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

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Complexes [AuR(acac-*C*)Cl] {R = pap (C_6H_4N=NPh-2) **1a** or mpap [C_6H_3(N=NC_6H_4Me-4)-2-Me-5] **1b**; Hacac = acetylacetone} or '$AuR(Cl)(OClO_3)$' (R = pap **2a** or mpap **2b**) react with various ketones MeC(O)R' to give [AuR{$CH_2C(O)R'$}Cl] [R = pap, R' = Et **3**, Pr^n **4**, Pr^i **5**, Bu^t **6** or $C_6H_2(OMe)_3$-3,4,5 **7**; R = mpap, R' = Me **8**]. Whereas **1a** does not react with $MeC(O)CH_2Cl$, **2a** gives a mixture of the expected [Au(pap){$CH_2C(O)CH_2Cl$}Cl] and [Au(pap)Cl_2]. However, other ketones [R'C(O)R"] (R' = Me; R" = Ph, CH_2=CH, *trans*-PhCH=CH or MeCO; R' = R" = CH_2Cl or Et) or 2-methylcyclohexanone do not react at room temperature with **2a**. The reactions of **2a** with other species containing activated methyl groups [$MeCO_2Et$, $MeC(O)NH_2$ or 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, [Au(pap)$(dmso)_2$][ClO_4]$_2$ **9**. It reacts with NaI to give [Au(pap)Cl(I)] **10**. Complex **8** reacts with $NaClO_4$·H_2O and pyridine (py) or 2,2'-bipyridine (bipy) to give [Au(mpap){$CH_2C(O)Me$}L]ClO_4 (L = py **11** or bipy **12**). The following reactions were also studied: [Au(pap)Cl(acac-*C*)] + PPh_3 or $AgClO_4$ to give [Au(pap)Cl(acac-*C*)(PPh_3)] **13** or [Au(pap)(acac-*O*,*O'*)]ClO_4 **14**, respectively. Complexes **13** and **14** do not give an acetonyl 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 [Au(mpap)Cl_2] [space group $P\bar{1}$, a = 7.902(2), b = 9.527(2), c = 10.378(3) Å, α = 86.77(2), β = 77.32(2), γ = 67.42(2)°, R = 0.024] and **11** [space group $P2_1/n$, a = 8.693(5), b = 15.800(8), c = 16.489(8) Å, β = 94.51(4)°, R = 0.027]. The latter is the first crystal structure of an acetonylgold(III) complex, and it could be shown conclusively that the $CH_2C(O)Me$ 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 unusual[3] 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 [Au(pap)Cl_2] [pap = 2-phenylazophenyl] in acetone with various reagents such as Tl(acac) (Hacac = acetylacetone), KCN, $AgClO_4$, 1,10-phenanthroline, HgR_2 (R = C_6F_5 or pap) or PdR_2 (R = $C_6H_4NO_2$-2) gives [Au(pap){$CH_2C(O)Me$}Cl]. Some intermediates in this process (see Scheme 1) were isolated. However, the reaction pathway when X = 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 [Au(mpap)Cl_2] [mpap = C_6H_3(N=NC_6H_4Me-4)-2-Me-5] and one ketonyl derivative to show conclusively that in the solid state, as in solution, this ligand is *C*-bonded.

Results

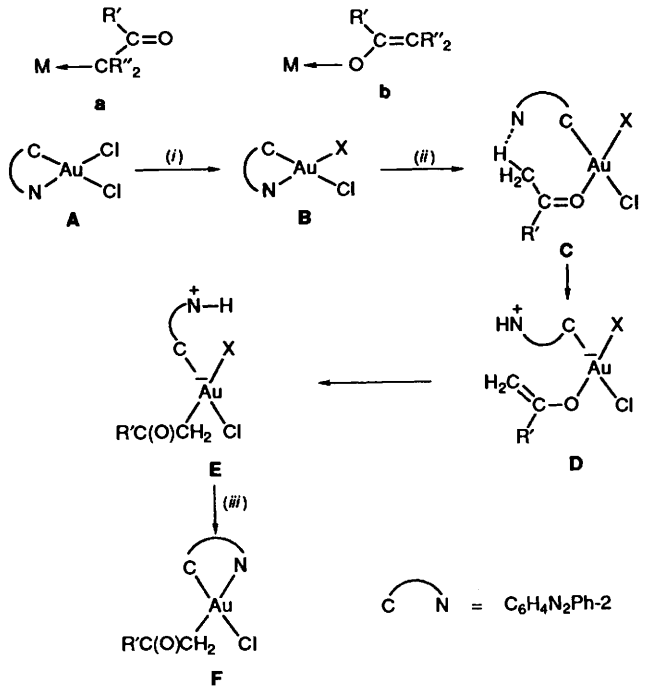
Complexes [AuR(acac-*C*)Cl] (R = pap **1a** or mpap **1b**) or '$AuR(Cl)(OClO_3)$' (R = pap **2a** or mpap **2b**, obtained by the reaction of [$AuRCl_2$] with Tl(acac) or $AgClO_4$, respectively,[4] react with various ketones MeC(O)R' to give [AuR{$CH_2C(O)R'$}Cl] [R = pap, R' = Et **3**, Pr^n **4**, Pr^i **5**, Bu^t **6**, or $C_6H_2(OMe)_3$-3,4,5 **7**; R = mpap, R' = Me **8**] (see Scheme 2).

The reaction between complex **1a** and MeC(O)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 $[AuRCl_2]$ with $AgClO_4$ [which gives complexes '$AuR(Cl)(OClO_3)$' **2a** and **2b**, see below] in the ketone as solvent (acetone) or, when $[AuRCl_2]$ 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, $C_6H_4N{=}NPh$-2, C_6F_5 or $C_6H_4NO_2$-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.

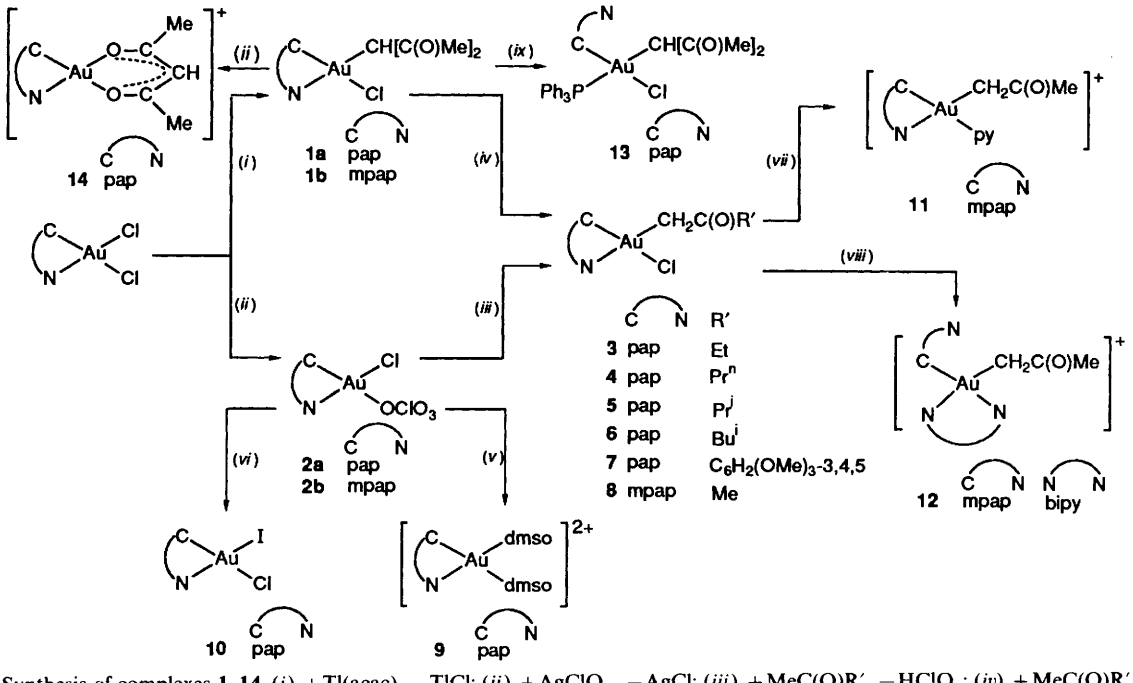
Complex **1a** was recovered unchanged after 110 or 91 h of stirring in $MeC(O)CH_2Cl$ or MeC(O)Ph, respectively. Method B also fails to activate MeC(O)Ph after 65 h. However, **1a** reacts with $MeC(O)CH_2Cl$ giving a mixture whose IR and NMR spectra indicate the presence of $[Au(pap)Cl_2]$ and $[Au(pap)Cl\{CH_2C(O)CH_2Cl\}]$. This mixture could neither be separated nor its formation prevented, because $[Au(pap)Cl_2]$ is formed even if the intermediate '$Au(pap)Cl(OClO_3)$' 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.

$$'Au(pap)Cl(OClO_3)' + MeC(O)CH_2Cl \longrightarrow [Au(pap)Cl_2] \quad (1)$$

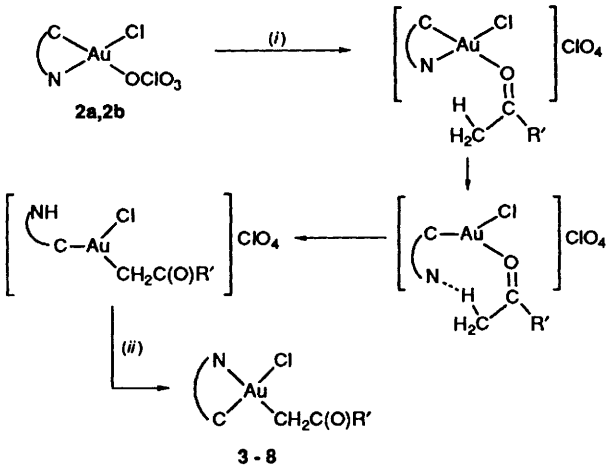
All remaining reactions were carried out using Method B because of the greater reactivity of the intermediate '$AuRCl(OClO_3)$' compared with the corresponding acac complexes **1a** and **1b**. Accordingly, 3,4,5-trimethoxyacetophenone gives $[Au(pap)\{CH_2C(O)C_6H_2(OMe)_3\text{-}3,4,5\}Cl]$ **7** using this method. However, the following ketones do not react: $MeC(O)R'$, where $R' = CH_2{=}CH$ (24 h), *trans*-PhCH=CH (24 h), MeCO (94 h), $(ClCH_2)_2CO$ (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 $[Au(pap)(dmso)_2][ClO_4]_2$ **9** and $[Au(pap)Cl_2]$ instead of a carbon–hydrogen activation product. Complex **9** can be obtained pure by reacting $[Au(pap)Cl_2]$ 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 $[AuCl_3(dmso)]$.[6]

In an attempt to identify complexes **2a** and **2b** they were isolated (see below) and **2a** was treated with NaI to give $[Au(pap)Cl(I)]$ **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*) +Tl(acac), −TlCl; (*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*) $-HClO_4$

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 $NaClO_4 \cdot H_2O$ and pyridine (py) or 2,2'-bipyridine (bipy) to give $[Au(mpap)\{CH_2C(O)Me\}L]ClO_4$ (L = py **11** or bipy **12**). The crystal structures of **11** and the starting complex $[Au(mpap)Cl_2]$ were determined.

We have also prepared other acac complexes to study their reactivities with acetone. Thus, **1a** reacts with PPh_3 (1:1) or $AgClO_4$ (1:1) to give [Au(pap)Cl(acac-*C*)(PPh_3)] **13** or [Au(pap)(acac-*O*,*O'*)]ClO_4 **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 $C_6H_4CH_2NMe_2$-2,[4] $[AuMe_2$(acac-*O*,*O'*)],[7] $[AuMe_2$(acac-*C*)L], of which only the complex with L = $PPhMe_2$ has been isolated,[8] and $[AuR_2(acac)]$, where R_2 = 2,2'-biphenyl[9] 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 suggested[4] on the basis of the isolation and properties of some of the proposed intermediates (see Scheme 1). However, when Method B (X = ClO_4) 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 = ClO_4). The reaction of $[AuRCl_2]$ (R = pap or mpap) with $AgClO_4$ (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 effect[11] 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' = CH_2Cl) 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 NH_2) 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 $CH_2C(O)R'$ to the metal through the CH_2 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 $Me_2SO \rightarrow M$ bonding.[14] For $[AuCl_3$(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 $M\{CH_2C(O)R'\}$ show the δ(CH_2) ^1H NMR resonance as a singlet in the range 1.3–2.6, whereas those of the related enolato complexes $M\{OC(R')=CH_2\}$ appear as two resonances at lower field (δ 4.0–4.6).[15]

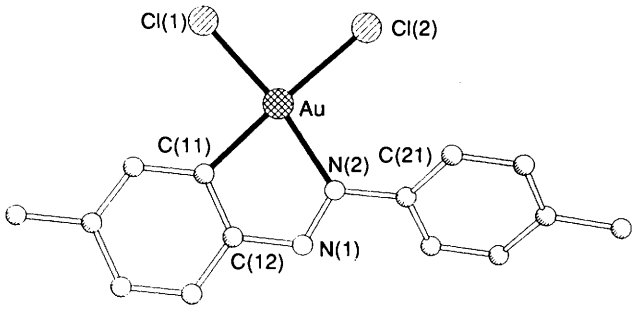


Fig. 1 The molecule of $[Au(mpap)Cl_2]$ in the crystal. Radii are arbitrary; H atoms omitted for clarity

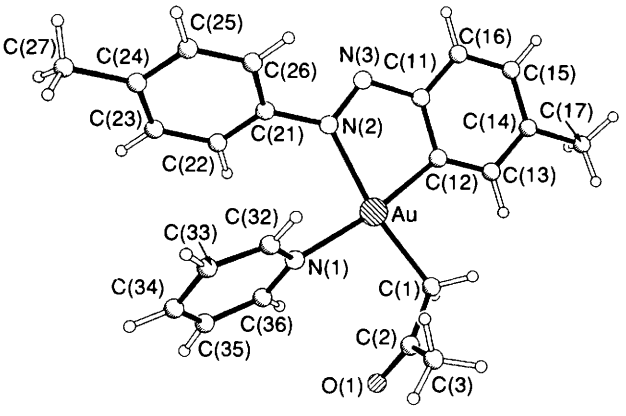


Fig. 2 The cation of compound **11** in the crystal. Radii are arbitrary

Table 1 Selected bond lengths (Å) and angles (°) for $[Au(mpap)Cl_2]$

Au–Cl(1)	2.274(1)	Au–Cl(2)	2.347(1)
Au–N(2)	2.069(4)	Au–C(11)	2.021(5)
N(1)–N(2)	1.283(5)	N(1)–C(12)	1.388(7)
N(2)–C(21)	1.415(7)		
Cl(1)–Au–Cl(2)	89.9(1)	Cl(1)–Au–N(2)	171.1(1)
Cl(2)–Au–N(2)	98.5(1)	Cl(1)–Au–C(11)	91.4(2)
Cl(2)–Au–C(11)	177.5(2)	N(2)–Au–C(11)	80.1(2)
N(2)–N(1)–C(12)	114.3(4)	Au–N(2)–N(1)	116.2(3)
Au–N(2)–C(21)	128.5(3)	N(1)–N(2)–C(21)	114.8(4)
Au–C(11)–C(12)	109.1(4)	N(1)–C(12)–C(11)	120.1(4)

Table 2 Selected bond lengths (Å) and angles (°) for compound **11**

Au–C(12)	2.011(5)	Au–N(2)	2.120(4)
Au–N(1)	2.112(4)	Au–C(1)	2.061(6)
C(11)–N(3)	1.412(7)	N(2)–N(3)	1.264(6)
N(2)–C(21)	1.440(7)	N(1)–C(32)	1.340(7)
N(1)–C(36)	1.342(7)	C(1)–C(2)	1.481(7)
C(2)–C(3)	1.486(8)	C(2)–O(1)	1.217(7)
C(12)–Au–N(2)	78.6(2)	C(12)–Au–N(1)	172.4(2)
N(2)–Au–N(1)	93.8(2)	C(12)–Au–C(1)	91.2(2)
N(2)–Au–C(1)	169.5(2)	N(1)–Au–C(1)	96.3(2)
Au–N(2)–N(3)	116.4(3)	Au–N(2)–C(21)	126.5(3)
N(3)–N(2)–C(21)	116.4(4)	C(11)–N(3)–N(2)	112.9(4)
Au–N(1)–C(32)	120.2(3)	Au–N(1)–C(36)	120.1(3)
Au–C(1)–C(2)	114.5(4)	C(1)–C(2)–C(3)	116.9(5)
C(1)–C(2)–O(1)	122.2(5)	C(3)–C(2)–O(1)	120.9(5)

However, a high oxidation state, as in $[Pt^{IV}\{CH_2C(O)Me\}Cl_4(NH_3)]^-$, can give a methylene resonance at low field (δ 4.72)[16] and certain ligands, such as in $[Rh\{CH_2C(O)Me\}(porphyrin)]$, can give a methylene resonance at very high field (δ −4.7).[3] Complexes **3**–**6**, **8**, **11** and **12** show the methylene singlet in the range δ 3.3–3.5 as expected for a ketonyl complex of a metal in oxidation state +3. The electron-releasing nature of the $C_6H_2(OMe)_3$-3,4,5 group in **7** shifts this resonance to δ 4.0.

The non-equivalence of the Me groups in the ^1H and ^{13}C NMR spectra of complex **13** indicates that rotation of the pap ligand around the Au–C bond does not take place. This could arise from steric hindrance by the *cis* PPh_3 ligand and/or from an N→Au axial interaction. The possibility of acac being *trans* to PPh_3 is also supported by the value of $^3J(HP)$ 16 Hz which is greater than that (12 Hz) for *cis*-$[AuMe_2(acac\text{-}C)(PMe_2Ph)]$.[8]

The molar conductivity in acetone of the new complexes **3**–**14** is in agreement with their proposed formulations; **3**–**8**, **10** and **13** are non-conducting in acetone solution.

The complexes $[Au(mpap)Cl_2]$ and **11** have been studied by X-ray diffraction methods (see Figs. 1 and 2, Tables 1 and 2). The precision of the low-temperature measurements was sufficient to confirm that the ketonyl ligand in **11** co-ordinates through the C atom; first, the H atoms were located in Fourier difference syntheses, secondly, the thermal parameters are normal and thirdly C–C [1.481(7) and 1.486(8) Å] and C=O [1.217(7) Å] bond lengths are normal for a ketonyl group.

Both complexes show square-planar co-ordination at the gold atom, but the chelate rings of the mpap ligand are associated with some distortion at the narrow C–Au–N bond angle [80.1(2) and 78.6(2)°, respectively] and a concomitant opening of Cl(2)–Au–N(2) [98.5(1)°] for $[Au(mpap)Cl_2]$ and of N(1)–Au–C(1) [96.3(2)°] and N(2)–Au–N(1) [93.8(2)°] in **11**. The Au–C(aryl) bond distances are similar [2.021(5) and 2.011(5) Å, respectively] in spite of the different *trans* ligands. Similar Au–C(aryl) bond lengths are observed *trans* to an oxygen donor, as in $[Au(\eta^2\text{-}C_6H_4CH_2NMe_2\text{-}2)(\eta^2\text{-quin})]$ (quin = quinolin-8-olate) [2.021(7) Å].[17] However, the Au–CH_2 bond in **11** [2.061(6) Å] is longer than Au–C(aryl), probably because of the different hybridization of the carbon atom. In contrast, the Au–N and Au–Cl bond distances are sensitive to the nature of the *trans* ligand. Thus, both Au–N bond lengths in **11** are similar [2.112(4) and 2.120(4) Å], because both have a *trans* carbon donor ligand, but are longer than the Au–N bond [2.069(4) Å] in $[Au(mpap)Cl_2]$, because of the lower *trans* influence of the chloride ligand. Similarly, the greater *trans* influence of an aryl ligand compared to an N-donor is reflected in Au–Cl(2) [2.347(1) Å] being longer than Au–Cl(1) [2.274(1) Å] in $[Au(mpap)Cl_2]$. These values are also consistent with previous and present assignments of the Au–Cl stretching modes.[4c,18]

The gold atom of complex **11** is involved in a short non-bonded contact to a perchlorate oxygen; Au···O(5) $(-1+x, y, z)$ 3.32 Å. No short contacts to gold are observed in $[Au(mpap)Cl_2]$.

Experimental

The IR spectra, the C, H and N analyses, conductance measurements, melting point determinations, NMR spectra, and fundamental reaction conditions were as described elsewhere.[4c] The starting complexes $[AuRCl_2]$ (R = pap or mpap),[4c,18] **1a**[4b] and **1b**[4c] were prepared as reported.

Synthesis of the Ketonyl Complexes **3**–**8**.—*Method A: for* **3**–**6** *and* **8**. A solution of complex **1a** or **1b** (50 mg, 0.1 mmol) in the corresponding ketone (30–35 cm^3) was stirred for 66, 80, 80, 90 or 15 h, respectively. The resulting solution was evaporated to dryness, the residue extracted with dichloromethane and filtered over anhydrous $MgSO_4$. The solution was concentrated (1 cm^3), whereupon addition of hexane (5 cm^3) and recrystallization from dichloromethane–hexane gave the corresponding complexes. Yields: **3**, 70; **4**, 60; **5**, 65; **6**, 70; and **8**, 80%.

Method B. The stoichiometric amount of solid $AgClO_4$ was added to a solution of the corresponding $[AuRCl_2]$ (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.); ν(AuCl) 300, ν(CO) 1668 cm^{-1}; δ(^{1}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, $^3J_{HH}$ = 7 Hz) and 1.0 (t, 3 H, Me); δ(^{13}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. $C_{16}H_{16}AuClN_2O$ requires C, 39.6; H, 3.3; Au, 40.6; N, 5.8%).

Complex **4**: m.p. 138 °C; ν(AuCl) 300, ν(CO) 1675 cm^{-1}; δ(^{1}H) 8.0 (m, 9 H, pap), 3.4 (s, 2 H, C^1H_2), 2.7 (t, 2 H, C^3H_2, $^3J_{HH}$ = 7), 1.6 (m, 2 H, C^4H_2, $^3J_{HH}$ = 7 Hz) and 0.9 (t, 3 H, Me); δ(^{13}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. $C_{17}H_{18}AuClN_2O$ requires C, 40.9; H, 3.6; Au, 39.5; N, 5.6%).

Complex **5**: m.p. 108 °C; ν(AuCl) 307, ν(CO) 1665 cm^{-1}; δ(^{1}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, $^3J_{HH}$ = 7 Hz) and 1.1 (d, 6 H, Me); δ(^{13}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. $C_{17}H_{18}AuClN_2O$ requires C, 40.9; H, 3.7; Au, 39.5; N, 5.6%).

Complex **6**: m.p. 117 °C (decomp.); ν(AuCl) 310, ν(CO) 1680 cm^{-1}; δ(^{1}H) 7.9 (m, 9 H, pap), 3.5 (s, 2 H, C^1H_2), 2.6 (d, 2 H, C^3H_2, $^3J_{HH}$ = 7), 2.2 (m, 1 H, C^4H, $^3J_{HH}$ = 7 Hz) and 0.9 (d, 6 H, Me); δ(^{13}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. $C_{18}H_{20}AuClN_2O$ requires C, 42.2; H, 3.9; Au, 38.4; N, 5.5%).

Complex **7**: m.p. 167 °C; ν(AuCl) 300, ν(CO) 1638 cm^{-1}; δ(^{1}H) 7.7 (m, 11 H, pap + H^2,H^6), 4.0 (s, 2 H, CH_2), 3.925 (s, 6 H, OMe) and 3.921 (s, 3 H, OMe); δ(^{13}C) 198.0 (CO), 60.9 (OMe) and 56.7 (OMe) (Found: C, 43.6; H, 3.9; Au, 31.3; N, 4.4. $C_{23}H_{22}AuClN_2O_4$ requires C, 44.4; H, 3.6; Au, 31.6; N, 4.5%).

Complex **8**: m.p. 189 °C; ν(AuCl) 300, ν(CO) 1670 cm^{-1}; δ(^{1}H) 8.0 [d, 1 H, mpap (H^{13}), $^3J_{HH}$ = 8], 7.9 [d, 2 H, mpap (H^{22}), $^3J_{HH}$ = 8 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); δ(^{13}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. $C_{17}H_{18}AuClN_2O$ requires C, 40.9; H, 3.6; Au, 39.5; N, 5.6%).

[Au(pap)(dmso)$_2$][ClO_4]$_2$ **9**.—One drop of dmso and solid $AgClO_4$ (40 mg, 0.22 mmol) were added to a suspension of [Au(pap)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; Λ_M = 182 Ω^{-1} cm^2 mol^{-1} (in acetone); δ(^{1}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. $C_{16}H_{21}AuCl_2N_2O_{10}S_2$ requires C, 26.2; H, 2.9; Au, 26.8; N, 3.8%).

[Au(pap)Cl(I)] **10**.—Solid $AgClO_4$ (23 mg, 0.1 mmol) was added to a solution of [Au(pap)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; ν(AuCl) 300 cm^{-1} (Found: C, 25.9; H, 2.0; Au, 36.1; N, 5.6. $C_{12}H_9AuClIN_2$ requires C, 26.7; H, 1.7; Au, 36.4; N, 5.2%).

[Au(mpap){$CH_2C(O)Me$}L]ClO_4 (L = *py* **11** *or bipy* **12**).—Pyridine (1 cm^3) or solid 2,2′-bipyridine (1:1) and solid $NaClO_4$·H_2O (1:1) were added to a solution of complex **8** (40–50 mg) in acetone (10–20 cm^3); the resulting suspension was stirred for 30 min, then concentrated to dryness and the residue extracted with dichloromethane (3 × 5 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.); Λ_M = 141 Ω^{-1} cm^2 mol^{-1} (in acetone); ν(CO) 1690 cm^{-1}; δ(^{1}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, ^{3}Me); δ(^{13}C) 206.1 (CO), 40.9 (CH_2), 30.0 (^{3}Me), 22.4 and 21.2 (Me of mpap) (Found: C, 41.9; H, 4.0; Au, 31.0; N, 6.0. $C_{22}H_{23}AuClN_3O_5$ requires C, 41.2; H, 3.6; Au, 30.7; N, 6.6%).

Complex **12**: yield 87%, m.p. 147 °C (decomp.); Λ_M = 130 Ω^{-1} cm^2 mol^{-1} (in acetone); ν(CO) 1670 cm^{-1}; δ(^{1}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, ^{3}Me); δ(^{13}C) 208.3 (CO), 32.8 (CH_2), 30.3 (^{3}Me), 21.5 and 21.3 (Me of pap) (Found: C, 45.7; H, 3.2; Au, 27.0; N, 7.6. $C_{27}H_{26}AuClN_4O_5$ requires C, 45.1; H, 3.6; Au, 27.4; N, 7.8%).

[Au(pap)Cl(acac-*C*)(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; ν(AuCl) 310, ν(CO) 1660 and 1680 cm^{-1}; δ(^{1}H) 7.4 (m, 24 H, Ph), 4.8 (d, 1 H, CH, $^3J_{HP}$ = 16 Hz), 2.1 and 2.0 (s, 3 H, Me); δ(^{13}C) 203.9 (CO), 203.7 (CO), 67.6 (CH, $^3J_{CP}$ = 86.4 Hz), 31.8 and 31.2 (Me); δ(^{31}P) 30.5 (Found: C, 54.2; H, 4.0; Au, 25.5; N, 3.6. $C_{35}H_{31}AuClN_2O_2P$ requires C, 53.6; H, 4.5; Au, 25.4; N, 3.6%).

[Au(pap)(acac-*O*,*O*′)]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; Λ_M = 118 Ω^{-1} cm^2 mol^{-1} (in acetone); ν(CO) 1565 and 1510 cm^{-1}; δ(^{1}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. $C_{17}H_{16}AuClN_2O_6$ requires C, 35.4; H, 2.8; Au, 34.2; N, 4.9%).

X-Ray Structure Determination of [Au(mpap)Cl_2].—*Crystal data.* $C_{14}H_{13}AuCl_2N_2$, M_r = 477.1, triclinic, space group $P\bar{1}$, a = 7.902(2), b = 9.527(2), c = 10.378(3) Å, α = 86.77(2), β = 77.32(2), γ = 67.42(2)°, U = 703.4 Å^3, Z = 2, D_c = 2.253 Mg m^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ = 10.8 mm^{-1}, F(000) = 448, T = −95 °C.

Data collection and reduction. An orange tablet *ca.* 0.5 × 0.3 × 0.2 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 $2\theta_{max}$ 50°, of which 2477 were unique (R_{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 2θ 20–23°. 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 $F_{corr} = F(1 + 0.002xF^2/\sin 2\theta)^{-0.25}$; x refined to 0.000 99(11). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. 179 Parameters; S 1.4; maximum Δ/σ 0.002; maximum $\Delta\rho$ 1.4 e Å^{-3}. Final atom coordinates are given in Table 3.

X-Ray Structure Determination of Compound **11**.—*Crystal data.* $C_{22}H_{23}AuClN_3O_5$, M_r = 641.8, monoclinic, space group $P2_1/n$, a = 8.693(5), b = 15.800(8), c = 16.489(8) Å,

Table 3 Atomic coordinates (× 10^4) for [Au(mpap)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 (× 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)

$\beta = 94.51(4)°$, $U = 2258$ Å^3, $Z = 4$, $D_c = 1.888$ Mg m^{-3}, λ(Mo-Kα) = 0.710 69 Å, $\mu = 6.66$ mm^{-1}, $F(000) = 1248$, $T = -95$ °C.

Data collection and reduction. As above, with the following differences. Orange prism *ca.* 0.45 × 0.4 × 0.3 mm, 5584 intensities, 3968 unique (R_{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 Δ/σ 0.005; maximum $\Delta\rho$ 1.0 e Å^{-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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