Synthesis of the First Acetonylgold(III) Complexes by C–H Activation of Acetone with 2-Phenylazophenylgold(III) Complexes

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The complex $[Au(C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}Cl]$ (**1**) can be obtained by treating $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$ with Tl(acac) (Hacac = acetylacetone) in acetone at room temperature. At 0 °C or using dichloromethane as solvent, the intermediate $[Au(C_6H_4N{=}NPh\text{-}2)(C\text{-acac})Cl]$ (**2**){*C*-acac $=CH[C(O)Me]_2$} can be isolated. Complex (**1**) can also be obtained by treating $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$, in acetone, (*i*) with KCN (1 : 1), (*ii*) with $[Hg(C_6F_5)_2]$ and Cl^- (2 : 1 : 2), (*iii*) with $[Pd\{C_6H_4N(O)O\text{-}2\}_2]$ (1 : 1), (*iv*) with $AgClO_4$ (1 : 1), (*v*) with $[Hg(C_6H_4N{=}NPh\text{-}2)_2]$ (1 : 1), or (*vi*) with 1,10-phenanthroline (phen). The probable intermediate in this last reaction $[Au(C_6H_4N{=}NPh\text{-}2)(phen)Cl_2]$ (**3**) can be isolated by use of dichloromethane as solvent. Complex (**3**) is converted into complex (**1**) when dissolved in acetone. Complex (**1**) is also obtained from an acetone solution of $[Au(C_6H_4N{=}NPh\text{-}2)(bipy)Cl]ClO_4$ (bipy = 2,2′-bipyridyl). This complex reacts in acetone with $AgClO_4$ (1 : 1) to give $[Au(C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}(bipy)]ClO_4$ (**4**). A similar reaction between *trans*-$[Au(C_6H_4N{=}NPh\text{-}2)(PPh_3)_2Cl]ClO_4$ and $AgClO_4$ (1 : 1) in acetone gives the dinuclear complex $[Au_2(C_6H_4N{=}NPh\text{-}2)_2(PPh_3)_4][ClO_4]_4$ (**5**). A parallel study with $[Au(C_6H_4CH_2NMe_2\text{-}2)Cl_2]$ shows a quite different behaviour. It does not react in acetone with $[Hg(C_6F_5)_2]$ and Cl^- (2 : 1 : 2), $[Pd\{C_6H_4N(O)O\text{-}2\}_2]$ (1 : 1), phen (1 : 1), phen and $NaClO_4$ (1 : 1 : 1), or bipy (1 : 1). However, it does react in acetone with Tl(acac) (1 : 1) giving $[Au(C_6H_4CH_2NMe_2\text{-}2)(C\text{-acac})Cl]$ (**6**) or with $AgClO_4$ (1 : 1) giving a solution from which, by addition of phen, the complex $[Au(C_6H_4CH_2NMe_2\text{-}2)(phen)Cl]ClO_4$ (**7**) can be isolated. Complex (**7**) reacts, in acetone, with $AgClO_4$ (1 : 1) to give $[Au(C_6H_4CH_2NMe_2\text{-}2)(phen)][ClO_4]_2$. A plausible reaction pathway for the C–H activation process is given.

There are several methods for preparing metallated ketones, $M'[CR_2C(O)R']$. Metallation of the ketone [equation (1)] is

$$HCR_2C(O)R' + M'X \longrightarrow HX + M'[CR_2C(O)R'] \quad (1)$$

the most direct. In this reaction M′X is usually a basic compound (*e.g.* $X = O^{2-}$ or OH^-)[1] or a metal hydride (*e.g.* KH)[2] but can also be an oxo- {*e.g.* $[O(AuPPh_3)_3]^+$}[3] or hydroxo-complex[4] {*e.g.* $[PtR(OH)L_2]$ (R = Ph or Me, L = PR_3)}. A new type of metallation process for acetone has recently been reported,[5,6] in which the intramolecular co-operation between a ligand and the metal centre results in the deprotonation of acetone. This paper deals with this type of process.

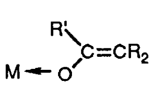
Other preparative methods utilize oxidative-addition reactions of an α-halogenocarbonyl compound,[7,8] or of an epoxide.[9] Attack on a co-ordinated ligand can also give a metallated ketone[10] [*e.g.* equations (2) and (3), cp = η⁵-C_5H_5]. Finally, the ketonyl (or enolate) anion can be transmetallated[2,3] [*e.g.* equation (4)].

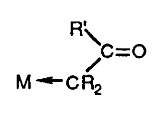
$$RC(O)Cl + [Ti(cp)_2({=}CH_2)] \longrightarrow [Ti(cp)_2\{CH_2C(O)R\}Cl] \quad (2)$$

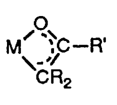
$$[ZrMe_2R_2] + CO \longrightarrow [Zr\{OC(Me){=}CMe_2\}MeR_2] \quad (3)$$

$$[CH_3C(O)CH_2Au(PPh_3)] + HgCl_2 \longrightarrow [CH_3C(O)CH_2HgCl] \quad (4)$$

Three types of co-ordination bonding are found in these complexes: *O* bonding (enolato complexes), *C* bonding (ketonyl complexes), and chelating bidentate.[2,7b,9] However,

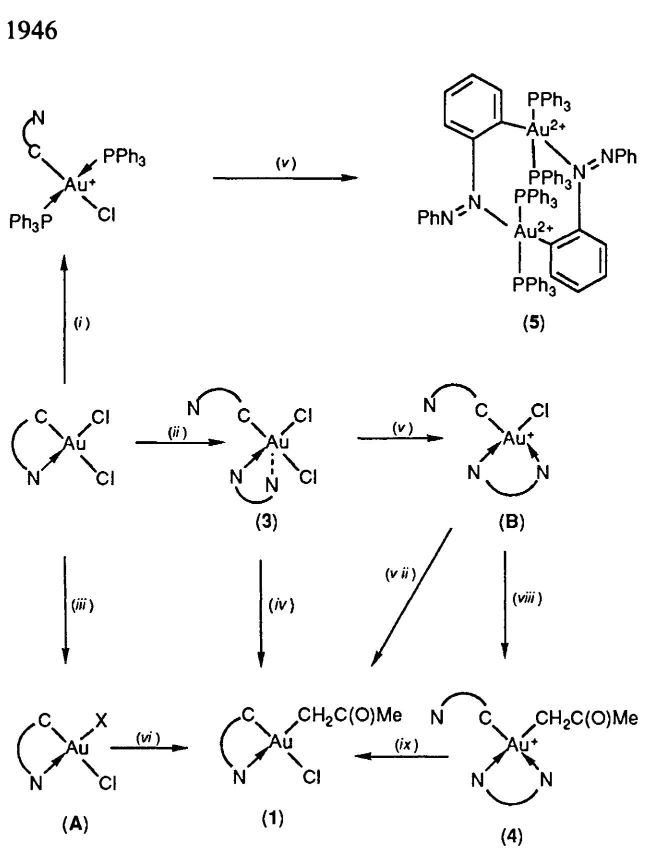






while complexes of the first two types have been isolated, the latter class have so far, to our knowledge, only been observed in solution. The only aurated ketones previously reported[3] are $[Au\{CH_2C(O)R\}(PPh_3)]$ [R = H, Me, Et, Ph, or $C_5H_4Fe(C_5H_5)$].

The synthesis of organogold(III) complexes through C–H activation is limited to arenes which react with $(AuCl_3)_2$ (the so called 'auration' reaction) to give $[(AuRCl_2)_2]$ (R = aryl) complexes.[11] There is as yet no report of an alkyl C–H activation by a gold(III) complex. Even the auration of arenes is of limited synthetic use because it is inhibited by the presence of a co-ordinating substituent on the aromatic ring.[12,13] However, we have prepared several examples of orthometallated arylgold(III) complexes by transmetallation reactions using organomercury compounds.[14] It is through the development of the chemistry of the orthometallated 2-(phenylazo)phenylgold(III) complexes that we have, fortuitously, found that metallation of acetone occurs in several processes. Some of these results have been the subject of a preliminary communication.[6]



Scheme 1. Synthesis of complexes (1)—(7). (A) $\widehat{CN}$ = 2-$C_6H_4N{=}NPh$, X = *C*-acac (2), CN, $OClO_3$, C_6F_5, or $C_6H_4NO_2$-2; $\widehat{CN}$ = 2-$C_6H_4CH_2NMe_2$, X = *C*-acac (6), C_6F_5,[14k] or $C_6H_4NO_2$-2.[14l] (B) $\widehat{CN}$ = 2-$C_6H_4N{=}NPh$, $\widehat{NN}$ = phen[14b] or bipy;[14i] $\widehat{CN}$ = 2-$C_6H_4CH_2NMe_2$ co-ordinated as chelating ligand with nitrogen *trans* to chloro ligand, $\widehat{NN}$ = phen (7) (see text). Step (*i*) +2PPh_3, $-Cl^-$; (*ii*) +$\widehat{NN}$; (*iii*) +X^-, $-Cl^-$; (*iv*) +Me_2CO, −[Hphen]Cl; (*v*) $-Cl^-$; (*vi*) + Me_2CO, −HX; (*vii*) +Me_2CO, $-[Hbipy]^+$; (*viii*) +Me_2CO, $-Cl^-$, $-H^+$; (*ix*) +HCl, −[Hbipy]Cl

Results and Discussion

Scheme 1 shows all reactions giving the complex $[\overline{Au(C_6H_4N{=}N}\text{-}Ph\text{-}2)\{CH_2C(O)Me\}Cl]$ (1), most of which were designed to prepare other complexes. We had already reported the formation of this complex (which we believed to be an acetone adduct) as one of the components of the mixture obtained when $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$ reacts with KCN (1:2.5).[14j] After we found the same type of 'adduct' in other reactions we decided to look at this complex more closely.

Complex (1) was also obtained when we tried to prepare $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)(C\text{-acac})Cl]$ (2) {*C*-acac = $CH[C(O)\text{-}Me]_2$} by treating $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$ with Tl(acac) (1:1) in acetone (15 min, room temperature). Subsequently, we isolated the intermediate (2) by carrying out the same reaction in dichloromethane or in acetone at low temperature (0 °C). Complex (2) reacts with acetone at room temperature to give (1) (15 h, 90% yield).

Again, in developing our method of synthesis of mixed diarylgold(III) complexes,[14e] we tried to prepare $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)(R)Cl]$ (R = C_6F_5 or $C_6H_4NO_2$-2) in acetone [by treating $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$ with HgR_2 and Cl^- (2:1:2; 48 h) or with $[\overline{Pd\{C_6H_4N(O)O}\text{-}2\}_2]$ (1:1; 40 h) at room temperature. However the only gold complex isolated was (1). We since have obtained the desired compounds, using chloroform as solvent, and proved that they decompose in acetone giving complex (1).[15]

The complexes $[Au(C_6H_4N{=}NPh\text{-}2)(L\text{-}L)Cl]ClO_4$ [L–L = 2,2′-bipyridyl (bipy)[14i] or 1,10-phenanthroline (phen)[14b]] were prepared by treating in acetone a mixture of $NaClO_4$, L–L, and $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$ (1:1:1).[14b] However, on standing, the final reaction product is complex (1) because when an acetone solution of $[Au(C_6H_4N{=}NPh\text{-}2)(bipy)Cl]ClO_4$ is left for 1 d at room temperature complex (1) and $[Hbipy]ClO_4$ were isolated. In addition, in an attempt to prepare the probable intermediate in the reaction with phen, $[Au(C_6H_4N{=}NPh\text{-}2)(phen)Cl_2]$ (3), complex (1) was obtained. Complex (3) however can be isolated using dichloromethane as solvent and, as expected, a solution of (3) in acetone yields complex (1).

The reaction of $[Au(C_6H_4N{=}NPh\text{-}2)(bipy)Cl]ClO_4$ with $AgClO_4$ (1:1) in acetone {hoped to yield $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)(bipy)][ClO_4]_2$} was reported[14i] instead to give an acetone adduct. A reinvestigation of this reaction revealed $[Au(C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}(bipy)]ClO_4$ (4) was the product (room temperature, 2 h). The desired dicationic complex was later prepared *via* a different procedure.[14d]

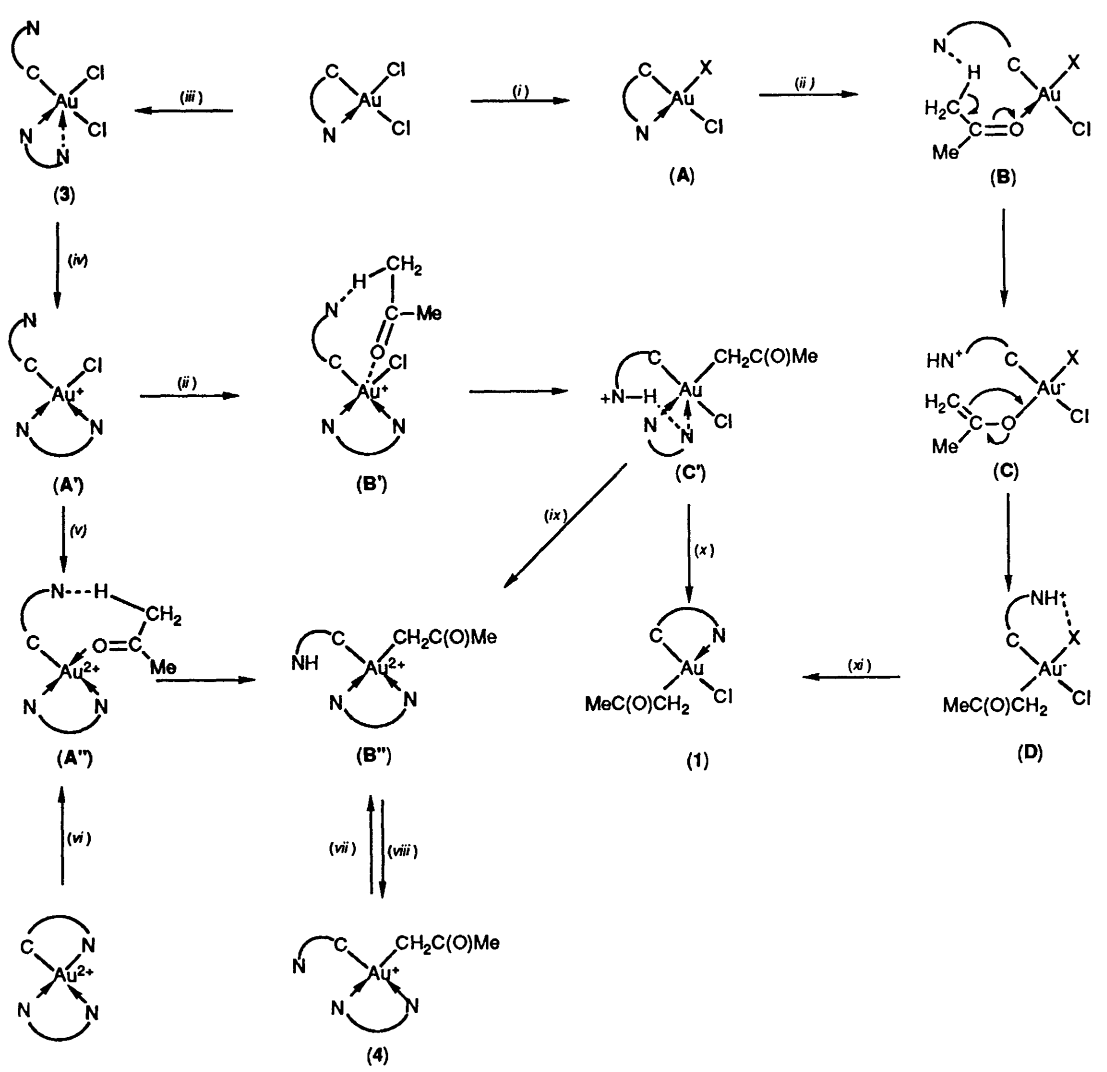
A similar reaction between *trans*-$[Au(C_6H_4N{=}NPh\text{-}2)(PPh_3)_2Cl]ClO_4$ and $AgClO_4$ (1:1) gave $[\overline{Au_2(C_6H_4N}{=}NPh\text{-}2)_2(PPh_3)_4][ClO_4]_4$ (5) instead of any acetonyl complex.

The synthesis of complexes (1) and (4), which are the first acetonylgold(III) complexes reported, represent the first example of alkyl C–H activation by a gold(III) complex.

As far as we know, the sole previous report of similar behaviour has only recently appeared.[5] In this report, a series of rhodium(III) complexes [Rh(L)Cl] (L = porphyrin) react with acetone (either at 50 °C or room temperature) to give the corresponding acetonyl complexes $[Rh\{CH_2C(O)Me\}L]$. The presence of a phenolic hydroxyl or a quinolyl nitrogen suitably located out of the plane of the porphyrinic molecule seems to be essential for the metallation to occur, thus suggesting that the oxygen or nitrogen atoms act as a base to promote enolization of acetone in co-operation with the central Rh^{III} atom.

Whatever the mechanistic details of the reactions leading to (1), it is reasonable to postulate the intermediates shown in Scheme 2. Two different pathways have been proposed depending on the nature, anionic or neutral, of the ligands that react with $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$. When the ligands are anionic the first step, which gives the intermediate (A), is essential because $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$ does not react with acetone alone (93 h at room temperature or refluxing for 3 h). Substitution of the chloro ligand *trans* to the nitrogen atom occurs in the case of X = *C*-acac, C_6F_5, or $C_6H_4NO_2$, and that these intermediates behave as precursors for complex (1) has been proved. When X = ClO_4^- it is more reasonable to assume that acetone replaces the ClO_4^- ion so giving a cationic intermediate. We postulate that the anionic CN, *C*-acac, C_6F_5, or $C_6H_4NO_2$ ligands activate the N→Au bond more so than the chloro ligand enabling co-ordination of acetone to give intermediate (B).

The importance of this N→Au bond cleavage in the C–H activation process can be illustrated as follows: $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$ always reacts with neutral ligands giving first the addition product of such cleavage {*e.g.* with PPh_3 to give $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)]$} while $[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)Cl_2]$, which always yields chelating gold(III) derivatives {*e.g.* with PPh_3 to give $[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)Cl(PPh_3)]Cl$[14c,h]}, fails to give any acetonyl complex when treated under the same conditions by which $[\overline{Au(C_6H_4N{=}N}Ph\text{-}2)Cl_2]$ gives (1) or (4). Thus, no reactions take place when $[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)Cl_2]$ is treated with Cl^- and $[Hg(C_6F_5)_2]$ (2:1:2), with



Scheme 2. Proposed reaction pathways for the synthesis of complexes (**1**) and (**4**). (*i*) $+X^-$, $-Cl^-$; (*ii*) $+Me_2CO$; (*iii*) +phen in CH_2Cl_2; (*iv*) $-Cl^-$; (*v*) $+Me_2CO$, $-Cl^-$; (*vi*) slow, $+Me_2CO$; (*vii*) $+H^+$; (*viii*) $-H^+$; (*ix*) $+Cl^-$; (*x*) $-\overset{\frown}{N\,N}H^+$; (*xi*) $-HX$

$[Pd\{C_6H_4N(O)O\text{-}2\}_2]$ (1:1), phen (1:1), phen and $NaClO_4$ (1:1:1), or with bipy (1:1). Sometimes the expected substitution products are formed. Thus, for example, $[Au(C_6H_4CH_2NMe_2\text{-}2)Cl_2]$ reacts in acetone with Tl(acac) (1:1) to give $[Au(C_6H_4CH_2NMe_2\text{-}2)(C\text{-acac})Cl]$ (**6**) or with $AgClO_4$ (1:1) to give a solution from which, by addition of phen, the complex $[Au(C_6H_4CH_2NMe_2\text{-}2)(phen)Cl]ClO_4$ (**7**) can be isolated. In addition, complex (**7**) reacts in acetone with $AgClO_4$ (1:1) to give $[Au(C_6H_4CH_2NMe_2\text{-}2)(phen)][ClO_4]_2$.[14h] Finally, complexes of type $[Au(C_6H_4CH_2NMe_2\text{-}2)(X)Cl]$ ($X = C_6F_5$ [14k] or $C_6H_4NO_2\text{-}2$ [14l]) have been obtained but they are stable in acetone solution.

The step (**B**) ⟶ (**C**) (Scheme 2) is similar to that proposed to rationalize the activation of acetone by the porphyrin complexes [Rh(L)Cl] [5] and also enolization processes catalysed by metalloenzymes such as aldolases.[16] The process is completed when the azonium cation (**D**) transfers a proton to the ligand X (to give HX) and chelation is re-established. The formation of HX is especially surprising for $X = ClO_4$ because it means that perchloric acid is displaced by the weak acid acetone.

It is reasonable to assume that the reaction between $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2]$ and phen in acetone gives first the adduct (**3**) which we have isolated using dichloromethane as solvent. Its structure could reasonably be similar to those of the complexes $[Au(C_4Ph_4)(phen)Cl]$ [17a] and $[Au(C_6H_4CH_2NMe_2\text{-}2)(PPh_3)(phen)][BF_4]_2$,[14g] whose crystal structures show a distorted square-pyramidal co-ordination around the gold atom with the common feature of having both one of the nitrogen atoms of the phen ligand in a distant axial position. The measurable conductivity of complex (**3**) in acetone, 17 Ω^{-1} cm^2 mol^{-1}, similar to the value of 13 Ω^{-1} cm^2 mol^{-1} measured for $[Au(C_4Ph_4)(phen)Cl]$,[17a] can be interpreted as a consequence of the formation of species (**A′**) containing a symmetrically bonded phen ligand. This intermediate might axially co-ordinate an acetone molecule to give species (**B′**) which should probably rearrange to intermediate (**C′**) and thence to complex (**1**) and [Hphen]Cl, similarly to the conversion of (**B**) ⟶ (**1**). The synthesis of (**1**) and $[Hbipy]ClO_4$ from an acetone solution of $[Au(C_6H_4N{=}NPh\text{-}2)(bipy)Cl]ClO_4$,[14i] a complex of type (**A′**), supports our proposal.

The synthesis of complex (**4**) by treating $[Au(C_6H_4N{=}NPh\text{-}2)(bipy)Cl]ClO_4$ with $AgClO_4$ must follow a different pathway. We postulate the initial formation of the solvento complex (**A″**) (Scheme 2), which undergoes rearrangement to the intermediate (**B″**) and thence to complex (**4**). Assuming our proposed reaction pathway, the synthesis of complex (**4**) from

$[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)(bipy)][ClO_4]_2}$ in acetone establishes that bipy can sufficiently labilize the N→Au bond to give, through a slow process, intermediate (**A''**) and finally complex (**4**).

The related reaction between *trans*-$\mathrm{[Au(C_6H_5N{=}NPh\text{-}2)(PPh_3)_2Cl]ClO_4}$ and $\mathrm{AgClO_4}$ fails to give any acetonyl complex, probably because the entering acetone molecule is unable to co-ordinate in a *cis* arrangement as in intermediate (**A''**). Thus, the metal–acetone ligand co-operative effect is precluded, or at least, is slower than the dimerization process that gives complex (**5**).

Noting that intermediate (**C'**) and complex (**4**) differ only by an HCl molecule we have tested the possibility of connecting both reaction pathways by treating complex (**4**) with HCl in dichloromethane. Two routes for the reaction can be proposed [equations (5) and (6)]. Although equation (6) seems more likely from an acid–base point of view (*i.e.* acetone is a weaker acid than $\mathrm{[Hbipy]ClO_4}$), according to our proposed reaction scheme, equation (5) should occur because it assumes that the strong electrophile (**B''**) would favour co-ordination of the nucleophile $\mathrm{Cl^-}$ over rearrangement to the intermediate (**A''**) *via* a multi-step process. Experimentally conversion of complex (**4**) into (**1**) is observed so confirming our proposal.

$$(\mathbf{4}) \longrightarrow (\mathbf{B''}) \longrightarrow (\mathbf{C'}) \longrightarrow (\mathbf{1}) + [\mathrm{Hbipy}]\mathrm{Cl} \tag{5}$$

$$(\mathbf{4}) \longrightarrow (\mathbf{B''}) \longrightarrow (\mathbf{A''}) \longrightarrow \mathrm{[Au(C_6H_4N{=}NPh\text{-}2)(bipy)Cl]ClO_4 + Me_2CO} \tag{6}$$

The possibility of the C–H activation of acetone being an intermolecular process between the monodentate 2-phenylazophenyl ligand and acetone (or, more probably, with its enol form) has been tested by stirring acetone solutions of *trans*-$\mathrm{[Au(C_6H_4N{=}NPh\text{-}2)(PPh_3)_2Cl]ClO_4}$ (4 d at room temperature or 8 h at reflux temperature) or *cis*-$\mathrm{[Au(C_6H_4N{=}NPh\text{-}2)(PPh_3)Cl_2]}$ (1 week at room temperature). The recovery of the starting complexes intact supports an intramolecular process in our systems.

The geometries proposed for complexes (**1**)—(**3**), (**6**), and (**7**) are supported by the assignment of the ν(AuCl) bands in their i.r. spectra.[14] Thus, complexes (**1**), (**2**), and (**6**) show a medium to strong band at 305—308 $\mathrm{cm^{-1}}$ assignable to ν(AuCl) *trans* to the phenyl group while (**3**) shows two bands at 285 and 350 $\mathrm{cm^{-1}}$ assignable to ν(AuCl) *trans* to the phenyl group in a quasi five-co-ordinate environment[17a] and to ν(AuCl) *trans* to a nitrogen-donor ligand, respectively. For complex (**7**) the ν(AuCl) band appears at 350 $\mathrm{cm^{-1}}$ suggesting that the chloro-ligand is *trans* to the $\mathrm{NMe_2}$ group.

For complex (**5**) the experimentally derived equation relating the equivalent conductivity ($\Lambda_{\mathrm{eq.}}$) in acetone with the equivalent concentration (c) is $\Lambda_{\mathrm{eq.}} = -1\,451\,c^{\frac{1}{2}} + 165$, which is consistent with a dinuclear 4:1 electrolyte.[17b] We assume that an eight-membered ring species, as shown in Scheme 1, is a reasonable proposal for its structure. The observation of a singlet in its ^{31}P n.m.r. spectrum suggests a *trans* geometry because an alternative *cis* geometry with rapid exchange of $\mathrm{PPh_3}$ ligands seems unlikely. Unfortunately, several attempts to grow single crystals of this compound led instead to decomposition products such as $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)_2]ClO_4}$ and $\mathrm{[Au(PPh_3)_2]ClO_4}$.

The band corresponding to the ν(CO) mode appears as a strong absorption at 1 675 $\mathrm{cm^{-1}}$ for the acetonyl complexes (**1**) and (**4**) and, as a doublet of bands, at *ca.* 1 690 and 1 675 $\mathrm{cm^{-1}}$ for the acetylacetonate complexes (**2**) and (**6**), which suggests co-ordination through $\mathrm{CH_2}$ and CH groups, respectively. However, this sole criterion is not enough to be sure of the co-ordination mode of the acetonyl ligand. The enolato complexes $\mathrm{[Zr\{OC(Me){=}CMe_2\}\{N(SiMe_3)_2\}_2Me]}$,[10b] $\mathrm{[Si\{OC(Bu^t){=}CH(Bu^t)\}\ Me_3]}$, and $\mathrm{\{Pd[Pd\{OC(Bu^t){=}CH(Bu^t)\}(NCPh)(\mu\text{-}Cl)_2]_2Pd\}}$[18] show bands at 1 668, 1 647, and 1 650 $\mathrm{cm^{-1}}$ respectively, assigned to a ν(C=C) mode.

The ^{1}H n.m.r. spectra of ketonyl complexes of the type $\mathrm{M\{CH_2C(O)R\}}$ show the methylene resonance in the range δ 1.3—2.6 and, as expected, those of the related enolato complexes, $\mathrm{M\{OC(R){=}CH_2\}}$, appear as two distinct resonances at a lower field (δ 4.0—4.6).[2,3,8,10c,19,20] However, a high oxidation state, as in $\mathrm{[Pt^{IV}\{CH_2C(O)Me\}(NH_3)Cl_4]^-}$, can give a methylene resonance at a field as low as δ 4.72[21] and the especial nature of a ligand such as in a porphyrin complex $\mathrm{[Rh\{CH_2C(O)Me\}L]}$ can give a methylene resonance at a field as high as δ −4.7.[5] Complexes (**1**) and (**4**) show the methylene resonances as singlets at δ 3.45 and 3.26, respectively. The methine resonance of the acetylacetonato complexes, which is related to the methylene resonances of the acetonyl complexes, also appears at a relatively low-field, occurring at 4.85 and 4.42 for complexes (**2**) and (**6**), respectively.

^{13}C N.m.r. spectra of complexes (**1**) and (**4**) show δ(CO) resonances at 207.6 and 208.3 p.p.m., respectively, which being very similar to that of acetone (205.2 p.p.m.) confirm the C–Au bonding for these complexes. The carbonyl carbon in the enolato complexes $\mathrm{[Zr(\eta^5\text{-}C_5Me_5)H(OCH{=}CH_2)]}$[10b] and $\mathrm{[Rh\{OC(R^1){=}CHR^2\}(CO)(PPh_3)]}$[2] resonate at 154.2 and 78—80 p.p.m., respectively. The ^{13}C n.m.r. spectrum of $\mathrm{[Sn\{CHMeC(O)Ph\}Et_3]}$, which exists in solution in equilibrium with $\mathrm{[Sn\{OC(Ph){=}CHMe\}Et_3]}$, shows δ(CO) resonances at 199.90 (ketonyl isomer) and 100.59 p.p.m. (enolato isomer).[22] Therefore, the observed value of δ(CO) is the best criterion for assigning the co-ordination mode of this type of ligand.

Because both pyridine rings of the bipy ligand in (**4**) are equivalent (according to ^{13}C n.m.r. spectroscopy) it is reasonable to assume that this ligand is rotating. Probably, such rotation occurs *via* five-co-ordinate species in which the bipy ligand is asymmetrically bonded, as has been assumed above, and observed in some related phenanthroline complexes.[14g,17a] Complex (**7**) is of low-solubility in organic solvents and its solutions too unstable to allow the assignment of the n.m.r. resonances.

The study of the reactivity of different ketones with $\mathrm{C_6H_4N{=}NPh\text{-}2}$ gold(III) and palladium(II) complexes is in progress.

Experimental

Recording of i.r. spectra, the C, H, and N analyses, conductance measurements, and melting point determinations were performed as described elsewhere.[14] N.m.r. spectra (in $\mathrm{CDCl_3}$) were recorded on Bruker 200AC and Varian FT80 spectrometers. Reactions were carried out with magnetic stirring without special precautions to exclude light or moisture unless otherwise stated. The preparations described below are those which led to the best yields. All complexes of $\mathrm{C_6H_4N{=}NPh\text{-}2}$ are orange in colour while all complexes of $\mathrm{C_6H_4CH_2NMe_2\text{-}2}$ are colourless. Table 1 gives yields, elemental analyses, melting points, molar conductivities, and some i.r. data. Table 2 includes selected n.m.r. spectroscopic data.

Preparations.—$[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)\{CH_2C(O)Me\}Cl]}$ (**1**). To an acetone solution (30 $\mathrm{cm^3}$) of $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)Cl_2]}$[14b] (40 mg, 0.09 mmol) solid $\mathrm{AgClO_4}$ (19 mg, 0.09 mmol) was added. After stirring in the dark for 1 h, the suspension was concentrated to dryness and the residue extracted with dichloromethane (3 × 5 $\mathrm{cm^3}$) and filtered through Celite. The resulting solution was concentrated to *ca.* 2 $\mathrm{cm^3}$ and n-hexane (15 $\mathrm{cm^3}$) added to give complex (**1**).

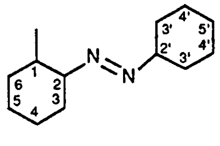
$[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)(}C\mathrm{\text{-}acac)Cl]}$ (**2**). To a dichloromethane solution (20 $\mathrm{cm^3}$) of $[\overline{\mathrm{Au(C_6H_4N{=}N}}\mathrm{Ph\text{-}2)Cl_2]}$ (81 mg, 0.18

Table 1. Analytical, spectroscopic, and other data for complexes (**1**)—(**7**)

	Compound	ν(Au–Cl)/cm^{-1}	ν(CO)/cm^{-1}	M.p. (°C)	Λ_M[a]	Analysis (%)[b] C	H	N	Au	Yield (%)
(**1**)	$[\overline{Au(C_6H_4N=N}Ph\text{-}2)\{CH_2C(O)Me\}Cl]$	305	1 675	163	1	38.4 (38.3)	3.1 (3.0)	5.5 (5.9)	41.3 (41.8)	90
(**2**)	$[\overline{Au(C_6H_4N=N}Ph\text{-}2)(C\text{-acac})Cl]$	308	1 690 1 678	137[c]	2	40.1 (39.8)	3.3 (3.1)	5.8 (5.5)	38.1 (38.4)	75
(**3**)	$[Au(C_6H_4N=NPh\text{-}2)(phen)Cl_2]$	350 285		106	17	49.1 (49.8)	2.8 (2.7)	8.1 (8.9)	31.7 (31.7)	81
(**4**)	$[Au(C_6H_4N=NPh\text{-}2)\{CH_2C(O)Me\}(bipy)]ClO_4$		1 675	167[c]	131	43.8 (43.5)	3.6 (3.2)	7.5 (8.1)	28.2 (28.5)	72
(**5**)	$[\overline{Au_2(C_6H_4N}=NPh\text{-}2)_2(PPh_3)_4][ClO_4]_4$			185[c]	330	51.6 (52.3)	3.6 (3.6)	1.7 (2.5)	19.1 (18.9)	83
(**6**)	$[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)(C\text{-acac})Cl]$	305	1 683 1 673	146[c]	0	36.6 (36.1)	4.2 (4.1)	2.8 (3.0)	41.9 (42.3)	70
(**7**)	$[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)(phen)Cl]ClO_4$	350		180[c]	137	45.4 (46.1)	3.4 (3.7)	7.5 (7.7)	35.3 (36.0)	60

[a] In Ω^{-1} cm^2 mol^{-1} (5×10^{-4} mol dm^{-3} acetone solvent). [b] Calculated values are given in parentheses. [c] With decomposition.

Table 2. Selected n.m.r. spectroscopic data (δ/p.p.m.) in $CDCl_3$ at 25 °C

Compound	^1H[a]	^{13}C[b]
(**1**)	2.38 (s, 3 H, CH_3), 3.45 (s, 2 H, CH_2), 7.44—7.94(m,9H, Ph)	31.16 (CH_3), 38.50 (CH_2), 124.69, 128.75 ($C^{3'}$, $C^{4'}$), 129.14, 131.97, 132.44, 132.70, 135.84 (C^3—C^6, $C^{5'}$), 147.76, 149.92 (C^2, $C^{2'}$), 162.24 (C^1), 207.61 (CO)
(**2**)	2.37 (s, 6 H, CH_3), 4.85 (s, 1 H, CH), 7.44—7.82(m,9H, Ph)	
(**4**)	2.13 (s, 3 H, CH_3), 3.26 (s, 2 H, CH_2), 7.52–7.77 (m, 9 H, Ph), 8.16—8.73 (m, 8 H, bipy)	30.47 (CH_3), 32.92 (CH_2), 122.51, 129.46 ($C^{3'}$, $C^{4'}$), 125.77, 127.52, 128.54, 128.90, 131.97, 133.26, 133.74, 134.51, 143.32, 148.37 (C^3—C^6, $C^{5'}$, bipy), 151.40, 152.18 (C^2, $C^{2'}$), 154.55 (C^1), 208.29 (CO)
(**6**)	2.38 [s, 6 H, $CH_3C(O)$], 3.00 (s, 6 H, CH_3N), 4.16 (s, 2 H, CH_2), 4.42 (s, 1 H, CH), 7.16—7.53(m,4H, Ph)	

[a] 80 MHz. [b] 50.32 MHz, $\delta = 0$ for $SiMe_4$ in both ^1H and ^{13}C spectra.

mmol) freshly prepared Tl(acac) (54.5 mg, 0.18 mmol) was added. After 10 min, the resulting suspension was filtered through anhydrous $MgSO_4$. The resulting solution was concentrated to *ca.* 1 cm^3 and n-hexane added (20 cm^3) to give complex (**2**).

$[Au(C_6H_4N=NPh\text{-}2)(phen)Cl_2]$ (**3**). To a dichloromethane suspension (10 cm^3) of $[\overline{Au(C_6H_4N=N}Ph\text{-}2)Cl_2]$ (22 mg, 0.11 mmol) solid phen•H_2O (22 mg, 0.11 mmol) was added. After 30 min, the solution was concentrated (1 cm^3) and diethyl ether added (10 cm^3) to give a solid which was recrystallized from dichloromethane–diethyl ether (1:5) to give complex (**3**).

$[Au(C_6H_4N=NPh\text{-}2)\{CH_2C(O)Me\}(bipy)]ClO_4$ (**4**). To an acetone solution (15 cm^3) of $[Au(C_6H_4N=NPh\text{-}2)(bipy)Cl]ClO_4$ (134 mg, 0.2 mmol) solid $AgClO_4$ (41 mg, 0.2 mmol) was added. After 2 h the solvent was removed, the residue extracted with dichloromethane (3×5 cm^3) and the suspension filtered off. The resulting solution was concentrated (1 cm^3) and diethyl ether added (10 cm^3) to give a solid which was recrystallized from dichloromethane–diethyl ether (1:5) to give complex (**4**).

$[\overline{Au_2(C_6H_4N}=NPh\text{-}2)_2(PPh_3)_4][ClO_4]_4$ (**5**). To an acetone solution (15 cm^3) of $[Au(C_6H_4N=NPh\text{-}2)(PPh_3)_2Cl]ClO_4$ (23 mg, 0.02 mmol) solid $AgClO_4$ (4.6 mg, 0.02 mmol) was added. After 1 h the solvent was removed and the residue extracted with dichloromethane (3×5 cm^3) and the suspension filtered through Celite. The solution was concentrated to *ca.* 1 cm^3 and diethyl ether added (10 cm^3) to give complex (**5**).

$[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)(C\text{-acac})Cl]$ (**6**). To an acetone solution (10 cm^3) of $[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)Cl_2]$ (100 mg, 0.25 mmol) solid Tl(acac) (76 mg, 0.25 mmol) was added. After 10 min the solvent was evaporated, the residue extracted with dichloromethane (3×5 cm^3) and the suspension filtered off. The resulting solution was concentrated to *ca.* 1 cm^3 and diethyl ether added (10 cm^3) to give complex (**6**).

$[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)(phen)Cl]ClO_4$ (**7**). To an acetone solution (10 cm^3) of $[\overline{Au(C_6H_4CH_2N}Me_2\text{-}2)Cl_2]$ (120 mg, 0.30 mmol) solid $AgClO_4$ (68 mg, 0.33 mmol) was added. After 10 min the solvent was evaporated, the residue extracted with dichloromethane (3×10 cm^3) and the suspension filtered. The resulting solution was concentrated (2 cm^3) and diethyl ether added (20 cm^3) to give an extremely air-sensitive solid which was dissolved in acetone, and phen•H_2O (60 mg, 0.30 mmol) added to give a solution which was concentrated (1 cm^3). After addition of diethyl ether (10 cm^3) a solid was formed which was recrystallized from dichloromethane–diethyl ether (1:5) to give complex (**7**).

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