \text{SiMe}_3$) **4**, respectively (Scheme 1). Conversely, treatment of the related ketimine $\text{Me}_3\text{SiN}=\text{C}(t\text{Bu})\text{CH}(\text{SiMe}_3)_2$ (**2c**) with PCl_3 generated the *trans*-1,3,2,4-diazadiphosphetidine **5** in moderate yield (Scheme 1). The key ketimines **2a** and **2c** were formed by the reactions of the 1-azaallyl $\text{RNC}(t\text{Bu})\text{C}(\text{Li})\text{HR}$ (**1a**) with Ph_2PCl or $\text{CF}_3\text{SO}_3\text{R}$ ($\text{R} = \text{SiMe}_3$), respectively.^[2] The successful preparation of compounds such as **1** is dependent on the availability of suitable 1-azaallyl precursors which react preferentially as C-centred rather than N-centred nucleophiles.^[4] For an ambidentate N,C-monoanionic ligand, C- over N-centred nucleophilicity is often favoured by utilising solvent-free 1-azaallyllithium precursors.^[4] The presence of donor solvents such as tetramethylethylenediamine significantly enhances N-nucleophilicity. In preliminary studies, the solvent-free 1-azaallyl, $\text{RNC}(\text{Ad})\text{C}(\text{Li})\text{HR}$ ($\text{Ad} = \text{adamantyl}$) (**1b**), was prepared by the reaction of LiCHR_2 and AdCN in pentane under ambient conditions.^[1] Consequently, it was envisaged that **1b** could be utilised as a C-

centred nucleophile to prepare adamantyl derivatives of **3**. This present study was stimulated by the emergence of interest in lipophilic cations as a new class of antitumour drugs with the potential to selectively target mitochondria in tumour cells.^[5] Several structurally diverse lipophilic cations have demonstrated strong activity by concentrating in mitochondria, for example, rhodamine 123,^[6] dequalinium,^[7] pyronine Y,^[8] ditercalinium,^[9] AA-1^[10] and MKT-077,^[11] the latter having been advanced to phase I clinical trials. Several classes of lipophilic cations have demonstrated that antitumour selectivity is increased as the lipophilic-hydrophilic balance is varied (e.g. bisquaternary ammonium heterocycles,^[12] $[\text{Au}(\text{P-P})_2]^+$, where P-P is a bisphosphane^[5,13] and triarylalkylphosphonium salts^[14]). Consequently, herein the preparation of lipophilic cations is reported, that is, the cyclic phosphonium salts derived from **1** and chlorophosphane precursors. The chemistry of formation and stability of these compounds is presented with a view of evaluating their potential as a new class of antitumour agent.

Results and Discussion

Synthesis

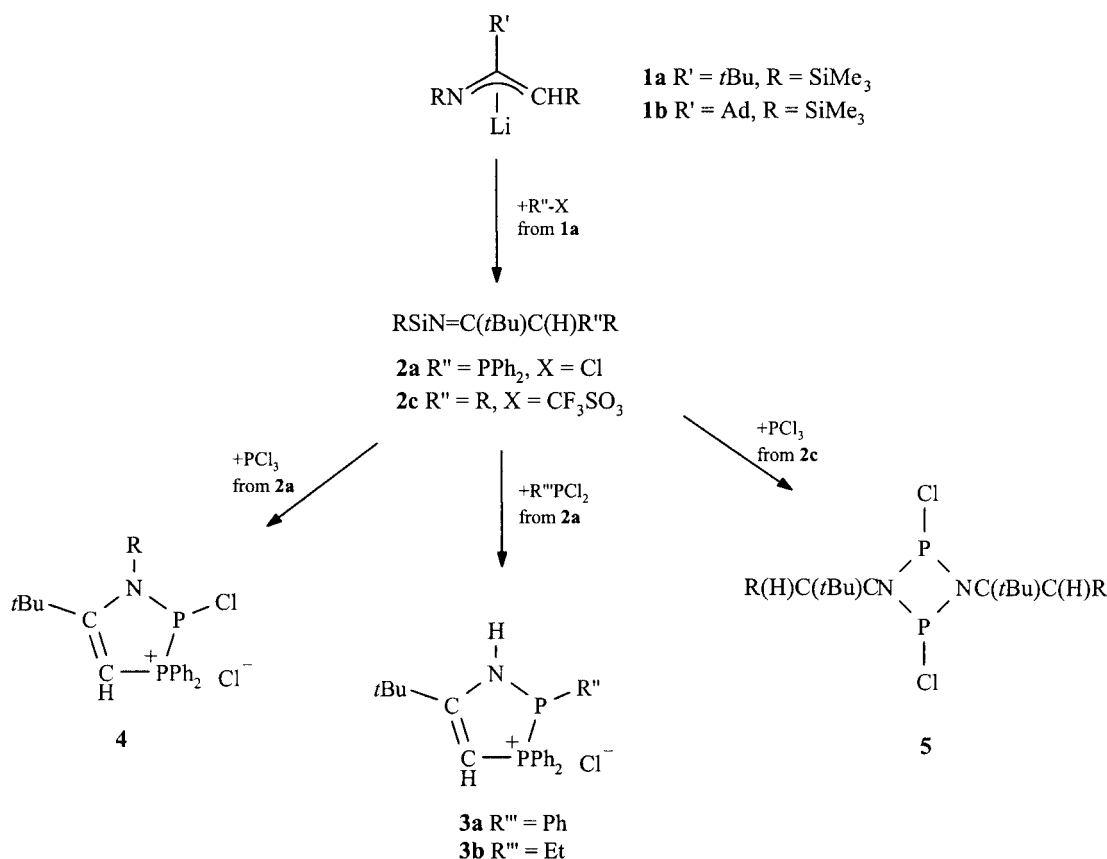
In the present study, the solvent-free 1-azaallyllithium, $\text{RNC}(\text{Ad})\text{C}(\text{Li})\text{HR}$ (**1b**) was prepared in high yield by the reaction of LiCHR_2 ($\text{R} = \text{SiMe}_3$) and AdCN ($\text{Ad} = \text{adamantyl}$) in hexane at low temperature. This type of reaction has previously been rationalised by insertion of the alkyl-lithium reagent into the CN bond of the organonitrile to form a lithioaldimine, followed by a 1,3- Me_3Si shift to give the 1-azaallyl.^[4] Compound **1b**, behaving as a C-centred nu-

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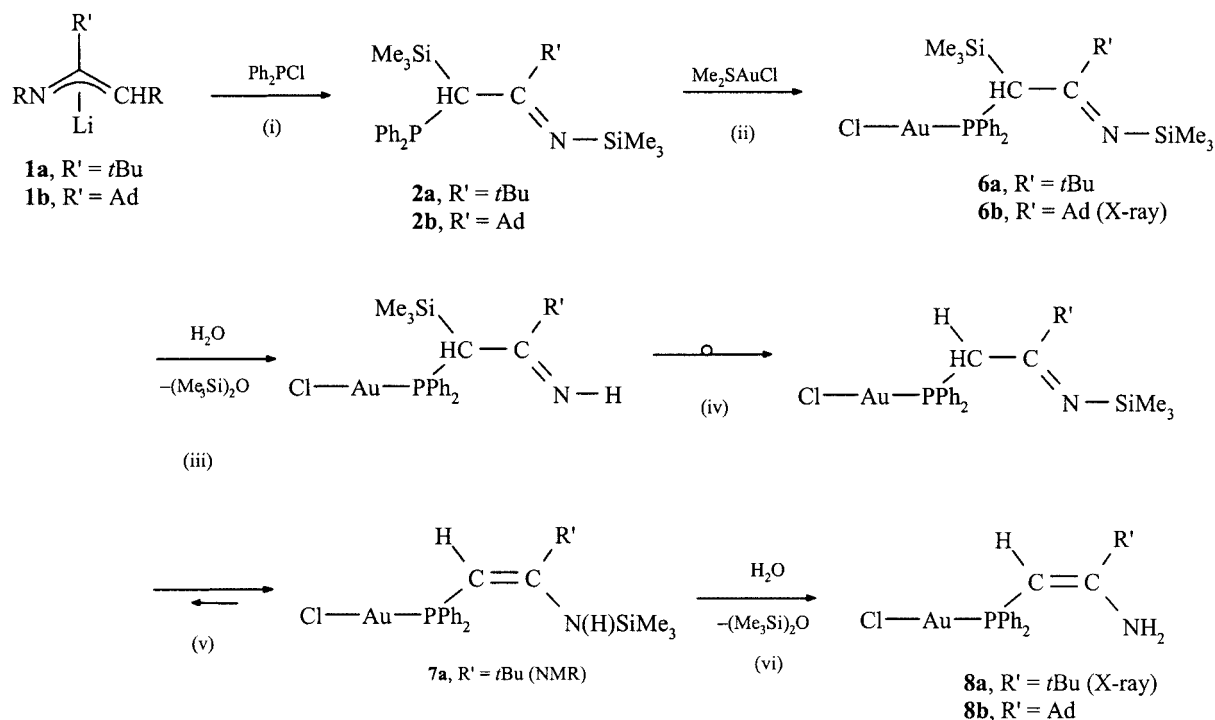
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Scheme 1. Reactions of ketimines with phosphorus halides.

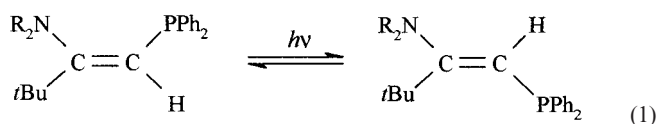
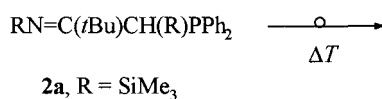
cleophile, was reacted with the phosphanyl chloride, Ph_2PCl , to give the novel ketimine $\text{RN}=\text{C}(\text{Ad})\text{CH(R)PPh}_2$ (**2b**) (i, Scheme 2) in a yield comparable to the analogous reaction involving $\text{RNC}(t\text{Bu})\text{C(Li)HR}$ and chlorodiphenylphosphane.^[2] The purification of **2b** by distillation was not attempted owing to reports that the corresponding *t*Bu derivative, $\text{RN}=\text{C}(t\text{Bu})\text{CH(R)PPh}_2$ (**2a**) isomerised to give the (*Z*)-enamine upon heating under reduced pressure, while subsequent irradiation of the (*Z*)-enamine using a medium-pressure mercury lamp afforded an equilibrium mixture of the *Z* and *E* isomers [Equation (1)].^[2] Owing to the stability that a number of transition metals can afford to phosphanes, by σ -donation of the ligand and backbonding from the metal to the vacant d-orbitals of the phosphane, the Au^{I} complex of **2b** was prepared (ii, Scheme 2). The expected stability and linear two-coordinate geometry of the complex was observed (**6b**), allowing unambiguous assignment of **2b** as a coordinated adduct by NMR and X-ray crystallographic analysis. Similarly, $[\text{Me}_3\text{SiN}=\text{C}(t\text{Bu})\text{CH}(\text{SiMe}_3)\text{PPh}_2(\text{AuCl})]$ (**6a**) was prepared in high yield from the reaction of $\text{Me}_3\text{SiN}=\text{C}(t\text{Bu})\text{CH}(\text{SiMe}_3)\text{PPh}_2$ (**2a**) and ClAuSMe_2 in THF. In both cases, the 1:1 complex was formed irrespective of stoichiometry, and an excess of ligand was typically used to ensure complete complexation. While enhanced thermal stabilities of the ketimines were achieved by coordination of P to Au^{I} it was found that the SiMe_3 group attached to N was readily hydrolysed in the presence of moisture (treatment of **6** with methanol) to give

the complexes $[\text{H}_2\text{NC(R')}=\text{C(H)PPh}_2(\text{AuCl})]$ (Scheme 2; **8a**, $\text{R}' = t\text{Bu}$; **8b**, $\text{R}' = \text{Ad}$) in high yields. The structure of the *t*Bu derivative was confirmed by crystallographic analysis. The process presumably involves cleavage of the terminal trimethylsilyl group (Scheme 2, iii), followed by a 1,3 trimethylsilyl shift from C to N (Scheme 2, iv) and isomerisation of the ketimine (the sequence of rearrangement iv and isomerisation v may well be reversed or a simultaneous process) to the thermodynamically favoured enamine (Scheme 2, v). The latter intermediate $[\text{H}(\text{SiMe}_3)\text{NC(R')}=\text{CHPPh}_2(\text{AuCl})]$ was NMR spectroscopically identified for $\text{R}' = t\text{Bu}$ (**7a**) as the major product (with **6a** and **8a** as side products) when **6a** was treated with a mixture of diethyl ether and hexane. Hydrolysis of the remaining trimethylsilyl group (Scheme 2, vi) completed a template-assisted synthesis of novel bidentate ligands. For comparison the non-hydrolysable ketimine $\text{Ph}_2\text{PCH}_2\text{C(Ph)=N(C}_6\text{H}_3\text{Me}_2\text{-2,6)}$ ^[15] was reacted with $\text{Me}_2\text{-SAuCl}$ to synthesise a *N*-aryl analogue of **6**. The gold complex was isolated in good yield (66%) and found to exist in solution as a mixture of four isomers (two tautomers analogous to the ones shown for equilibrium v in Scheme 2 and their respective *Z/E* isomers). No decomposition or change in the isomer ratio was observed in acetone solution over a period of two weeks. The described synthesis of **8** represents a new route to mixed P, N donor ligands with C–C backbone. Typically, ligands of this sort are generated by the AIBN-assisted free radical-catalysed^[16] (or base-cat-



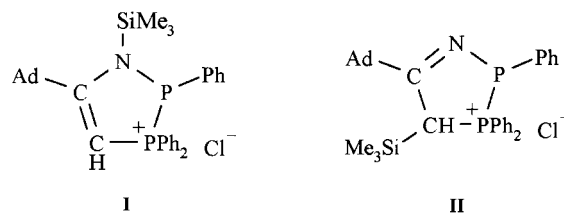
Scheme 2. Synthesis of gold phosphane complexes.

alysed^[17]) addition of P–H bonds to vinylamides [e.g. $\text{CH}_2=\text{C}(\text{O})\text{NH}_2$] or possibly the reaction of N-nucleophiles to ω -chloroalkylphosphanes. The procedure reported here, beginning with C-centred nucleophilic attack of a 1-azaallyl on a phosphanyl chloride, followed by template-assisted hydrolysis, not only provides a route to mixed P, N donor ligands, but allows for further alkyl substitution at a single carbon atom.



Since the reaction of $\text{Me}_3\text{SiN}=\text{C}(t\text{Bu})\text{CH}(\text{SiMe}_3)\text{PPh}_2$ (**2a**) with $\text{R}'''\text{PCl}_2$ proceeded to give the cyclic phosphonium salts $[\text{Ph}_2\text{PP}(\text{R}''')\text{N}(\text{H})\text{C}(t\text{Bu})=\text{CH}]\text{Cl}$ (**3a**, $\text{R}''' = \text{Ph}$, **3a** or **Et**, **3b**),^[2] the Ad-substituted analogue, $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(\text{Ad})=\text{CH}]\text{Cl}$ (**3c**) was prepared by a similar reaction involving $\text{Me}_3\text{SiN}=\text{C}(\text{Ad})\text{CH}(\text{SiMe}_3)\text{PPh}_2$ (**2b**) and PhPCl_2 , albeit in lower yield. In a process that was used to rationalise the formation of the *t*Bu-substituted cyclic phosphonium salts,^[2] the formation of $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(\text{Ad})=\text{CH}]\text{Cl}$ (**3c**) from $\text{Me}_3\text{SiN}=\text{C}(\text{Ad})\text{CH}(\text{SiMe}_3)\text{PPh}_2$

(**2b**) is likely to involve, firstly, N-centred nucleophilic attack of $\text{Me}_3\text{SiN}=\text{C}(\text{Ad})\text{CH}(\text{SiMe}_3)\text{PPh}_2$ at the P atom of PhPCl_2 , yielding the ketimido-phosphorous(III) chloride $\text{PhP}(\text{Cl})\text{N}=\text{C}(\text{Ad})\text{CH}(\text{R})\text{PPh}_2$ with concomitant Me_3SiCl elimination. Secondly, cyclisation is invoked by a rearrangement (1,3-SiMe₃ shift from C to N) of $\text{PhP}(\text{Cl})\text{N}=\text{C}(\text{Ad})\text{CH}(\text{R})\text{PPh}_2$ into the isomeric enamidophosphorous(III) chloride $\text{PhP}(\text{Cl})\text{N}(\text{R})\text{C}(\text{Ad})=\text{C}(\text{R})\text{PPh}_2$ followed by intramolecular nucleophilic displacement of the chloride to give the cyclic phosphonium salt **I**. Hydrolysis completes the conversion to $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(\text{Ad})=\text{CH}]\text{Cl}$ (**3c**). Alternatively, the transformation could proceed through cyclisation of the ketimido-phosphorous(III) chloride $\text{PhP}(\text{Cl})\text{N}=\text{C}(\text{Ad})\text{CH}(\text{R})\text{PPh}_2$, to give the cycloketimido-phosphonylphosphonium salt $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}=\text{C}(\text{Ad})\text{CHR}]\text{Cl}$ **II**, which subsequently undergoes rearrangement to **I** and hydrolysis to complete the process.



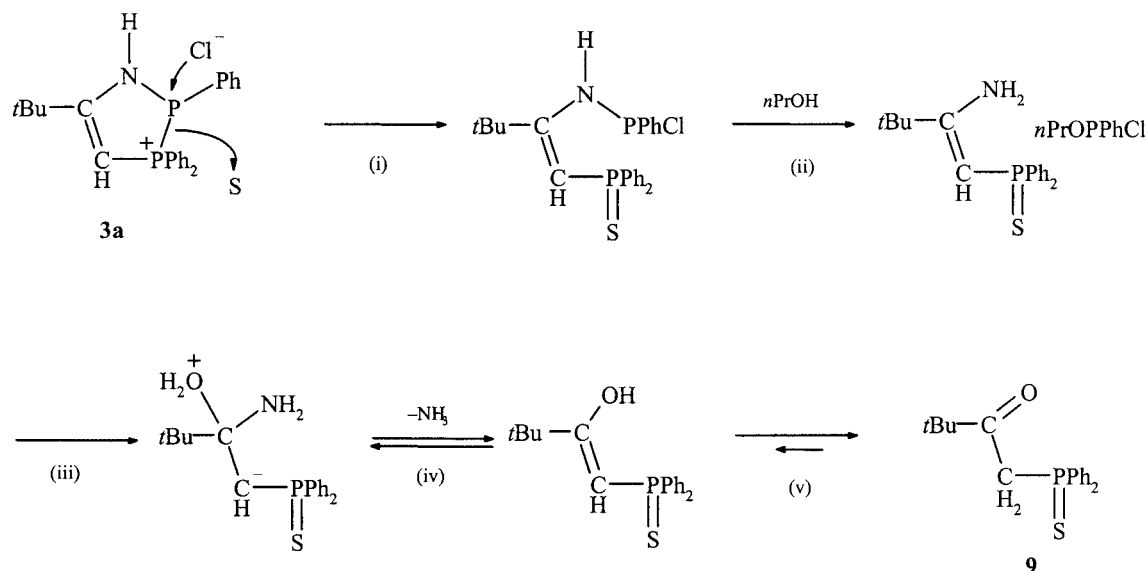
Fulfilment of the requirement of stability is necessary before proceeding with biological evaluations. While isolation and characterisation of the cyclic phosphonium salts were possible under inert gas conditions, instability of the five-membered ring (a solution of **3c** in CDCl_3 decomposed

within 24 h completely into two major products on exposure to moist air) necessitated strategies to attempt to induce stability. Consequently, metathesis reactions involving replacement of the chloride with bulkier anions were undertaken. The reaction of $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(\text{Ad})=\text{CH}]\text{Cl}$ (**3c**) with NaBPh_4 proceeded almost quantitatively to give $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(\text{Ad})=\text{CH}]\text{BPh}_4$ (**3d**), while the synthesis of related compounds with NO_3^- , CH_3CO_2^- , BF_4^- or ClO_4^- as counterion from **3c** and the corresponding silver salts was unsuccessful. ^{31}P NMR analysis of **3d**, however, revealed that the instability under atmospheric conditions was persistent, with decomposition of the five-membered ring being particularly rapid in foetal calf serum (fcs) containing cell-culture medium. Subsequently, in an attempt to acquire an insight into the factors which were responsible for this decomposition, a reaction was undertaken with $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(t\text{Bu})=\text{CH}]\text{Cl}$ (**3a**) and one equivalent of sulfur in dichloromethane, since thiol-containing compounds are constituents of fcs and the interaction with sulfur is a reasonable comparison for the observed oxygen- and moisture-facilitated decomposition pathways. Removal of the solvent in vacuo, and recrystallisation of the crude product from propan-1-ol, gave colourless crystals in good yield. Crystallographic analysis of the product revealed that a rare example of a β -keto thiophosphane, i.e. $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{C}(\text{O})t\text{Bu}$ (**9**) was obtained. It is plausible that the formation of the β -keto thiophosphane oxide involved initial sulfuration of the quarternary P and concomitant P–P bond scission of the cyclic phosphonium salt $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(t\text{Bu})=\text{CH}]\text{Cl}$ to give an intermediary chlorophosphane $\text{Ph}_2\text{P}(\text{S})\text{CH}=\text{C}(t\text{Bu})\text{N}(\text{H})\text{P}(\text{Ph})\text{Cl}$ (Scheme 3, i). Facile elimination of ClPPhOPr or a related species (Scheme 3, ii), followed by nucleophilic attack of water on the $t\text{Bu}$ -substituted carbon in a Michael-type addition reaction (the related P^{III} compounds **8** in Scheme 2 are in contrast unreactive) produces a zwitterionic intermediate (Scheme 3, iii) whose negative charge is stabilised by the $\text{P}=\text{S}$ double bond. Ethene bond

reformation is accompanied by the elimination of ammonia (Scheme 3, iv), with enol-keto tautomerism (Scheme 3, v) completing the envisaged reaction pathway involving the formation of $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{C}(\text{O})t\text{Bu}$ (**9**) from $[\text{Ph}_2\text{PP}(\text{Ph})\text{N}(\text{H})\text{C}(t\text{Bu})=\text{CH}]\text{Cl}$. Reaction of **3c** with oxygen-free water in CH_2Cl_2 resulted in a solid that showed two major signals at $\delta = 22.5$ and 23.3 ppm in the ^{31}P NMR spectrum that were within 1 ppm identical to those found in the above-mentioned decomposition study of **3c** in CDCl_3 . This implicates the reaction with water as a major reason for the instability of the phosphonium salts. Attempts to isolate the products were unsuccessful and a mass spectrum of the product mixture was inconclusive. The further reaction of **3c** with dry oxygen yielded after removal of the solvent a solid that consisted of a mixture of numerous compounds with unreacted starting material being one of the major components. The mass spectrum of the mixture showed m/z values consistent with **3c** and an oxygen analogue $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Ad}]$ of **9**. The persistent instability of the phosphonium salts under atmospheric conditions precluded further biological testing and further development as potential antitumour drugs is at this stage doubtful.

Solid-State Structures of Compounds **6b**, **8a** and **9**

The molecular structures of $[\text{RN}=\text{C}(\text{Ad})\text{CH}(\text{R})\text{PPh}_2(\text{AuCl})]$ (**6b**) ($\text{R} = \text{SiMe}_3$) and $[\text{H}_2\text{NC}(t\text{Bu})=\text{C}(\text{H})\text{PPh}_2(\text{AuCl})]$ (**8a**) with the atom numbering scheme are shown in Figure 1 and Figure 2, while selected bond lengths are compared in Table 1. Complex **6b** crystallises as a discrete monomer with the Au atom adopting a linear geometry $[\text{P}-\text{Au}-\text{Cl}] 178.74(9)^\circ$. The Au–P and Au–Cl distances of 2.245(2) and 2.296(2) Å are unexceptional and compare well to those found in related two-coordinate phosphane complexes such as $i\text{Bu}_3\text{PAuCl}$,^[18] Et_3PAuCl ,^[19] Ph_3PAuCl ,^[20] $(2\text{-Pyr})_3\text{PAuCl}$ ^[21] or $i\text{Pr}_3\text{PAuCl}$.^[22] The short



Scheme 3. Possible reaction mechanism for the formation of **9**.

C2–N [1.266(6) Å] and long C1–C2 [1.558(6) Å] distances are consistent with the alkyl substituent at P being an iminoalkyl. There is considerable steric repulsion between the bulky adamantyl and trimethylsilyl groups attached to the two sp^2 hybridised atoms C2 and N, respectively, as is evident from the deviation of the angles C3–C2–N [123.9(4)°] and C2–N–Si3 [151.9(4)°] from the idealised geometry of 120°.

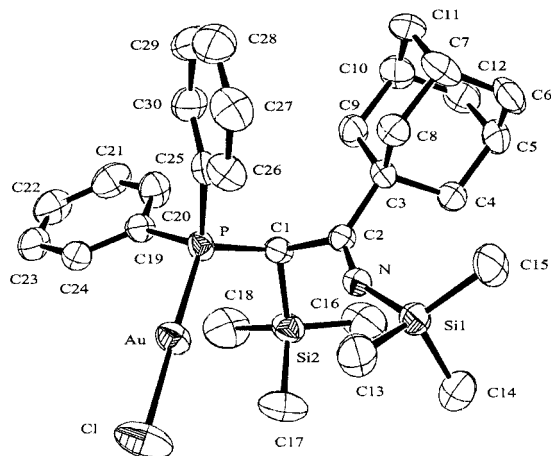


Figure 1. Molecular structure of ClAuPPh₂CH(SiMe₃)C(Ad)-NSiMe₃ (**6b**). Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

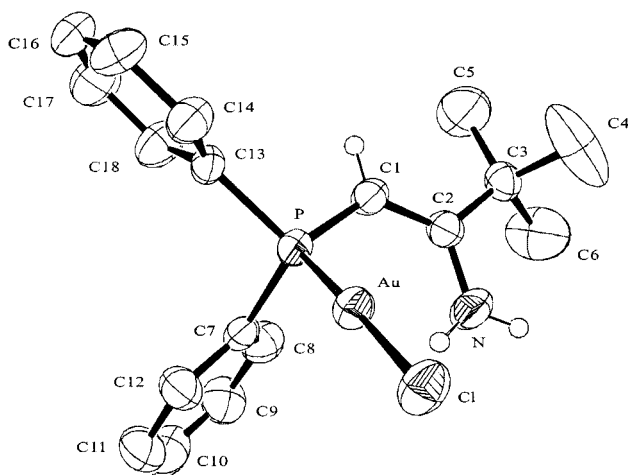


Figure 2. Molecular structure of ClAuPPh₂CHC(*t*Bu)NH₂ (**8a**). Thermal ellipsoids are drawn at the 50% probability level. H atoms (except at N, C1) have been omitted for clarity.

Compound **8a** crystallises as a centrosymmetric dimer (Figure 3) as a consequence of conventional hydrogen bonding between the Cl and NH₂ groups of adjacent molecules hereby forming a 14-membered heterocycle R₂²(14). The Cl $\cdots$ N contacts [3.345(7) Å] are close to the mean value of 3.299(6) Å reported in the literature.^[23] The dimers are further weakly hydrogen-bonded by short C–H $\cdots$ Cl interactions (C4–H4 $\cdots$ Cl: 2.76 Å, 172°) between the Cl atom and one of the methyl groups of the *t*Bu substituent in the backbone of an adjacent dimer (Figure 3, Table 2). The existence of C–H $\cdots$ Cl (H $\cdots$ A) interactions has been discussed in se-

Table 1. Selected bond lengths [Å] and angles [°] for compound **6b**, **8a** and **9**.

Bond length/angle	6b	8a	9
Au/S–P	2.245(2)	2.243(2)	1.9563(9)
Au–Cl	2.296(2)	2.295(2)	–
P–C1	1.825(6)	1.777(7)	1.822(2)
P–C ^[a]	1.838(5)	1.837(7)	1.820(2)
P–C ^[b]	1.830(6)	1.819(6)	1.821(2)
N/O–C2	1.266(6)	1.369(9)	1.209(3)
C1–C2	1.558(6)	1.361(9)	1.523(3)
P–Au–Cl	178.74(6)	177.24(6)	–

[a] C = carbon C19 (**6b**); carbon C7 (**8a**, **9**). [b] C = carbon C25 (**6b**); carbon C13 (**8a**, **9**).

veral recent papers^[24] and a C–H $\cdots$ Cl distance of close to 3 Å has been suggested as reasonable.^[24a] The closest contact in compound **6b** (C9–H9B $\cdots$ Cl: 2.94 Å, 148°) is in comparison considerably longer. In this context it is noteworthy that the distance between the methyl group (C4) involved in non-classical H-bonding and the central carbon atom of the *t*Bu group (C3) in **8a** [1.54(1) Å] is longer than those to the non-hydrogen-bonded methyl groups [1.52(1), 1.50(1) Å].

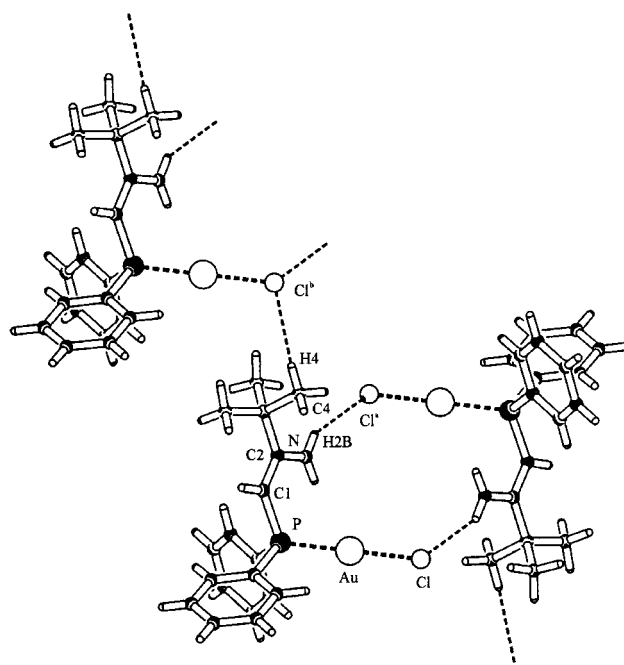


Figure 3. H bonding and intermolecular contacts in compound **8a**. (For symmetry codes see Table 2).

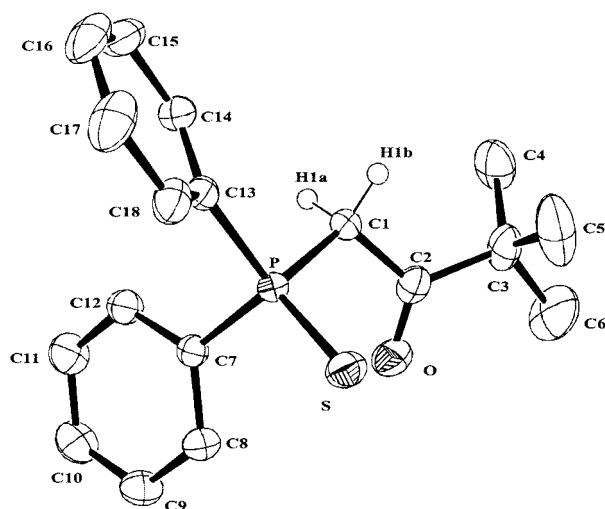
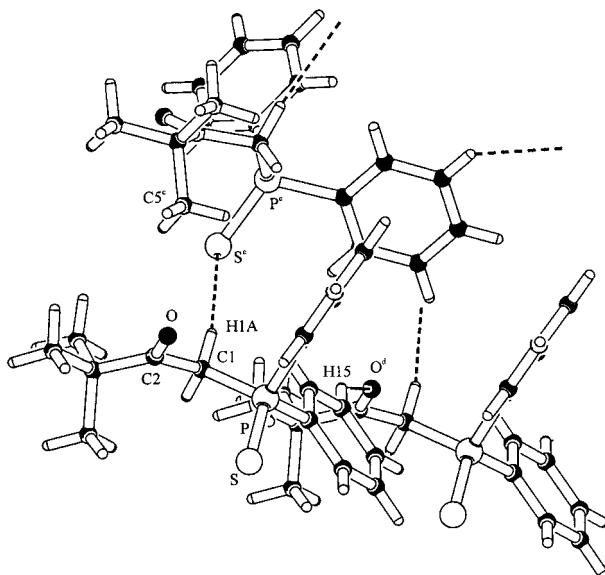
The bond lengths and geometry of the Au atom [Au–P: 2.243(2) Å, Au–Cl: 2.295(2) Å, P–Au–Cl 177.24(6)°] in complex **8a** are similar to those in complex **6b**. The short CN single bond [C1–N 1.369(9) Å] and comparatively long CC double bond [C1–C2 1.361(9) Å] in the phosphane substituent indicate considerable delocalisation within the enamine backbone (*Z* isomer) of the ligand that may extend to some degree to the phosphorus atom (c.f. short P–C1 as compared to long P–Ph distances).

Aurophilic Au $\cdots$ Au contacts^[25] that have been found to influence the solid-state structures of gold phosphane com-

Table 2. Intermolecular contact distances [Å] and angles [°] for compounds **8a** and **9**.

D–H...A	D–H	H...A	D...A	D–H...A
Compound 8a				
N–H2B...C ^[a]	0.86	2.57	3.345(7)	151
C4–H4...C ^[b]	0.96	2.76	3.717(13)	172
Compound 9				
C1–H1A...S ^[c]	0.99	2.80	3.755(2)	163
C15–H15...O ^[d]	0.95	2.42	3.241(3)	145

[a] Symmetry codes: $-x + 1, -y + 1, -z$. [b] $x, 1 + y, z$. [c] $x, -y, -1/2 + z$. [d] $1/2 + x, -1/2 + y, z$.

Figure 4. Molecular structure of $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{C}(\text{O})t\text{Bu}$ (**9**). Thermal ellipsoids are drawn at the 50% probability level. H atoms (except at C1) have been omitted for clarity.Figure 5. Intermolecular contacts in compound **9**. (For symmetry codes see Table 2).

plexes^[26] in the case of less bulky phosphanes are not observed in compound **6b** or **8a**.

The molecular structure of compound **9** and the atom numbering scheme is illustrated in Figure 4. The bond lengths and angles (Table 1) are unexceptional and compare well to the related dimethyl and diphenylphosphane sulfides $\text{Me}_2\text{P}(\text{S})\text{C}(\text{Me})\text{OHC}(\text{O})\text{Me}$,^[27] $\text{Me}_2\text{P}(\text{S})\text{C}(\text{Ph})\text{OHC}(\text{O})\text{Ph}$ ^[27] and $\text{Ph}_2\text{P}(\text{S})\text{CHC}(\text{O})(\text{CH}_2)_4$.^[28] The PS and CO groups are not coplanar as indicated by an angle of $71.5(2)^\circ$ between the two planes formed by the atoms S, P, Cl and C1, C2, O. This facilitates weak intermolecular C–H(Ph)...O and C–H(CH₂)...S interactions (Table 2) between adjacent molecules of **9** (Figure 5). There is also a close contact between C5 and O (C5...O: 3.130 Å).

Experimental Section

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in CDCl_3 , $[\text{D}_6]\text{acetone}$ and $[\text{D}_6]\text{DMSO}$ at ambient probe temperature by using the following Bruker instruments: DRX 400 (^1H 400.13; ^{31}P 161.9; ^{13}C 100.6 MHz), Avance 300 (^1H 300.13; ^{13}C 75.5 MHz) or AC200 (^1H 200.13 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C and ^{31}P NMR spectra were all proton-decoupled. Elemental analyses were determined by the Institute for Soil, Climate and Water, Pretoria, South Africa. The following abbreviations are used throughout the experimental section: s = singlet, br. s = broad singlet, d = doublet, dd = doublet of doublet, m = multiplet, mm = multiple multiplets. Coupling constants (J) are given in Hz.

Synthesis of $\text{Me}_3\text{SiNC}(\text{Ad})\text{CH}(\text{SiMe}_3)\text{PPh}_2$ (2b**):** Ph_2PCl (0.38 g, 1.71 mmol) in hexane (15 cm^3) was added dropwise to a magnetically stirred solution (-80°C) of the 1-azaallyllithium complex **1b** (0.56 g, 1.71 mmol) in hexane (30 cm^3). After stirring for 12 hours, the solution was filtered and the solvent removed in vacuo to give **2b** as a yellow oil (0.73 g, 80%). ^1H NMR (CDCl_3): $\delta = -0.04$ (s, 9 H, CSiMe_3), 0.28 (s, 9 H, NSiMe_3), 1.25–1.83 (mm, 15 H, Ad), 3.95 [d, $^2J_{\text{H,P}} = 6.1$ Hz, 1 H, CH] and 7.19–7.74 (mm, 10 H, Ph) ppm. ^{31}P NMR (CDCl_3): $\delta = -2.1$ ppm. ^{13}C NMR (CDCl_3): $\delta = 0.4$ (s, CSiMe_3), 0.5 (s, NSiMe_3), 28.6 (s, CH-Ad), 36.5 (s, $\text{CH}_2\text{-Ad}$), 31.6 (s, *ipso*-C-Ad), 38.9 [d, $^1J_{\text{C,P}} = 27.3$ Hz, CH], 39.5 (s, $\text{CH}_2\text{-Ad}$), 127.7 [d, $^3J_{\text{C,P}} = 7.1$ Hz, *m*-Ph], 128.2 [d, $^3J_{\text{C,P}} = 7.7$ Hz, *m*-Ph], 128.5 (s, *p*-Ph), 129.0 (s, *p*-Ph), 134.3 [d, $^2J_{\text{C,P}} = 21.8$ Hz, *o*-Ph], 134.6 [d, $^2J_{\text{C,P}} = 19.1$ Hz, *o*-Ph], 138.7 [d, $^1J_{\text{C,P}} = 16.3$ Hz, *ipso*-C], 140.3 [d, $^1J_{\text{C,P}} = 28.5$ Hz, *ipso*-C] and 183.1 [d, $^2J_{\text{C,P}} = 2.2$ Hz, CN] ppm.

Synthesis of $\text{Ph}_2\text{P}^+\text{P}(\text{Ph})\text{N}(\text{H})\text{C}(\text{Ad})\text{CH Cl}^-$ (3c**):** PhPCl_2 (0.57 g, 3.16 mmol) was added to $\text{Me}_3\text{SiN}=\text{C}(\text{Ad})\text{CH}(\text{SiMe}_3)\text{PPh}_2$ (**2b**) (1.60 g, 3.16 mmol). After complete addition, the mixture was heated at 50°C for 30 min. It liquefied as the ClSiMe_3 was given off. The mixture was then dried in vacuo to give a yellow solid (1.43 g, 90%). $\text{C}_{27}\text{H}_{32}\text{ClNP}_2$: calcd. C 69.30, H 6.85, N 2.99; found C 68.52, H 6.87, N 2.47 (the compound incorporates varying amounts of toluene). Pale yellow crystals were obtained from hot toluene (0.40 g, 25%). ^1H NMR (CDCl_3): $\delta = 1.71$ –1.84 (mm, 15 H, Ad), 4.63 [d, $^2J_{\text{H,P}} = 15.6$ Hz, 1 H, NH], 6.90–7.20 (mm, 5 H, Ph), 7.38–7.87 (mm, 10 H, Ph) and 9.99 [dd, $^2J_{\text{H,P}} = 32.0$, $^3J_{\text{H,P}} = 21.2$ Hz, 1 H, CH] ppm. ^{31}P NMR (CDCl_3): $\delta = 13.5$ [d, $^1J_{\text{P,P}} = 239.2$ Hz, $\lambda^3\text{P}$], 41.9 [d, $^1J_{\text{P,P}} = 239.2$ Hz, $\lambda^4\text{P}^+$] ppm. ^{13}C NMR (CDCl_3): $\delta = 28.3$ (s, CH-Ad), 36.2 (s, $\text{CH}_2\text{-Ad}$), 40.4 [d, $^3J_{\text{C,P}} =$

11.3 Hz, *ipso*-C-Ad), 41.0 (s, CH₂-Ad), 64.1 [d, ¹J_{C,P} = 72.9 Hz, CH], 118.1, [d, ¹J_{C,P} = 82.5 Hz, *ipso*-C], 124.2 [dd, ²J_{C,P} = 75.0, ³J_{C,P} = 18.8 Hz, *ipso*-C], 125.2 (s, *ipso*-C), 128.7 (mm of aromatic C atoms) and 186.8 [overlapping dd, ²J_{C,P} = 27.9, ³J_{C,P} = 14.4 Hz, CN] ppm.

Synthesis of Ph₂P⁺P(Ph)N(H)C(Ad)CH BPh₄[−] (3d): NaBPh₄ (0.37 g, 1.08 mmol) was added to a magnetically stirred solution of CH₂Cl₂ (20 cm³) and Ph₂P⁺P(Ph)N(H)C(Ad)CH Cl[−] (3c) (0.54 g, 1.07 mmol) at −30 °C. The reaction mixture was stirred for 12 hours and warmed to room temperature giving an off-white solution. It was filtered and the solvent removed in vacuo to give a yellow solid. Various recrystallisation attempts led to the decomposition of the compound. **3d** (crude: 0.76 g, 92%). ¹H NMR (CDCl₃): δ = 1.57–1.89 (mm, 15 H, Ad), 4.64 [d, 1 H, ²J_{H,P} = 15.3 Hz, NH], 6.00 [dd, ²J_{H,P} = 22.0, ³J_{H,P} = 8.0 Hz, 1 H, CH], 6.84–7.10 (mm, 5 H, Ph) and 7.36–7.64 (mm, 10 H, Ph) ppm. ³¹P NMR (CDCl₃): δ = 10.8 [d, ¹J_{P,P} = 241.4 Hz, λ³P], 43.8 [d, ¹J_{P,P} = 241.4 Hz, λ⁴P⁺] ppm. ¹³C NMR (CDCl₃): δ = 28.0 (s, CH-Ad), 36.0 (s, CH₂-Ad), 39.8 (s, *ipso*-C-Ad), 41.0 (s, CH₂-Ad), 66.4 [d, ¹J_{C,P} = 71.4 Hz, CH], 117.3 [d, ¹J_{C,P} = 81.0 Hz, *ipso*-C], 121.7 (s, BPh), 122.4 [d, ¹J_{C,P} = 32.5 Hz, *ipso*-C], 125.5 (s, BPh), 129.2 [d, ¹J_{C,P} = 5.6 Hz, Ph], 129.5 [d, ¹J_{C,P} = 19.0 Hz, Ph], 130.3 [d, ¹J_{C,P} = 12.6 Hz, Ph], 132.8 [d, ¹J_{C,P} = 10.4 Hz, Ph], 136.3 (s, BPh), 164.2 [q, ¹J_{C,B} = 49.3 Hz, *ipso*-C] and 184.8 [d, ²J_{C,P} = 13.0 Hz, CN] ppm.

Synthesis of ClAuPPh₂CH(SiMe₃)C(*t*Bu)NSiMe₃ (6a): ClAuSMe₂[²⁹] (0.24 g, 0.82 mmol) was added to a solution of Ph₂PCH(SiMe₃)C(*t*Bu)NSiMe₃ (**2a**) (0.30 g, 0.85 mmol) in THF (10 cm³) at 0 °C. The solution was stirred at 0 °C for 10 minutes, warmed to room temperature and stirred for further 15 minutes. The solvent was removed in vacuo to yield a sticky yellow compound (**6a**, 0.45 g, 83%). ¹H NMR (CDCl₃): δ = 0.17 (s, 9 H, CSiMe₃), 0.33 (s, 9 H, NSiMe₃), 0.88 (s, 9 H, *t*Bu), 4.46 [d, ²J_{H,P} = 15.8 Hz, 1 H, CH] and 7.44–7.81 (mm, 10 H, Ph) ppm. ³¹P NMR (CDCl₃): δ = 40.7 ppm. ¹³C NMR (CDCl₃): δ = 0.8 [d, ³J_{C,P} = 4.3 Hz, CSiMe₃], 3.1 (s, NSiMe₃), 29.0 (s, CMe₃), 38.8 [d, ¹J_{C,P} = 30.4 Hz, CH], 43.6 (s, CMe₃), 128.5 [d, ²J_{C,P} = 11.6 Hz, *o*-Ph], 131.0 [d, ³J_{C,P} = 9.9 Hz, *m*-Ph], 131.8 [d, ⁴J_{C,P} = 2.4 Hz, *p*-Ph], 132.8 [d, ¹J_{C,P} = 79.0 Hz, *ipso*-C] and 179.4 [d, ²J_{C,P} = 6.0 Hz, CN] ppm.

Synthesis of ClAuPPh₂CH(SiMe₃)C(Ad)NSiMe₃ (6b): ClAuSMe₂[²⁹] (0.30 g, 1.02 mmol) was added to a solution of Ph₂PCH(SiMe₃)C(Ad)NSiMe₃ (**2b**) (0.78 g, 1.54 mmol) in THF (20 cm³) at 0 °C. The solution was stirred for 15 minutes and the solvent was removed in vacuo to yield a yellow solid. Colourless crystals of **6b** (0.25 g, 33%) were obtained from CH₂Cl₂ at −60 °C. ¹H NMR (CDCl₃): δ = 0.07 (s, 9 H, CSiMe₃), 0.25 (s, 9 H, NSiMe₃), 1.26–1.86 (mm, 15 H, adamantyl), 4.37 [d, ²J_{H,P} = 15.9 Hz, 1 H, CH], 7.41–7.43 (mm, 6 H, Ph), 7.71–7.74 (mm, 2 H, Ph) and 7.92–7.98 (mm, 2 H, Ph) ppm. ³¹P NMR (CDCl₃): δ = 40.9 ppm. ¹³C NMR (CDCl₃): δ = 1.0 [d, ³J_{C,P} = 4.0 Hz, CSiMe₃], 3.7 (s, NSiMe₃), 28.5 (s, CH-Ad), 36.2 (s, CH₂-Ad), 37.6 [d, ¹J_{C,P} = 30.2 Hz, CH], 39.6 (s, CH₂-Ad), *ipso*-C-Ad not observed, 128.5 [d, ³J_{C,P} = 11.7 Hz, *m*-Ph], 131.3 [d, ⁴J_{C,P} = 2.8 Hz, *p*-Ph], 132.3 [d, ¹J_{C,P} = 79.9 Hz, *ipso*-C], 134.3 [d, ²J_{C,P} = 14.2 Hz, *o*-Ph] and 179.5 (s, CN) ppm.

Synthesis of ClAuPPh₂CHC(*t*Bu)N(H)SiMe₃ (7a): ClAuPPh₂CH-(SiMe₃)C(*t*Bu)NSiMe₃ (**6a**) was dissolved in a mixture of ether/hexane. A yellow powder of **7a** (0.37 g, 66%) was obtained at −60 °C. ¹H NMR (CDCl₃): δ = 0.14 (s, 9 H, SiMe₃), 1.23 (s, 9 H, *t*Bu), 4.33 [d, ²J_{H-P} = 5.6 Hz, 1 H, CH], 4.81 [br. s, 1 H, NH], 7.42–7.69 (mm, 10 H, Ph) ppm. ³¹P NMR (CDCl₃): δ = 10.6 ppm. ¹³C NMR (CDCl₃): δ = 2.5 (s, SiMe₃), 29.8 (s, CMe₃), 38.3 [d, ³J_{C,P} =

8.5 Hz, CMe₃], 86.4 [d, ¹J_{C,P} = 72.3 Hz, CH], 129.1 [d, ³J_{C,P} = 11.7 Hz, *m*-Ph], 131.2 [d, ¹J_{C,P} = 84.5 Hz, *ipso*-C], 131.4 [d, ⁴J_{C,P} = 2.6 Hz, *p*-Ph], 133.2 [d, ²J_{C,P} = 13.6 Hz, *o*-Ph] and 173.3 (s, CN) ppm.

Synthesis of ClAuPPh₂C(H)C(*t*Bu)NH₂ (8a): ClAuPPh₂CHC(*t*Bu)-N(H)SiMe₃ (**7a**) was dissolved in hot methanol. Colourless crystals of **8a** (0.06 g, 14%) were obtained after slow cooling of the solution at room temperature. C₁₈H₂₂AuClNP: calcd. C 41.92, H 4.30, N 2.72; found C 41.20, H 4.33, N 2.70. ¹H NMR (CDCl₃): δ = 1.23 (s, 9 H, *t*Bu), 4.32 [d, ²J_{H-P} = 8.8 Hz, 1 H, CH], 4.82 (br. s, 2 H, NH₂), 7.44 (6 H, Ph) and 7.57–7.63 (mm, 4 H, Ph) ppm. ³¹P NMR (CDCl₃): δ = 7.1 ppm. ¹³C NMR (CDCl₃): δ = 29.1 (s, CMe₃), 37.2 [d, ³J_{C,P} = 9.8 Hz, CMe₃], 72.8 [d, ¹J_{C,P} = 71.9 Hz, CH], 129.0 [d, ³J_{C,P} = 11.7 Hz, *m*-Ph], 131.2 [d, ⁴J_{C,P} = 2.3 Hz, *p*-Ph], 131.9 [s, *ipso*-C], 132.9 [d, ²J_{C,P} = 13.5 Hz], *o*-Ph and 168.9 (s, CN) ppm.

Crude **6a** (0.45 g, 0.68 mmol) was dissolved in methanol (20 cm³) and after a period of 5 minutes a white precipitate started to form. After stirring the reaction mixture for 30 minutes at room temperature the solvent was carefully decanted and the residue dried in vacuo to give 0.31 g (88%) of **8a**.

Synthesis of ClAuPPh₂C(H)C(Ad)NH₂ (8b): ClAuPPh₂CH(SiMe₃)C(Ad)NSiMe₃ (**6b**) was dissolved in hot methanol. It was cooled slowly and yielded **8b** (0.13 g, 65%) as a pale yellow powder. C₂₄H₂₈AuClNP: calcd. C 48.50, H 4.75, N 2.36; found C 48.33, H 4.85, N 2.27. ¹H NMR (CDCl₃): δ = 1.67–1.83 (mm, 15 H, adamantyl), 4.28 [d, ²J_{H-P} = 9.1 Hz, 1 H, CH], 4.81 (br. s, 2 H, NH₂), 7.42–7.44 (mm, 6 H, Ph) and 7.56–7.64 (mm, 4 H, Ph) ppm. ³¹P NMR (CDCl₃): δ = 7.1 ppm. ¹³C NMR (CDCl₃): δ = 28.4 (s, CH-Ad), 36.5 (s, CH₂-Ad), 38.9 [d, ³J_{C,P} = 9.5 Hz, *ipso*-C, Ad], 40.9 (s, CH₂-Ad), 72.5 [d, ¹J_{C,P} = 72.0 Hz, CH], 129.0 [d, ³J_{C,P} = 11.8 Hz, *m*-Ph], 131.2 [d, ⁴J_{C,P} = 2.5 Hz, *p*-Ph], 132.1 (s, *ipso*-C), 132.9 [d, ²J_{C,P} = 13.4 Hz, *o*-Ph] and 169.1 (s, CN) ppm.

Synthesis of ClAuPPh₂CH₂C(Ph)N(C₆H₃Me₂-2,6): ClAuPPh₂CH₂C(Ph)N(C₆H₃Me₂-2,6) was obtained from PPh₂CH₂C(Ph)N(C₆H₃Me₂-2,6)[¹⁵] (0.18 g, 0.44 mmol) and ClAu(SMe₂) (0.11 g, 0.38 mmol) following the same procedure as described for compound **6**. The solvent was removed and the residue recrystallised by layering a toluene solution of the title compound with hexane (approx. ratio 1:4) yielding ClAuPPh₂CH₂C(Ph)N(C₆H₃Me₂-2,6) as a colourless powder (0.16 g, 66%). In solution the compound was found to exist as a mixture of two tautomers and their respective *Z/E* isomers (the ratio is given in bracket):

ClAuPPh₂CH₂C(Ph)=N(C₆H₃Me₂-2,6). Major Isomer (4): ¹H NMR (CDCl₃): δ = 1.73 (s, 6 H, Me), 3.86 (d, ²J_{H-P} = 13.5 Hz, 2 H, CH) ppm. ³¹P NMR (CDCl₃): δ = 23.8 ppm. ¹³C NMR ([D₆] acetone) (only CH₂ and CN are assigned): δ = 39.9 [d, ¹J_{C,P} = 44 Hz, CH], 165.5 (s, CN) ppm. **Minor Isomer (3):** ¹H NMR (CDCl₃): δ = 1.88 (s, 6 H, Me), 4.24 (d, ²J_{H-P} = 9.9 Hz, 2 H, CH) ppm. ³¹P NMR (CDCl₃): δ = 25.8 ppm. ¹³C NMR ([D₆] acetone): not observed.

ClAuPPh₂CH=C(Ph)N(H)(C₆H₃Me₂-2,6). Major Isomer (8): ¹H NMR (CDCl₃): δ = 2.33 (s, 6 H, Me), 4.33 (d, ²J_{H-P} = 5.3 Hz, 1 H, CH), 5.64 (d, ⁴J_{H-P} = 3.3 Hz, 1 H, NH) ppm. ³¹P NMR (CDCl₃): δ = 17.9 ppm. ¹³C NMR ([D₆] acetone) (only CH and CN are assigned): δ = 78.9 [d, ¹J_{C,P} = 87 Hz, CH], 163.3 (d, ²J_{C,P} = 21 Hz, CN) ppm. **Minor Isomer (1.2):** ¹H NMR (CDCl₃): δ = 2.11 (s, 6 H, Me), 4.74 (d, ²J_{H-P} = 9.9 Hz, 1 H, CH), 6.55 (br. s, 1 H, NH) ppm. ³¹P NMR (CDCl₃): δ = 8.8 ppm. ¹³C NMR ([D₆] acetone): not observed. FAB-Mass spectrum: *m/z* (%) = 1243 (21) [(M⁺)₂ – Cl], 639 (20) [M⁺], 604 (92) [M⁺ – Cl].

Table 3. Crystal data and refinement for compounds **6b**, **8a** and **9**.

Compound	6b	8a	9
Empirical formula	C ₃₀ H ₄₄ AuClNP ₂ Si ₂	C ₁₈ H ₂₂ AuClNP	C ₁₈ H ₂₁ OPS
<i>M</i>	738.23	515.75	316.38
<i>T</i> [K]	293(2)	293(2)	173(2) K
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>Cc</i>
<i>a</i> [Å]	13.630(3)	8.841(6)	16.2497(19)
<i>b</i> [Å]	16.154(3)	10.228(7)	9.8721(11)
<i>c</i> [Å]	14.574(3)	11.224(7)	10.9257(12)
<i>α</i> [°]	90	68.113(11)	90
<i>β</i> [°]	93.783(4)	89.650(12)	98.304(2)
<i>γ</i> [°]	90	86.744(12)	90
<i>V</i> [Å ³]	3201.9(11)	940.1(11)	1734.3(3)
<i>Z</i>	4	2	4
<i>D</i> (calcd.) [Mg/m ³]	1.531	1.822	1.212
<i>μ</i> [mm ^{−1}]	4.822	8.047	0.276
<i>F</i> (000)	1480	496	672
Crystal size [mm ³]	0.36 × 0.09 × 0.06	0.26 × 0.22 × 0.04	0.56 × 0.10 × 0.09
Reflections collected	18516	6345	5906
Independent reflections	6273 [<i>R</i> (int.) = 0.074]	4426 [<i>R</i> (int.) = 0.062]	3054 [<i>R</i> (int.) = 0.024]
Data/restraints/parameters	6273/0/332	4426/0/202	3054/2/193
Goodness-of-fit on <i>F</i> ²	0.932	1.032	0.971
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.037, <i>wR</i> ₂ = 0.075	<i>R</i> ₁ = 0.040, <i>wR</i> ₂ = 0.099	<i>R</i> ₁ = 0.030, <i>wR</i> ₂ = 0.064
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.072, <i>wR</i> ₂ = 0.084	<i>R</i> ₁ = 0.052, <i>wR</i> ₂ = 0.105	<i>R</i> ₁ = 0.039, <i>wR</i> ₂ = 0.067
Extinction coefficient	—	—	0.04(6)
Largest diff. peak and hole [e·Å ^{−3}]	1.25 and −0.80	2.34 and −1.24	0.26 and −0.16

Synthesis of Ph₂P(S)CH₂C(O)*t*Bu (9**):** Sulfur (0.026 g, 0.81 mmol) was added to a magnetically stirred solution of Ph₂P⁺P(Ph)N(H)C(*t*Bu)CH Cl[−] (**3a**) (0.33 g, 0.77 mmol) in CH₂Cl₂ (15 cm³) at −30 °C. The colourless solution was stirred for 12 hours at room temperature; the solvent was then removed in vacuo to yield a white compound. Colourless crystals of **9** (0.15 g, 61%) were obtained from propanol at −60 °C. Melting point: 210–212 °C. Mass spectrum: *m/z* = 316 (85) [M⁺], 259 (15) [M⁺ − *t*Bu], 231 (65) [Ph₂PSCH₂]. ¹H NMR (DMSO): δ = 1.07 (s, 9 H, *t*Bu), 4.32 [d, ²*J*_{H-P} = 13.1 Hz, 2 H, CH₂], 7.47–7.52 (mm, 6 H, Ph) and 7.88–7.95 (mm, 4 H, Ph) ppm. ³¹P NMR (DMSO): δ = 38.9 ppm. ¹³C NMR (DMSO): δ = 25.3 (s, CMe₃), 26.1 [d, ¹*J*_{C,P} = 76.1 Hz, CH₂], 44.4 (s, CMe₃), 128.1 [d, ²*J*_{C,P} = 12.4 Hz, *o*-Ph], 130.7 [d, ³*J*_{C,P} = 10.6 Hz, *m*-Ph], 131.0 [d, ⁴*J*_{C,P} = 2.7 Hz, *p*-Ph], 133.3 [d, ¹*J*_{C,P} = 82.9 Hz, *ipso*-C] and 207.1 [d, ²*J*_{C,P} = 6.7 Hz, C=O] ppm.

X-ray Crystallography: Intensity data were collected with a Bruker SMART 1K CCD area detector diffractometer with graphite-monochromated Mo-*K*_α radiation (50 kV, 30 mA). The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program SAINT⁺,^[30] with face-indexed absorption corrections (compounds **6b** and **8a**) and semi-empirical absorption corrections (compound **9**) carried out using the program XPRED^[30] and SADABS,^[30] respectively. The crystal structures were solved by direct methods using SHELXTL.^[31] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on *F*² using SHELXTL. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Further crystallographic data are summarised in Table 3. Diagrams and publication material were generated using SHELXTL,^[31] PLATON^[32] and ORTEP3.^[33]

CCDC-244675 to -244677 contain the supplementary crystallographic data for this paper. These data can be obtained free of

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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