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

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† 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.

Complexes [AuR(acac-C)Cl] (R = pap = C6H4(N=NPh-2) 1a or mpap = C6H4(N=NC6H4Me-4)-2-Me-5) 1b; Hacac = acetylacetone or 'AuR(Cl)(OCIO3)' (R = pap 2a or mpap 2b) react with various ketones MeC(O)R' to give [AuR(CH2C(O)R')Cl] (R = pap, R' = Et 3, Pra 4, Prb 5, Bu 6 or C6H5(OMe)2 7; R = mpap, R' = Me 8). Whereas 1a does not react with MeC(O)CH2Cl, 2a gives a mixture of the expected [Au(pap){CH2C(O)CH2Cl}2Cl] and [Au(pap)Cl2]. However, other ketones [R'C(O)R'Cl] (R' = Me; R' = Ph, CH2=CH, trans-PhCH=CH or MeCO; R' = CH3Cl or Et) or 2-methylcyclohexanone do not react at room temperature with 2a. The reactions of 2a with other species containing activated methyl groups [MeCO2Et, MeC(O)NH 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)].[ClO4] 9. It reacts with NaI to give [Au(pap)Cl(II)] 10. Complex 8 reacts with NaClO4·H2O and pyridine (py) or 2,2'-bipyridine (bipy) to give [Au(mpap)(CH2C(O)Me)2]ClO4 (L = py 11 or bipy 12). The following reactions were also studied: [Au(pap)(Cl(acac-C)) + PPh3 or AgClO4 to give [Au(pap)(Cl(acac-C))(PPh3)] 13 or [Au(pap)(acac-C)Cl] 14, respectively. Complexes 13 and 14 do not give an acetyl 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]L [space group Pt, 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 [Au(mpap)Cl]L [space group P21/n, a = 8.693(5), b = 15.800(8), c = 16.489(8) Å, â = 94.51(4)°, R = 0.027]. The latter is the first crystal structure of an acetylonylgold(III) complex, and it could be shown conclusively that the CH2C(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). Metallated ketones play an important role in organic synthesis. There are several syntheses of these compounds involving e.g. direct metallation of the ketone by deprotonating agents, oxidative-addition reactions (with α-halogenocarboxyl compounds or epoxides), or transmetallation reactions. We have recently reported that an unusual carbon–hydrogen activation of acetone occurs by intramolecular co-operation between the metal centre and a ligand attached to it. Thus, the reaction of [Au(pap)Cl2] [pap = 2-phenylazophenyl] in acetone with various reagents such as Ti(acac) (Hacac = acetylacetone), KCN, AgClO4, 1,10-phenanthroline, HgR2 (R = C6F5 or pap) or PrR2 (R = C6H5NO2 -2) gives [Au(pap){CH2C(O)Me}Cl]. Some intermediates in this process (see Scheme 1) were isolated. However, the reaction pathway when X = ClO4, 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)Cl2] [mpap = C6H4(N=NC6H4Me-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)(OCIO3)' (R = pap 2a or mpap 2b, obtained by the reaction of [AuRCl2] with Ti(acac) or AgClO4, respectively) react with various ketones MeC(O)R' to give [AuR(CH2C(O)R')Cl] [R = pap, R' = Et 3, Pr 4, Pr 5, Bu 6, or C6H5(OMe)2 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
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(0)R' where R' = Pr", Pr' or Bu' were not complete after 72 h; for R' = Pr" or Pr', 80 h and for Bu' 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 [AuRCI₂] with AgCIO₄ [which gives complexes ‘AuR(Cl)(OCIO₃)’] 2a and 2b, see below] in the ketone as solvent (acetone) or, when [AuRCI₂] was sparingly soluble, in a mixture of chloroform or dichloromethane with the ketone (Method B). This method gives similar yields (50-90\%) and is faster. Thus, ketones MeC(0)R' require 1, 40, 40, 40 and 80 h for R' = Me, Et, Pr", Pr' and Bu', respectively, to complete the activation process.

Complex \(1a\) was recovered unchanged after 110 or 91 h of stirring in MeC(O)CH₂Cl or MeC(O)Ph, respectively. Method B also fails to activate MeC(O)Ph after 65 h. However, \(1a\) reacts with MeC(O)CH₂Cl giving a mixture whose IR and NMR spectra indicate the presence of [Au(pap)Cl₂] and [Au(pap)Cl(CH₂C(O)CH₂Cl)]. This mixture could neither be separated nor its formation prevented, because [Au(pap)Cl₂] 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 ‘AuRCI(Cl)(OCIO₃)’ compared with the corresponding acac complexes \(1a\) and \(1b\). Accordingly, 3,4,5-trimethoxyacetophenone gives [Au(pap)(CH₂C(O)C₆H₃(OMe)₃-3,4,5)Cl] 7 using this method. However, the following ketones do not react: MeC(0)R', where R' = Me, Et, Pr", Pr' and Bu', respectively, to complete the activation process. This complex does react with excess of dimethyl sulfoxide (dmso) to give a mixture of [Au(pap)(dmso)₂][ClO₄]₂, 9 and [Au(pap)Cl₂] instead of a carbon–hydrogen activation product. Complex 9 can be obtained pure by reacting [Au(pap)Cl₂] with AgClO₄ (1:2) and excess of dmso. As far as we are aware, there is only one reported gold complex with dmso, the unstable [AuCl₃(dmso)]\(^+\).

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

![Diagram](attachment:Scheme3.png)

tried to prepare similar complexes with the aryl group mpap, which had given good results in the case of 1b. Since the corresponding acetylone 8 also does not give suitable crystals, we tried to crystallize derivatives obtained by reaction with NaClO₄, tert-butanol, and pyridine or 2,2'-bipyridine to give [Au(mpap)CH₂C(O)Me]ClO₄, LClO₄ (L = py or bpy 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,0')]ClO₄, 14, respectively. However, these complexes do not give neutral complexes with acetone. Reported acac-gold(III) complexes are limited to 1a and 1b and homologues with the aryl ligand C₆H₅CH₂NMe₂⁺. For [Au(mpap)(acac-O,0')], [AuMe₂(acac-C)L], of which only the complex with L = PPh₂Me₂ has been isolated, and [AuR₂(acac)], where R = 2,2'-biphenyl or 1,2,3,4-tetraphenylbuta-1,3-dien-1,4-diyl Complex 14 is the first cationic acetylacetonato-gold(III) complex.

**Discussion**

A plausible reaction pathway of keto-carbon–hydrogen activation starting from complexes 1 has been suggested on the basis of the isolation and properties of some of the proposed intermediates. For the reaction of 1b with acetone, we considered it more reasonable to postulate that the weakly bonding perchlorate ligand is replaced by acetone, instead of labilizing the ligand and allowing 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 v(Au-Cl), that of 2b has a band at 365 cm⁻¹, assignable to v(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 antisymmetric effect can explain both results. Because perchlorate is a harder ligand than chloride it should co-ordinate trans to the softer iodine 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. This isomerization is also consistent with the antisymmetric 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 cooperation 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 ketonyle complexes. Our experience suggests that at least one of the substituents should be a methyl group (+1 effect, low steric requirement) and the other an alkyl group with +1 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 −1 effect the reaction may (R’ = CH₃CH₂) or may not (R’ = MeCO, R’CH=CH₂ or Ph) occur. The importance of electronic effects on the activation process is emphasized by the fact that a crystal activation starting from complexes 10, 11, 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 CH₃C(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 ligand in either the 2a and 2b complexes. For [Au(mpap)(dmso)] the v(S≡O) mode is the v(CC≡O), whereas the acac-QO' complex displays a pair of well separated bands at 1565 and 1650 cm⁻¹ for the ketonyl 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). The dmso complex 9 shows two strong bands at 900 and 925 cm⁻¹ assignable to v(SO). Such frequencies, lower than that of the free ligand (1053 cm⁻¹), have been interpreted as implying Me₂SO—M bonding. For [AuCl₃(dmso)] the v(SO) mode appears at 1198 cm⁻¹, which, in combination with the v(CC≡O) assignment, suggests 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.

Ketonyle complexes of the type M[CH₃C(O)R'] show the δ(CH₂) H NMR resonance as a singlet in the range 1.3-2.6, whereas those of the related enolato complexes M[OC(CHR')₂] appear as two resonances at lower field (δ 4.0-4.6).
of a metal in oxidation state \( +3 \). The electron-releasing nature of the \( \text{C}_6\text{H}_3\text{(OMe)}_3 \) group in 7 shifts this resonance to \( \delta 4.0 \).

The non-equivalence of the \( \text{Me} \) groups in the \( ^1H \) and \( ^13C \) 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 \( J(\text{HP}) \) which is greater than that (12 Hz) for cis-[\( \text{AuMe}_2(\text{(acac-C)}\text{PMe}_2\text{Ph})\)]\(_2\).

The Au–C(aryl) bond lengths of the new complexes are in agreement with their proposed formulations; 3–10 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 \( C \) atoms, normal and thirdly \( C(1) \{1.487(1) \text{ Å}\} \) and \( C(0) \{1.217(1) \text{ Å}\} \) 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 \( \text{C}(2)-\text{Au}-\text{N}(2) \) (Table 2) for [Au(mpap)Cl\(_2\)] and of \( \text{N}(1)-\text{Au}-\text{C}(1) \) [93.8(2)"], respectively] and a concomitant opening of \( \text{C}(2)-\text{Au}-\text{N}(2) \) [98.5(1)"], respectively] and a concomitant opening of \( \text{N}(1)-\text{Au}-\text{C}(1) \) [96.3(2)"], respectively] and a concomitant opening of \( \text{N}(2)-\text{Au}-\text{N}(1) \) [93.8(2)"], respectively] in 11. The Au–C(aryl) bond distances are similar \( 2.021(5) \) and \( 2.011(5) \), respectively] in spite of the different trans ligands. Similar Au–C(aryl) bond lengths are observed trans to an oxygen donor, as in \( [\text{Au}(\text{n}^5-\text{C}_6\text{H}_4\text{CH}_2\text{NMMe}_2-2)(\text{n}^5-\text{quin})] \) (quin = quinolin-8-olate) \( 2.021(7) \).\(^\mathrm{1}\) However, the Au–Cl bond is longer \( 2.210(4) \) than \( 2.112(4) \) in \( \{\text{Au(C}2\text{H}5\text{Cl})_{2}\}\text{Na} \).\(^\mathrm{1}\)\(^\mathrm{1}\), probably because of the different hybridization of the carbon atom. In contrast, the Au–N and Au–Cl bond distances are sensitive to the trans ligand. Thus, both Au–N bond lengths in 11 are similar \( 2.112(4) \) and \( 2.120(4) \), respectively] because both have a trans carbon donor ligand, but are longer than the Au–N bond \( 2.069(4) \) 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) \( 2.347(1) \) being longer than Au–Cl(1) \( 2.274(1) \) in [Au(mpap)Cl\(_2\)]. These values are also consistent with previous and present assignments of the Au–Cl stretching modes.\(^\mathrm{10}\)\(^\mathrm{18}\)

The gold atom of complex 11 is involved in a short non-bonded contact to a perchlorate oxygen; \( \text{Au} \cdots \text{O}(5) = 3.32 \text{ Å} \). No short contacts to gold are observed in \( [\text{Au(mpap)Cl}_2] \).

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.\(^\mathrm{10}\) The starting complexes [AuRCI\(_2\)] \( (R = \text{mpap or mpap}) \).\(^{4,18}\) \( \text{Ia}\) and \( \text{Ib}\) were prepared as reported.

**Synthesis of the Ketonyl Complexes 3–8** —**Method A**: for 3–6 and 8. A solution of complex \( \text{Ia} \) or \( \text{Ib} \) (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 \( [\text{Au(mpap)Cl}_2] \) (50 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...
Diethyl ether (12.0; Au, 36.1; N, 5.2. C, H, AuClIN, requires C, 26.7; H, 1.7; Au, 26.8; N, 3.8%).

Complex 3: m.p. 117 °C (decomp.); [Au(pap)Cl,"] (50 mg, 0.1 mmol) in dichloromethane (30 cm3); the resulting suspension was stirred for 3 h and concentrated (1 cm3). Addition of diethyl ether (5 cm3) added to precipitate complex 11 as a yellow-orange or orange solid, respectively.

Complex 11: yield 75%, m.p. 187 °C (decomp.); [Au(pap)(acac-O,O')]+ClO4- (Found: C, 41.5; H, 3.6; Au, 27.4; N, 3.6%).

[Au(pap)(Clac-c)(PPh3)]-13.—Solid PPh3 (77 mg, 0.3 mmol) was added to a solution of complex 11a (150 mg, 0.5 mmol) in dichloromethane (20 cm3); the resulting suspension was stirred for 1 h and concentrated (1 cm3). Addition of diethyl ether (5 cm3) precipitated complex 11a as an orange solid. Yield 85%, m.p. 154 °C; [Au(pap)(Clac-c)(PPh3)]-ClO4- (Found: C, 41.3; H, 3.1; Au, 26.8; N, 5.8%; Cl, 24.2; H, 0.5; Me; ClO4- 203.9 (CO), 203.7 (CO), 67.6 (CH2, 13C) = 86.4 Hz). 318.1 and 31.2 (Me; ClO4-) 30.5 (Found: C, 52.4; H, 4.0; Au, 25.5; N, 3.6. C3H13AuClIN204P requires C, 53.6; H, 4.5; Au, 25.4; N, 3.6%).

[Au(pap)(Clac-c)(PPh3)]-14.—Solid AgClO4 (21 mg, 0.1 mmol) was added to a solution of complex 11a (50 mg, 0.1 mmol) in dichloromethane (15 cm3); the resulting suspension was stirred for 3 h and filtered over anhydrous MgSO4. The solution was concentrated for 30 min, then concentrated to dryness and the residue was extracted with dichloromethane (3 × 5 cm3), filtered over anhydrous MgSO4, the concentrated (1 cm3), and diethyl ether (5 cm3) added to precipitate complex 11 or 12 as a yellow-orange or orange solid, respectively.

Complex 12: yield 87%, m.p. 147 °C (decomp.); [Au(pap)(acac-O,O')]+ClO4- (Found: C, 41.5; H, 3.6; Au, 27.4; N, 3.6%).

5: [Au(pap)(acac-O,O')]+ClO4- 14.—Solid AgClO4 (21 mg, 0.1 mmol) was added to a solution of complex 11a (50 mg, 0.1 mmol) in dichloromethane (20 cm3); the resulting suspension was stirred for 1 h and concentrated (1 cm3). Addition of diethyl ether (5 cm3) precipitated complex 11a as an orange solid. Yield 85%, m.p. 154 °C; [Au(pap)(acac-O,O')]+ClO4- (Found: C, 41.3; H, 3.1; Au, 26.8; N, 5.8%; Cl, 24.2; H, 0.5; Me; ClO4- 203.9 (CO), 203.7 (CO), 67.6 (CH2, 13C) = 86.4 Hz). 318.1 and 31.2 (Me; ClO4-) 30.5 (Found: C, 52.4; H, 4.0; Au, 25.5; N, 3.6. C3H13AuClIN204P requires C, 53.6; H, 4.5; Au, 25.4; N, 3.6%).

X-Ray Structure Determination of [Au(mppap)]+-15.—Solid C4H12AuClIN204 requires C, 53.6; H, 4.5; Au, 25.8; N, 3.4.9%.

1.25 (8) h and filtered over anhydrous MgSO4. The solution was concentrated (1 cm3) and addition of diethyl ether (1 cm3) and hexane (10 cm3) gave the corresponding complexes as yellow solids. Differences from this general method were that the solid kept from evaporation (11 mg, 0.055 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, 7, 65; and 7, 92%.

Complex 3: m.p. 138 °C; [Au(III)] (50 μg, 0.2 mmol) in acetone (10-20 cm3); the resulting suspension was concentrated (1 cm3) and addition of hexane (10 cm3) to precipitate complex 9 as a yellow solid. Yield 75%, m.p. 154 °C; v(AuCl) 300 cm-' (in acetone); [Au(III)] (510 cm3) added to a solution of [Au(pap)Cl,"] (50 mg, 0.1 mmol) in acetone (50 mg) in acetone (1 cm3); the resulting suspension was filtered over anhydrous MgSO4, the solution concentrated (1 cm3) and addition of hexane (10 cm3) to precipitate complex 11 as a yellow-orange or orange solid, respectively.

Complex 11: yield 75%, m.p. 187 °C (decomp.); [Au(pap)(acac-O,O')]+ClO4- (Found: C, 41.5; H, 3.6; Au, 27.4; N, 3.6%).

[Au(pap)(dmso)]2+[ClO4]- 9.—One drop of dmso and solid AgClO4 (40 mg, 0.22 mmol) were added to a suspension of [Au(pap)]+ (30 mg, 0.1 mmol) in dichloromethane (30 cm3); after (117 mg, 0.55 mmol) was added to precipitate complex 9 as a yellow solid. Yield 75%, m.p. 171 °C; [Au(III)] = 182 Ω cm2 mol-1 (in acetone); [Au(III)] (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. C3H13AuClIN2O4 requires C, 26.2; H, 2.9; Au, 26.8; N, 3.8%).

[Au(pap)(Clac-c)]10.—Solid AgClO4 (23 mg, 0.1 mmol) was added to a solution of [Au(pap)]+ (50 mg, 0.1 mmol) in dichloromethane (40 cm3); the suspension was stirred for 4 h and then filtered through Celite. To the resulting solution solid NaI (20 mg, 0.22 mmol) was added and stirred for 2 h. The excess of NaI was removed by filtration over anhydrous MgSO4, the resulting solution concentrated (1 cm3) and addition of ethyl ether (1:1) precipitated complex 10 as a brick-red solid. Yield 75%, m.p. 154 °C; [Au(III)] 300 cm-1 (Found: C, 25.9; H, 2.0; Au, 36.1; N, 5.6. C3H13AuClIN2O4 requires C, 26.7; H, 1.7; Au, 36.4; N, 5.2%).
Table 3 Atomic coordinates (× 10^4) for [Au(mpap)Cl₂]

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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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References

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