

Carbon-Hydrogen Activation of Ketones by 2-Phenylazo-phenylgold(III) Complexes to give Ketonylgold(III) Complexes†

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Complexes $[\text{AuR}(\text{acac-C})\text{Cl}]$ ($\text{R} = \text{pap}$ ($\text{C}_6\text{H}_4\text{N}=\text{NPh-2}$) **1a** or mpap [$\text{C}_6\text{H}_3(\text{N}=\text{NC}_6\text{H}_4\text{Me-4})\text{-2-Me-5}$] **1b**; $\text{Hacac} = \text{acetylacetone}$) or $[\text{AuR}(\text{Cl})(\text{OCIO}_3)]$ ($\text{R} = \text{pap}$ **2a** or mpap **2b**) react with various ketones $\text{MeC}(\text{O})\text{R}'$ to give $[\text{AuR}\{\text{CH}_2\text{C}(\text{O})\text{R}'\}\text{Cl}]$ [$\text{R} = \text{pap}$, $\text{R}' = \text{Et}$ **3**, Pr^n **4**, Pr^i **5**, Bu^i **6** or $\text{C}_6\text{H}_2(\text{OMe})_{3-3,4,5}$ **7**; $\text{R} = \text{mpap}$, $\text{R}' = \text{Me}$ **8**]. Whereas **1a** does not react with $\text{MeC}(\text{O})\text{CH}_2\text{Cl}$, **2a** gives a mixture of the expected $[\text{Au}(\text{pap})\{\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{Cl}\}\text{Cl}]$ and $[\text{Au}(\text{pap})\text{Cl}_2]$. However, other ketones $[\text{R}'\text{C}(\text{O})\text{R}'']$ ($\text{R}' = \text{Me}$; $\text{R}'' = \text{Ph}$, $\text{CH}_2=\text{CH}$, *trans*- $\text{PhCH}=\text{CH}$ or MeCO ; $\text{R}' = \text{R}'' = \text{CH}_2\text{Cl}$ or Et) or 2-methylcyclohexanone do not react at room temperature with **2a**. The reactions of **2a** with other species containing activated methyl groups $[\text{MeCO}_2\text{Et}$, $\text{MeC}(\text{O})\text{NH}_2$ or $\text{MeCN}]$ either do not occur or give products in which there is no carbon-hydrogen activation. Thus, **2a** reacts with dimethyl sulfoxide (dmsO) to give the first organogold(III) complex with this ligand, $[\text{Au}(\text{pap})(\text{dmsO})_2][\text{ClO}_4]_2$ **9**. It reacts with NaI to give $[\text{Au}(\text{pap})\text{Cl}(\text{I})]$ **10**. Complex **8** reacts with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and pyridine (py) or 2,2'-bipyridine (bipy) to give $[\text{Au}(\text{mpap})\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{L}][\text{ClO}_4]$ ($\text{L} = \text{py}$ **11** or bipy **12**). The following reactions were also studied: $[\text{Au}(\text{pap})\text{Cl}(\text{acac-C})] + \text{PPh}_3$ or AgClO_4 to give $[\text{Au}(\text{pap})\text{Cl}(\text{acac-C})(\text{PPh}_3)]$ **13** or $[\text{Au}(\text{pap})(\text{acac-O,O'})][\text{ClO}_4]$ **14**, respectively. Complexes **13** and **14** do not give an acetonoyl complex with acetone; **14** is the first cationic acetylacetonatogold(III) complex. A plausible reaction pathway is proposed for ketone carbon-hydrogen activation starting from complexes **2**. Low-temperature crystal structures were determined for $[\text{Au}(\text{mpap})\text{Cl}_2]$ [space group $P\bar{1}$, $a = 7.902(2)$, $b = 9.527(2)$, $c = 10.378(3)$ Å, $\alpha = 86.77(2)^\circ$, $\beta = 77.32(2)^\circ$, $\gamma = 67.42(2)^\circ$, $R = 0.024$] and **11** [space group $P2_1/n$, $a = 8.693(5)$, $b = 15.800(8)$, $c = 16.489(8)$ Å, $\beta = 94.51(4)^\circ$, $R = 0.027$]. The latter is the first crystal structure of an acetonoylgold(III) complex, and it could be shown conclusively that the $\text{CH}_2\text{C}(\text{O})\text{Me}$ group is bonded through the carbon atom. Both structures show the expected square-planar co-ordination around the gold atom, with some distortion from the narrow chelate rings. In the first complex the higher *trans* influence of the aryl group leads to a lengthening of the *trans* Au-Cl bond (2.347 Å) with respect to the *cis* bond (2.274 Å).

Metallated ketones play an important role in organic synthesis.¹ There are several syntheses of these compounds involving e.g. direct metallation of the ketone by deprotonating agents, oxidative-addition reactions (with α -halogenocarbonyl compounds or epoxides), or transmetallation reactions.² We have recently reported that an unusual³ carbon-hydrogen activation of acetone occurs by intramolecular co-operation between the metal centre and a ligand attached to it.⁴ Thus, the reaction of $[\text{Au}(\text{pap})\text{Cl}_2]$ [$\text{pap} = 2\text{-phenylazophenyl}$] in acetone with various reagents such as $\text{Ti}(\text{acac})$ ($\text{Hacac} = \text{acetylacetone}$), KCN , AgClO_4 , 1,10-phenanthroline, HgR_2 ($\text{R} = \text{C}_6\text{F}_5$ or pap) or PdR_2 ($\text{R} = \text{C}_6\text{H}_4\text{NO}_2\text{-2}$) gives $[\text{Au}(\text{pap})\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]$. Some intermediates in this process (see Scheme 1) were isolated. However, the reaction pathway when $\text{X} = \text{ClO}_4$, the most effective reagent for this activation, was assumed to be different. In this paper we propose a

plausible reaction pathway for the carbon-hydrogen activation of ketones when starting from this type of perchlorato-complex.

We have limited our previous studies to the metallation of acetone and shown that, in solution, all the isolated complexes are ketonyl (**a**) rather than enolate (**b**) derivatives (see Scheme 1). In this paper we extend the study (i) to different ketones and other compounds containing at least one activated methyl group and (ii) to other gold(III) complexes related to those known to be carbon-hydrogen activating agents. Finally, we characterize structurally the starting material $[\text{Au}(\text{mpap})\text{Cl}_2]$ [$\text{mpap} = \text{C}_6\text{H}_3(\text{N}=\text{NC}_6\text{H}_4\text{Me-4})\text{-2-Me-5}$] and one ketonyl derivative to show conclusively that in the solid state, as in solution, this ligand is C-bonded.

Results

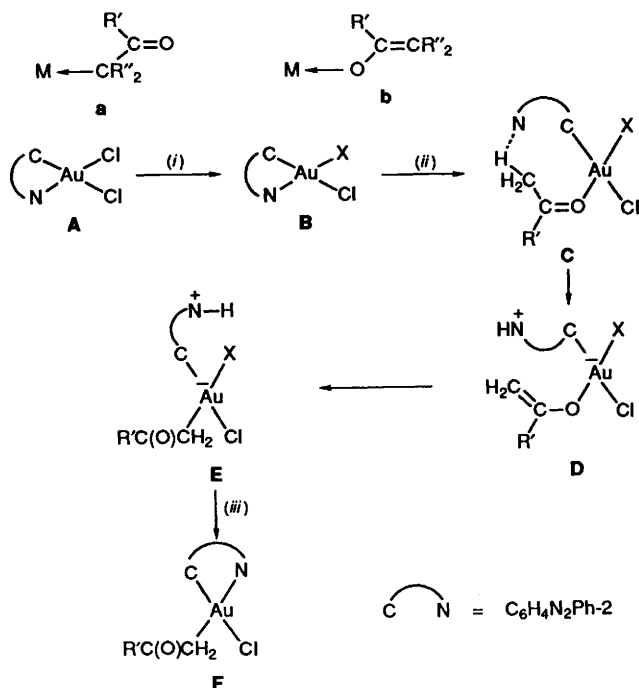
Complexes $[\text{AuR}(\text{acac-C})\text{Cl}]$ ($\text{R} = \text{pap}$ **1a** or mpap **1b**) or $[\text{AuR}(\text{Cl})(\text{OCIO}_3)]$ ($\text{R} = \text{pap}$ **2a** or mpap **2b**, obtained by the reaction of $[\text{AuRCl}_2]$ with $\text{Ti}(\text{acac})$ or AgClO_4 , respectively,⁴ react with various ketones $\text{MeC}(\text{O})\text{R}'$ to give $[\text{AuR}\{\text{CH}_2\text{C}(\text{O})\text{R}'\}\text{Cl}]$ [$\text{R} = \text{pap}$, $\text{R}' = \text{Et}$ **3**, Pr^n **4**, Pr^i **5**, Bu^i **6**, or $\text{C}_6\text{H}_2(\text{OMe})_{3-3,4,5}$ **7**; $\text{R} = \text{mpap}$, $\text{R}' = \text{Me}$ **8**] (see Scheme 2).

The reaction between complex **1a** and $\text{MeC}(\text{O})\text{Et}$ (Method A) for 48 h at room temperature gives complex **3** along with the

† Supplementary data available: Complete bond lengths and angles, H-atom coordinates, structure factors and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 56170.

starting complex, whereas reaction is complete after 66 h. With acetone the reaction is accomplished at 15 h.⁴ The same reaction time allows complete reaction between acetone and the mpap complex **1b**. Similarly, reactions of **1a** with MeC(O)R' where R' = Pr^n , Pr^i or Bu^i were not complete after 72 h; for R' = Pr^n or Pr^i , 80 h and for Bu^i 90 h were sufficient for activation. The reaction products **3–6** and **8** were isolated in 60–80% yields.

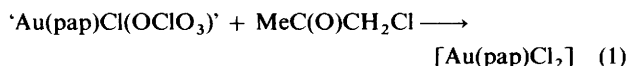
The same complexes can be obtained by treating the corresponding $[\text{AuRCl}_2]$ with AgClO_4 [which gives complexes 'AuR(Cl)(OCIO₃)' **2a** and **2b**, see below] in the ketone as solvent (acetone) or, when $[\text{AuRCl}_2]$ was sparingly soluble, in a mixture of chloroform or dichloromethane with the ketone



Scheme 1 Proposed reaction pathway for the carbon-hydrogen activation process of ketones with 2-phenylazophenylgold(III) complexes. (i) + X (X = acac-C, CN, $\text{C}_6\text{H}_4\text{N}=\text{NPh}-2$, C_6F_5 or $\text{C}_6\text{H}_4\text{NO}_2-2$), -Cl; (ii) + R'C(O)Me ; (iii) -XH

(Method B). This method gives similar yields (50–90%) and is faster. Thus, ketones MeC(O)R' require 1, 40, 40, 40 and 80 h for R' = Me, Et, Pr^n , Pr^i and Bu^i , respectively, to complete the activation process.

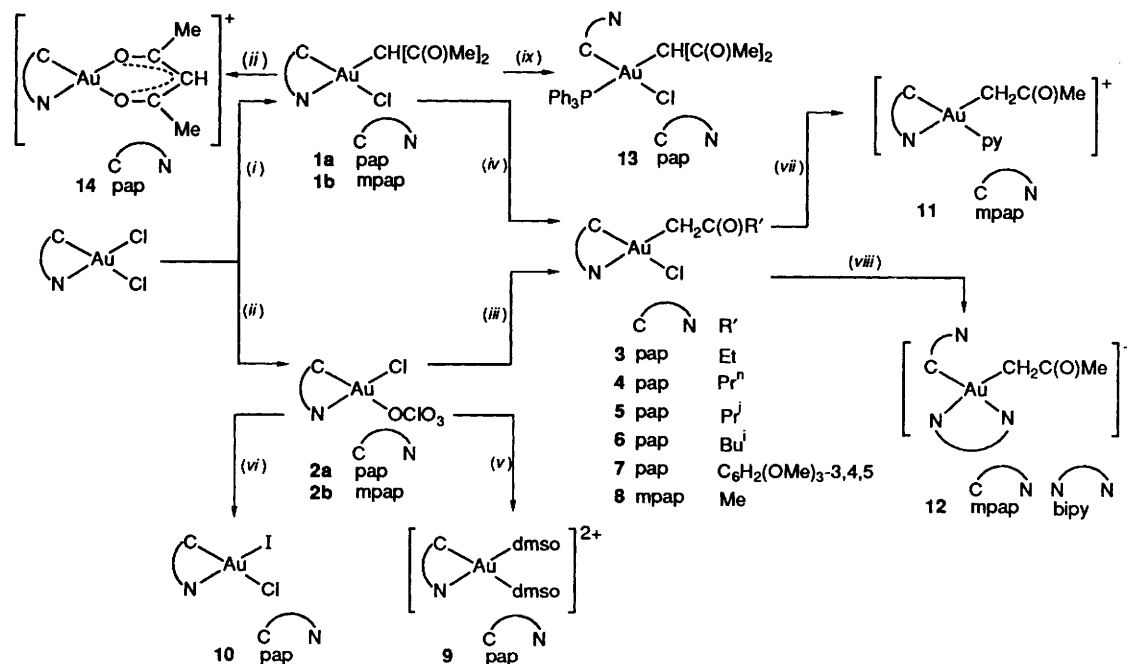
Complex **1a** was recovered unchanged after 110 or 91 h of stirring in $\text{MeC(O)CH}_2\text{Cl}$ or MeC(O)Ph , respectively. Method B also fails to activate MeC(O)Ph after 65 h. However, **1a** reacts with $\text{MeC(O)CH}_2\text{Cl}$ giving a mixture whose IR and NMR spectra indicate the presence of $[\text{Au(pap)Cl}_2]$ and $[\text{Au(pap)Cl}\{\text{CH}_2\text{C(O)CH}_2\text{Cl}\}]$. This mixture could neither be separated nor its formation prevented, because $[\text{Au(pap)Cl}_2]$ is formed even if the intermediate 'Au(pap)Cl(OCIO₃)' is used as starting material. A process parallel to carbon-hydrogen activation could be loosely formulated as (1) although we have not investigated the nature of the organic by-products.



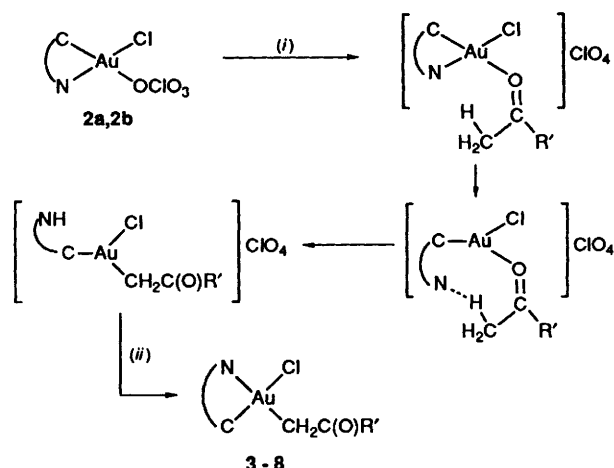
All remaining reactions were carried out using Method B because of the greater reactivity of the intermediate 'AuRCl(OCIO₃)' compared with the corresponding acac complexes **1a** and **1b**. Accordingly, 3,4,5-trimethoxyacetophenone gives $[\text{Au(pap)}\{\text{CH}_2\text{C(O)C}_6\text{H}_2(\text{OMe})_3-3,4,5\}\text{Cl}]$ **7** using this method. However, the following ketones do not react: MeC(O)R' , where $\text{R' = CH}_2=\text{CH}$ (24 h), *trans*- PhCH=CH (24 h), MeCO (94 h), $(\text{ClCH}_2)_2\text{CO}$ (24 h), Et_2CO (48 h) and 2-methylcyclohexanone (24 h).

Other species containing activated methyl groups, such as MeCO_2Et , MeC(O)NH_2 or MeCN , do not react with complex **2a** after 48 h of stirring at room temperature. However, this complex does react with excess of dimethyl sulfoxide (dmsO) to give a mixture of $[\text{Au(pap)(dmsO)}_2][\text{ClO}_4]$ **9** and $[\text{Au(pap)Cl}_2]$ instead of a carbon-hydrogen activation product. Complex **9** can be obtained pure by reacting $[\text{Au(pap)Cl}_2]$ with AgClO_4 (1:2) and excess of dmsO. As far as we are aware,⁵ there is only one reported gold complex with dmsO, the unstable $[\text{AuCl}_3(\text{dmsO})]$.⁶

In an attempt to identify complexes **2a** and **2b** they were isolated (see below) and **2a** was treated with NaI to give $[\text{Au(pap)Cl(I)}]$ **10**. Because none of the above ketonyl complexes gives suitable crystals for an X-ray diffraction study, we



Scheme 2 Synthesis of complexes **1–14**. (i) + Ti(acac)_3 , - TiCl_3 ; (ii) + AgClO_4 , - AgCl ; (iii) + MeC(O)R' , - HClO_4 ; (iv) + MeC(O)R' , - Hacac ; (v) + AgClO_4 + 2 dmsO, - AgCl ; (vi) + NaI, - NaClO_4 ; (vii) + py + NaClO_4 , - NaCl ; (viii) + bipy + NaClO_4 , - NaCl ; (ix) + PPh_3



Scheme 3 Proposed reaction pathway for the synthesis of complexes 3-8 starting from 2a and 2b. (i) + MeC(O)R'; (ii) - HClO₄

tried to prepare similar complexes with the aryl group mpap, which had given good results in the case of 1b.^{4c} Since the corresponding acetonyl 8 also does not give suitable crystals, we tried to crystallize derivatives obtained by reaction with NaClO₄·H₂O and pyridine (py) or 2,2'-bipyridine (bipy) to give [Au(mpap){CH₂C(O)Me}L]ClO₄ (L = py 11 or bipy 12). The crystal structures of 11 and the starting complex [Au(mpap)Cl₂] were determined.

We have also prepared other acac complexes to study their reactivities with acetone. Thus, 1a reacts with PPh₃ (1:1) or AgClO₄ (1:1) to give [Au(pap)Cl(acac-C)(PPh₃)] 13 or [Au(pap)(acac-O,O')]ClO₄ 14, respectively. However, these complexes do not give acetonyl complexes with acetone. Reported acac-gold(III) complexes are limited to 1a and 1b^{4b,c} and homologues with the aryl ligand C₆H₄CH₂NMe₂-2,4 [AuMe₂(acac-O,O')],⁷ [AuMe₂(acac-C)L], of which only the complex with L = PPhMe₂ has been isolated,⁸ and [AuR₂(acac)], where R₂ = 2,2'-biphenyl⁹ or 1,2,3,4-tetraphenylbuta-1,3-dien-1,4-diyl.¹⁰ Complex 14 is the first cationic acetylacetonato-gold(III) complex.

Discussion

A plausible reaction pathway of ketone carbon-hydrogen activation starting from complexes 1 has been suggested⁴ on the basis of the isolation and properties of some of the proposed intermediates (see Scheme 1). However, when Method B (X = ClO₄) was used the reaction pathway was assumed to be different; we considered it more reasonable to postulate that the weakly bonding perchlorate ligand is replaced by acetone, instead of labilizing the ligand *trans* to it to allow the co-ordination of acetone *cis* to the nitrogen atom, as postulated for all other X (see B → C in Scheme 1).

We first attempted to determine the substitution position in the process A → B by isolating B (X = ClO₄). The reaction of [AuRCl₂] (R = pap or mpap) with AgClO₄ (1:1, dichloromethane, 4 h) gives unstable complexes 2a and 2b (which we could not obtain analytically pure) which show a splitting of the band at 1100 cm⁻¹ corresponding to co-ordination of the perchlorate anion. However, whereas the IR spectrum of complex 2a shows no band assignable to ν(Au-Cl), that of 2b has a band at 365 cm⁻¹, assignable to ν(Au-Cl) *trans* to the N atom (see below). In contrast, the substitution product of perchlorate in 2a by iodide, 10, has the chloro ligand *trans* to carbon, as shown by the IR band at 300 cm⁻¹. The antisymbiotic effect¹¹ can explain both results. Because perchlorate is a harder ligand than chloride it should co-ordinate *trans* to the softer carbon donor, whereas the softer iodide ligand should co-ordinate *trans* to the harder nitrogen donor.

Assuming that both complexes 2a and 2b have the same

geometry, the steps in Scheme 3 can account for the carbon-hydrogen activation. The isomerization in this process is facilitated by the three-co-ordination of gold(III) proposed for some intermediates. Three-co-ordinate gold(III) intermediates have been established previously.¹² This isomerization is also consistent with the antisymbiotic effect because the softer C donor atoms prefer to be mutually *cis*.

The reaction pathways in Schemes 1 and 3 have in common the co-ordination of the ketone and the metal/ligand co-operation in carbon-hydrogen activation. The first process should be favoured by substituents on the ketone with +I or +M effects (electron-releasing substituents), whereas those with -I or -M effects (electron-withdrawing substituents) should increase the acid character of the proton and favour the activation reaction. An increase in substituent sizes should inhibit both processes. It is thus difficult to predict which ketones should give ketonyl complexes. Our experience suggests that at least one of the substituents should be a methyl group (+I effect, low steric requirement) and the other an alkyl group with +I effect (R' = Et, Pr or Bu). The negative effect of increasing the size of one of the substituents in the ketone is in agreement with the above results. If the second substituent has a -I effect the reaction may (R' = CH₂Cl) or may not (R' = MeCO, RCH=CH or Ph) occur. The importance of electronic effects on the activation process is emphasized by the fact that the three electron-releasing substituents MeO on the phenyl ring lead to activation, while the unsubstituted phenyl group fails. Substituents on the MeC(O) moiety with pronounced electron-releasing properties (R' = OEt or NH₂) inhibit the activation process.

The failure of the acac complexes 13 and 14 to activate acetone can also be explained by the pathway proposed in Scheme 1. In the first case the co-ordination of acetone is inhibited by the P-Au bond, which is much stronger than the N-Au bond in 1a. The cationic nature of 14 and the reduced *trans* influence and effect of an oxygen rather than a carbon donor should strengthen the N-Au bond, preventing the co-ordination of acetone.

Spectroscopic Properties and Structures of Complexes 1-14.

The band corresponding to ν(CO) appears as a strong absorption at ca. 1675 cm⁻¹ for the ketonyl complexes 3-6, 8, 11 and 12, whereas the electron-releasing nature of the 3,4,5-trimethoxyphenyl group shifts the absorption to 1630 cm⁻¹. These data suggest the co-ordination of the ligand CH₂C(O)R' to the metal through the CH₂ group. However, this criterion alone does not allow an unambiguous assignment of the co-ordination mode of the acetonyl ligand; some enolato complexes show a band at ca. 1650 cm⁻¹, assigned to ν(C=C).¹³

The acac-C complexes 1a and 1b and 13 show two bands at ca. 1670 cm⁻¹ assignable to ν(CO), whereas the acac-O,O' complex 14 displays a pair of well separated bands at 1565 and 1510 cm⁻¹, arising from the different nature of the *trans* ligands. The lowering of the ν(CO) frequency is thus associated with the different co-ordination modes of the acac ligand.

The chloro complexes 3-8, 10 and 13 show a medium or strong band at ca. 300 cm⁻¹, which indicates that the chloride ligand is *trans* to the phenyl group (see below).⁴ The dmso complex 9 shows two strong bands at 900 and 925 cm⁻¹ assignable to ν(SO). Such frequencies, lower than that of the free ligand (1053 cm⁻¹), have been interpreted as implying Me₂SO → M bonding.¹⁴ For [AuCl₃(dmso)] the ν(SO) mode appears at 1198 cm⁻¹, which was interpreted as an indication that the ligand is S-bonded to gold. It is probable that the 2+ charge of complex 9 changes the nature of the metal centre from the usual class b to class a, thus favouring the co-ordination with the harder donor atom of the ligand.

Ketonyl complexes of the type M{CH₂C(O)R'} show the δ(CH₂) ¹H NMR resonance as a singlet in the range 1.3-2.6, whereas those of the related enolato complexes M{OC(R')=CH₂} appear as two resonances at lower field (δ 4.0-4.6).¹⁵

Method B. The stoichiometric amount of solid AgClO_4 was added to a solution of the corresponding $[\text{AuRCl}_2]$ (50–100 mg) in chloroform (15–30 cm^3)–ketone (8–10 cm^3). The resulting suspension was stirred for 40 (3–5), 80 (6), 24 (7) or

1.25 (8) h and filtered over anhydrous MgSO_4 . The solution was concentrated (1 cm^3) and addition of diethyl ether (1 cm^3) and hexane (10 cm^3) gave the corresponding complexes as yellow solids. Differences from this general method were that the solid ketone (117 mg, 0.55 mmol) was used in the synthesis of **7** and that chloroform was not used in the synthesis of **8**. Yields: **3**, 60; **4** and **5**, 52; **6**, 50; **7**, 65; and **8**, 92%.

Complex **3**: m.p. 196°C (decomp.); $\nu(\text{AuCl})$ 300, $\nu(\text{CO})$ 1668 cm^{-1} ; $\delta(^1\text{H})$ 8.1, 7.9, 7.5 (m, 9 H, pap), 3.4 (s, 2 H, C^1H_2), 2.7 (q, 2 H, C^3H_2 , $^3J_{\text{HH}} = 7 \text{ Hz}$) and 1.0 (t, 3 H, Me); $\delta(^{13}\text{C})$ 210.4 (CO), 37.3 (C^1H_2), 36.8 (C^3H_2) and 8.4 (Me) (Found: C, 39.3; H, 3.2; Au, 40.1; N, 5.2. $\text{C}_{16}\text{H}_{16}\text{AuClIN}_2\text{O}$ requires C, 39.6; H, 3.3; Au, 40.6; N, 5.8%).

Complex **4**: m.p. 138°C ; $\nu(\text{AuCl})$ 300, $\nu(\text{CO})$ 1675 cm^{-1} ; $\delta(^1\text{H})$ 8.0 (m, 9 H, pap), 3.4 (s, 2 H, C^1H_2), 2.7 (t, 2 H, C^3H_2 , $^3J_{\text{HH}} = 7$), 1.6 (m, 2 H, C^4H_2 , $^3J_{\text{HH}} = 7 \text{ Hz}$) and 0.9 (t, 3 H, Me); $\delta(^{13}\text{C})$ 210.0 (CO), 45.3 (C^3H_2), 37.7 (C^1H_2), 18.0 (C^4H_2) and 13.7 (Me) (Found: C, 39.9; H, 3.3; Au, 39.1; N, 5.6. $\text{C}_{17}\text{H}_{18}\text{AuClIN}_2\text{O}$ requires C, 40.9; H, 3.6; Au, 39.5; N, 5.6%).

Complex **5**: m.p. 108°C ; $\nu(\text{AuCl})$ 307, $\nu(\text{CO})$ 1665 cm^{-1} ; $\delta(^1\text{H})$ 8.2, 8.1, 7.5 (m, 9 H, pap), 3.5 (s, 2 H, C^1H_2), 3.2 (sxt, 1 H, C^3H , $^3J_{\text{HH}} = 7 \text{ Hz}$) and 1.1 (d, 6 H, Me); $\delta(^{13}\text{C})$ 214.0 (C^2O), 40.3 (C^3H), 36.2 (C^1H_2) and 19.2 (Me) (Found: C, 41.0; H, 3.6; Au, 39.0; N, 6.2. $\text{C}_{17}\text{H}_{18}\text{AuClIN}_2\text{O}$ requires C, 40.9; H, 3.7; Au, 39.5; N, 5.6%).

Complex **6**: m.p. 117°C (decomp.); $\nu(\text{AuCl})$ 310, $\nu(\text{CO})$ 1680 cm^{-1} ; $\delta(^1\text{H})$ 7.9 (m, 9 H, pap), 3.5 (s, 2 H, C^1H_2), 2.6 (d, 2 H, C^3H_2 , $^3J_{\text{HH}} = 7$), 2.2 (m, 1 H, C^4H , $^3J_{\text{HH}} = 7 \text{ Hz}$) and 0.9 (d, 6 H, Me); $\delta(^{13}\text{C})$ 209.7 (CO), 52.2 (C^3H_2), 38.3 (C^1H_2), 25.4 (C^4H) and 22.5 (Me) (Found: C, 41.2; H, 3.9; Au, 38.8; N, 4.8. $\text{C}_{18}\text{H}_{20}\text{AuClIN}_2\text{O}$ requires C, 42.2; H, 3.9; Au, 38.4; N, 5.5%).

Complex **7**: m.p. 167°C ; $\nu(\text{AuCl})$ 300, $\nu(\text{CO})$ 1638 cm^{-1} ; $\delta(^1\text{H})$ 7.7 (m, 11 H, pap + H^2H^6), 4.0 (s, 2 H, CH_2), 3.925 (s, 6 H, OMe) and 3.921 (s, 3 H, OMe); $\delta(^{13}\text{C})$ 198.0 (CO), 60.9 (OMe) and 56.7 (OMe) (Found: C, 43.6; H, 3.9; Au, 31.3; N, 4.4. $\text{C}_{23}\text{H}_{22}\text{AuClIN}_2\text{O}_4$ requires C, 44.4; H, 3.6; Au, 31.6; N, 4.5%).

Complex **8**: m.p. 189°C ; $\nu(\text{AuCl})$ 300, $\nu(\text{CO})$ 1670 cm^{-1} ; $\delta(^1\text{H})$ 8.0 [d, 1 H, mpap (H^{13}), $^3J_{\text{HH}} = 8$], 7.9 [d, 2 H, mpap (H^{22}), $^3J_{\text{HH}} = 8 \text{ Hz}$], 7.8 (s, 1 H, H^{16}), 7.3 [m, 3 H, mpap (H^{23} , H^{14})], 3.4 (s, 2 H, C^1H_2), 2.57, 2.49 (s, 6 H, Me of mpap) and 2.42 (s, 3 H, Me); $\delta(^{13}\text{C})$ 207.6 (CO), 38.4 (CH_2), 31.1 (Me), 22.6 and 21.5 (Me of mpap) (Found: C, 41.8; H, 4.3; Au, 39.1; N, 5.6. $\text{C}_{17}\text{H}_{18}\text{AuClIN}_2\text{O}$ requires C, 40.9; H, 3.6; Au, 39.5; N, 5.6%).

$[\text{Au}(\text{pap})(\text{dmso})_2][\text{ClO}_4]_2$ **9**.—One drop of dmso and solid AgClO_4 (40 mg, 0.22 mmol) were added to a suspension of $[\text{Au}(\text{pap})\text{Cl}_2]$ (50 mg, 0.1 mmol) in dichloromethane (30 cm^3); after stirring for 5 min the resulting suspension was filtered over anhydrous MgSO_4 , the solution concentrated (1 cm^3) and diethyl ether added (30 cm^3) to precipitate complex **9** as a yellow solid. Yield 72%, m.p. 171°C ; $\Lambda_{\text{M}} = 182 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetone); $\delta(^1\text{H})$ 8.0 (m, 9 H, Ph) and 3.0 (s, 12 H, Me) (Found: C, 26.8; H, 3.0; Au, 26.4; N, 4.0. $\text{C}_{16}\text{H}_{21}\text{AuCl}_2\text{N}_2\text{O}_{10}\text{S}_2$ requires C, 26.2; H, 2.9; Au, 26.8; N, 3.8%).

$[\text{Au}(\text{pap})\text{Cl}(\text{I})]$ **10**.—Solid AgClO_4 (23 mg, 0.1 mmol) was added to a solution of $[\text{Au}(\text{pap})\text{Cl}_2]$ (50 mg, 0.1 mmol) in dichloromethane (40 cm^3); the suspension was stirred for 4 h and then filtered through Celite. To the resulting solution solid NaI (20 mg, 0.2 mmol) was added and stirred for 2 h. The excess of NaI was removed by filtration over anhydrous MgSO_4 , the resulting solution concentrated (1 cm^3) and addition of hexane–diethyl ether (1:1) precipitated complex **10** as a brick-red solid. Yield 75%, m.p. 154°C ; $\nu(\text{AuCl})$ 300 cm^{-1} (Found: C, 25.9; H, 2.0; Au, 36.1; N, 5.6. $\text{C}_{12}\text{H}_9\text{AuClIN}_2$ requires C, 26.7; H, 1.7; Au, 36.4; N, 5.2%).

$[\text{Au}(\text{mpap})\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2\text{L}]\text{ClO}_4$ (L = py **11** or bipy **12**).—Pyridine (1 cm^3) or solid 2,2'-bipyridine (1:1) and solid $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (1:1) were added to a solution of complex **8** (40–50 mg) in acetone ($10\text{--}20 \text{ cm}^3$); the resulting suspension was

stirred for 30 min, then concentrated to dryness and the residue extracted with dichloromethane ($3 \times 5 \text{ cm}^3$), filtered over anhydrous MgSO_4 , the solution concentrated (1 cm^3), and diethyl ether (5 cm^3) added to precipitate complex **11** or **12** as a yellow-orange or orange solid, respectively.

Complex **11**: yield 75%, m.p. 187°C (decomp.); $\Lambda_{\text{M}} = 141 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetone); $\nu(\text{CO})$ 1690 cm^{-1} ; $\delta(^1\text{H})$ 8.7–7 (m, 12 H, mpap + py), 3.4 (s, 2 H, CH_2), 2.5, 2.3 (s, 6 H, Me of mpap) and 2.1 (s, 3 H, ^3Me); $\delta(^{13}\text{C})$ 206.1 (CO), 40.9 (CH_2), 30.0 (^3Me), 22.4 and 21.2 (Me of mpap) (Found: C, 41.9; H, 4.0; Au, 31.0; N, 6.0. $\text{C}_{22}\text{H}_{23}\text{AuClIN}_3\text{O}_5$ requires C, 41.2; H, 3.6; Au, 30.7; N, 6.6%).

Complex **12**: yield 87%, m.p. 147°C (decomp.); $\Lambda_{\text{M}} = 130 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetone); $\nu(\text{CO})$ 1670 cm^{-1} ; $\delta(^1\text{H})$ 8.9–7.1 (m, 15 H, mpap + bipy), 3.3 (s, 2 H, CH_2), 2.5, 2.4 (s, 3 H, Me of pap) and 1.8 (s, 3 H, ^3Me); $\delta(^{13}\text{C})$ 208.3 (CO), 32.8 (CH_2), 30.3 (^3Me), 21.5 and 21.3 (Me of pap) (Found: C, 45.7; H, 3.2; Au, 27.0; N, 7.6. $\text{C}_{27}\text{H}_{26}\text{AuClIN}_4\text{O}_5$ requires C, 45.1; H, 3.6; Au, 27.4; N, 7.8%).

$[\text{Au}(\text{pap})\text{Cl}(\text{acac-C})(\text{PPh}_3)]$ **13**.—Solid PPh_3 (77 mg, 0.3 mmol) was added to a solution of complex **1a** (150 mg, 0.3 mmol) in dichloromethane (20 cm^3); the solution was stirred for 1 h and concentrated (1 cm^3). Addition of diethyl ether (5 cm^3) precipitated complex **13** as an orange solid. Yield 88%, m.p. 154°C ; $\nu(\text{AuCl})$ 310, $\nu(\text{CO})$ 1660 and 1680 cm^{-1} ; $\delta(^1\text{H})$ 7.4 (m, 24 H, Ph), 4.8 (d, 1 H, CH , $^3J_{\text{HP}} = 16 \text{ Hz}$), 2.1 and 2.0 (s, 3 H, Me); $\delta(^{13}\text{C})$ 203.9 (CO), 203.7 (CO), 67.6 (CH , $^3J_{\text{CP}} = 86.4 \text{ Hz}$), 31.8 and 31.2 (Me); $\delta(^{31}\text{P})$ 30.5 (Found: C, 54.2; H, 4.0; Au, 25.5; N, 3.6. $\text{C}_{35}\text{H}_{31}\text{AuClIN}_2\text{O}_2\text{P}$ requires C, 53.6; H, 4.5; Au, 25.4; N, 3.6%).

$[\text{Au}(\text{pap})(\text{acac-O,O'})]\text{ClO}_4$ **14**.—Solid AgClO_4 (21 mg, 0.1 mmol) was added to a solution of complex **1a** (50 mg, 0.1 mmol) in dichloromethane (15 cm^3); the resulting suspension was stirred for 3 h and filtered over anhydrous MgSO_4 . The solution was concentrated (1 cm^3) and addition of diethyl ether precipitated complex **14** as a yellow solid. Yield 91%, m.p. = 150°C ; $\Lambda_{\text{M}} = 118 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (in acetone); $\nu(\text{CO})$ 1565 and 1510 cm^{-1} ; $\delta(^1\text{H})$ 8.1 (m, 4 H, C_6H_4), 7.6 (m, 5 H, Ph), 5.6 (s, 1 H, C^1H), 2.4 and 2.2 (s, 3 H, Me) (Found: C, 35.8; H, 2.8; Au, 35.0; N, 5.4. $\text{C}_{17}\text{H}_{16}\text{AuClIN}_2\text{O}_6$ requires C, 35.4; H, 2.8; Au, 34.2; N, 4.9%).

X-Ray Structure Determination of $[\text{Au}(\text{mpap})\text{Cl}_2]$.—Crystal data. $\text{C}_{14}\text{H}_{13}\text{AuCl}_2\text{N}_2$, $M_r = 477.1$, triclinic, space group $P\bar{1}$, $a = 7.902(2)$, $b = 9.527(2)$, $c = 10.378(3) \text{ \AA}$, $\alpha = 86.77(2)$, $\beta = 77.32(2)$, $\gamma = 67.42(2)^\circ$, $U = 703.4 \text{ \AA}^3$, $Z = 2$, $D_c = 2.253 \text{ Mg m}^{-3}$, $\lambda(\text{Mo-K}\alpha) = 0.71069 \text{ \AA}$, $\mu = 10.8 \text{ mm}^{-1}$, $F(000) = 448$, $T = -95^\circ\text{C}$.

Data collection and reduction. An orange tablet ca. $0.5 \times 0.3 \times 0.2 \text{ mm}$ was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens P3 with LT-2 low-temperature attachment). 2672 Intensities were recorded to $2\theta_{\text{max}} 50^\circ$, of which 2477 were unique ($R_{\text{int}} 0.016$) and 2337 with $F > 4\sigma(F)$ considered observed. Cell constants were refined from setting angles of 50 reflections in the range $2\theta 20\text{--}23^\circ$. An absorption correction based on ω scans was applied, with transmission factors 0.41–1.00.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined anisotropically on F to $R 0.024$, $R' 0.031$. Hydrogen atoms were included using a riding model. An extinction correction was applied according to $F_{\text{corr}} = F(1 + 0.002xF^2/\sin 2\theta)^{-0.25}$; x refined to 0.00099(11). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. 179 Parameters; $S 1.4$; maximum $\Delta/\sigma 0.002$; maximum $\Delta\rho 1.4 \text{ e \AA}^{-3}$. Final atom coordinates are given in Table 3.

X-Ray Structure Determination of Compound 11.—Crystal data. $\text{C}_{22}\text{H}_{23}\text{AuClIN}_3\text{O}_5$, $M_r = 641.8$, monoclinic, space group $P2_1/n$, $a = 8.693(5)$, $b = 15.800(8)$, $c = 16.489(8) \text{ \AA}$,

Table 3 Atomic coordinates ($\times 10^4$) for $[\text{Au}(\text{mpap})\text{Cl}_2]$

Atom	x	y	z
Au	5081.1(2)	7274.4(2)	5365.7(2)
Cl(1)	3051(2)	7966(2)	7359(1)
Cl(2)	3208(2)	9485(1)	4458(1)
N(1)	8289(6)	4975(5)	3768(4)
N(2)	7069(6)	6311(5)	3666(4)
C(11)	6678(7)	5317(6)	6089(6)
C(12)	8120(7)	4417(5)	5035(5)
C(13)	9389(8)	2970(6)	5255(5)
C(14)	9205(8)	2426(6)	6522(6)
C(15)	7801(8)	3289(6)	7546(6)
C(16)	6561(8)	4742(6)	7307(6)
C(17)	7591(10)	2653(7)	8917(6)
C(21)	7149(7)	6853(5)	2365(5)
C(22)	7615(7)	5828(6)	1303(5)
C(23)	7773(8)	6355(6)	33(6)
C(24)	7523(7)	7861(6)	-219(6)
C(25)	7078(8)	8853(6)	846(6)
C(26)	6874(7)	8376(6)	2137(5)
C(27)	7758(10)	8376(8)	-1624(6)

Table 4 Atomic coordinates ($\times 10^4$) for compound 11

Atom	x	y	z
Au	1972.6(2)	1571.5(1)	5141.1(1)
C(1)	2223(6)	311(3)	5446(3)
C(2)	2652(6)	152(3)	6320(3)
C(3)	4327(7)	114(5)	6579(4)
O(1)	1689(5)	45(3)	6807(2)
C(11)	2003(6)	2038(3)	3485(3)
C(12)	1931(5)	1294(3)	3950(3)
C(13)	1858(6)	541(4)	3549(3)
C(14)	1872(6)	496(4)	2695(3)
C(15)	1986(6)	1244(4)	2257(3)
C(16)	2038(6)	2005(4)	2645(3)
C(17)	1738(8)	-343(4)	2271(3)
N(2)	1827(5)	2796(3)	4615(2)
N(3)	1992(5)	2840(3)	3861(3)
C(21)	1795(6)	3588(3)	5044(3)
C(22)	669(6)	3716(3)	5566(3)
C(23)	608(6)	4486(3)	5974(3)
C(24)	1684(7)	5115(3)	5870(3)
C(25)	2824(7)	4960(4)	5344(3)
C(26)	2890(6)	4213(4)	4928(3)
C(27)	1650(8)	5937(4)	6326(4)
N(1)	2036(5)	2033(3)	6345(2)
C(32)	3163(6)	2560(3)	6626(3)
C(33)	3106(7)	3003(4)	7345(3)
C(34)	1882(7)	2875(4)	7808(3)
C(35)	735(7)	2304(4)	7529(3)
C(36)	834(6)	1905(3)	6794(3)
Cl	6818(2)	2045(1)	5244(1)
O(2)	5648(6)	1632(4)	4762(3)
O(3)	6991(7)	1646(3)	6033(3)
O(4)	6456(8)	2912(3)	5354(3)
O(5)	8223(5)	1981(4)	4866(3)

$\beta = 94.51(4)^\circ$, $U = 2258 \text{ \AA}^3$, $Z = 4$, $D_c = 1.888 \text{ Mg m}^{-3}$, $\lambda(\text{Mo-K}\alpha) = 0.71069 \text{ \AA}$, $\mu = 6.66 \text{ mm}^{-1}$, $F(000) = 1248$, $T = -95^\circ\text{C}$.

Data collection and reduction. As above, with the following differences. Orange prism *ca.* $0.45 \times 0.4 \times 0.3 \text{ mm}$, 5584 intensities, 3968 unique ($R_{\text{int}} 0.026$), 3245 observed, transmission factors 0.43–0.81.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined anisotropically on F to $R 0.027$, $R' 0.030$. Hydrogen atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$.

298 Parameters; $S 1.2$; maximum $\Delta/\sigma 0.005$; maximum $\Delta\rho 1.0 \text{ e \AA}^{-3}$. Final atom coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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