Gold-acetonyl complexes: from side-products to valuable synthons

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Abstract: A novel synthetic strategy was devised leading to the formation of complexes such as [Au(IPr)(CH_2COCH_3)]. The approach capitalizes on the formation of a decomposition product observed in the course of the synthesis of [Au(IPr)(Cl)]. A library of gold acetonyl complexes bearing the most common N-heterocyclic carbene (NHC) ligands has been synthesized. These acetonyl complexes are good synths for the preparation of numerous organogold complexes. Moreover, they have proven to be precatalysts in common gold(I)-catalyzed reactions. Among these complexes, [Au(NHC)(Cl)] compounds have been recognized as valuable precursors for several organogold complexes. An improved protocol for their synthesis has recently been developed. This straightforward synthetic procedure allows for the preparation of [Au(NHC)(Cl)] complexes by reacting the corresponding imidazol(1-yl)ium salt (NHC-HCl) with [Au(SMe_2)(Cl)] in the presence of a weak base, such as K_2CO_3, in acetone at 60 °C (eq. a, Scheme 1). The reaction time was found to depend on the nature of the NHC-HCl salt. While [Au(IPr)(Cl)] (1a) and [Au(IMes)(Cl)] (1b) were obtained in 1 h and 3 h respectively, the synthesis of [Au(SIPr)(Cl)] (1c) or [Au(SiMes)(Cl)] (1d) required 24 h, under the same reaction conditions.

In an effort to reduce the reaction time for the synthesis of the gold(I)-chloride complexes bearing a saturated NHC ligand (1c), a large excess of K_2CO_3 (6 equiv.) was added to the reaction mixture. To our surprise, a mixture of complexes was obtained. The expected [Au(SiPr)(Cl)] (1c) and a new Au-SiPr derivative were obtained in a 1.3:1 ratio. H and ^13C NMR analysis of the mixture allowed the characterization of the desired Au-Ci complex and of a new species identified as the acetonyl complex [Au(SiPr)(CH_2COCH_3)] (2c) (eq. b, Scheme 1).

Introduction

The interest in gold chemistry has grown exponentially in the last decades. Gold species have been found to be highly active catalysts for both homogeneous and heterogeneous transformations. Moreover, organogold complexes present luminescent and biological properties, which make them attractive for the synthesis of new materials and for biomedical applications.

Initially, the use of simple gold salts as catalysts, such as AuCl, AuCl_3 or NaAuCl_4, was ubiquitous in gold catalysis. More recently, particular attention has been focused on the development of well-defined Au(I) and Au(III) complexes bearing ancillary ligands in order to examine whether or not enhanced catalytic activity could be achieved.

N-heterocyclic carbene (NHC) species have appeared as excellent ligands for the synthesis of a wide range of organometallic complexes. Their strong σ-donating ability and steric hindrance allow for strong metal-ligand bonds and prevent complex decomposition. The use of NHC ligands in gold chemistry has allowed for the synthesis of a plethora of organogold complexes. Indeed, highly unstable species have been isolated due to the unique properties of such ligands, e.g. the first Au(I)-tert-butoxide, Au(I)-fluoride and Au(I)-hydride species reported by the group of Sadighi, as well as the Au(I)-hydroxide and Au(I)-alky/peroxo complexes synthesized by Nolan and co-workers.

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These new species, bearing an acetonyl fragment, are members of the family of organogold-enolates. The term "enolate" usually refers to the tautomeric structures of a ketone; this structure reacts with a metal unit forming enol-M bonds (I), \( \eta^3 \)-oxoallyl-M (II) and 2-oxoalkyl-M complexes (III) (Figure 1).\(^{17}\)

**Figure 1.** Different types of Metal-enolate bonding.

Type III C-enolates or ketonyl complexes,\(^{18}\) are interesting organometallic compounds, proposed to be involved as short-lived intermediates in organic transformations.\(^{19}\) A range of synthetic methodologies have been used to form these M-ketonyl derivatives,\(^{18, 20}\) e.g., oxidative addition to organometallic compounds of \( \alpha \)-halogen carbonyl compounds\(^{21}\) or epoxides,\(^{22}\) transmetallation reactions promoted by Hg salts\(^{18, 23}\) or reactions of Main-group enolates with electrophilic metal centers.\(^{19a, 24}\) Other methodologies involve reactions of carbonyl compounds with metal-hydroxide\(^{25}\) or metal-chloride complexes in the presence of bases such as Ag\(_2\)O, KOH and NaOH.\(^{20c, 26}\)

Following these procedures, various M-ketonyl species have been isolated using late-transition metals, such as Rh, Ni, Pt, Pd and Au.\(^{18, 20c, 20e, 20g, 27}\) With regard to the latter, in 1989 Vicente reported the synthesis of Au(III)-ketonyl complexes by C-H bond activation of acetone promoted by the ancillary bidentate ligand bound to the metal center.\(^{28}\) Cinellu reported a similar structure of Au(III)-acetonyl complex bearing a C-N-cyclometallated ligand in 1996.\(^{29}\) Similar Au(III)-ketonyl complexes, bearing a chelating ligand, 2-phenylpyridine (ppy), were reported by Fan in 2004.\(^{30}\) Furthermore, Its synthesized and fully characterized stable Au(I)(PPh\(_3\)) -ketonyl and -homoketonyl complexes by adding silylated vinyl ethers or epoxides to Au(I)(PPh\(_3\))-chloride, in the presence of cesium fluoride.\(^{31}\) Crystal structures of Au(I)-acetonyl phosphine complexes and analogues were reported by the groups of Kuzmina and Laguna (Figure 2).\(^{19d, 32}\)

**Figure 2.** Some examples of reported Au(I) and Au(III)-ketonyl complexes

To the best of our knowledge, no examples of Au-NHC ketonyl compounds have been reported to date. Herein, we report the serendipitous discovery of the first gold(I)-NHC acetonyle complexes and the study of their stoichiometric and catalytic reactivity.

**Results and Discussion**

**Characterization of [Au(IPr)(acetonyl)] (2a)**

As previously stated, 2a was obtained as a single species, when mixing IPr-HCl (a-HCl), [Au(SMe\(_2\))][Cl] and K\(_2\)CO\(_3\) (6 equiv.) in acetone at 60 °C for 48 h (Scheme 2). The new air- and moisture-stable derivative was isolated as a white solid in 80% yield. Complex 2a was fully characterized by NMR and IR spectroscopies, elemental analysis and X-ray diffraction studies. The \(^1\)H NMR spectrum in CDCl\(_3\) indicated the presence of a functionalized acetone moiety: a singlet at 2.06 ppm that was assigned to the -CH\(_2\) group, and a singlet at 1.54 ppm corresponding to the -CH\(_3\) moiety. The \(^{13}\)C\(_{\text{H}}\) NMR spectrum showed a signal at 212.13 ppm that was assigned to the carbonyl group. This signal is shifted downfield with respect to free acetone (207.07 ppm). The FTIR (ATR) spectrum of 2a showed a strong absorption band at 1643 cm\(^{-1}\), corresponding to the stretching frequency of the carbonyl group (\(\nu\text{CO}\)), in agreement with previously reported Au-acetonyl compounds.\(^{26}\)

Suitable crystals for X-ray diffraction analysis were grown by slow diffusion of pentane into a saturated solution of 2a in DCM.\(^{33}\) The crystallographic representation of 2a is presented in Figure 3. The structure of 2a displays the usual linear geometry for Au(I) complexes, with a \(\text{C}_{\text{acetone}}\)-Au-CH\(_2\) angle of 175.7(3)°.\(^{33a}\) The Au-C_{acetone} distance of 2.024(7) Å lies in the typical range for gold(I)-NHC species.\(^{7c, 31a}\) Other relevant distances are Au-CH\(_3\) of 2.091(9) Å, CH\(_2\)-CO, 1.456(12) Å, and C=O, 1.230(11) Å, which are in agreement with previously reported Au-acetonyl complexes.\(^{7c, 30-31}\)
observed when NEt₃ was used as base, suggesting that the precipitation of KCl is the driving force of the reaction.

Figure 3. Thermal ellipsoid representation of 2a showing 50% probability. Most of the H atoms were omitted for clarity. Selected bond angles (deg) and lengths (Å): C1-Au-C31 175.7(3)*; Au-C1 2.024(7) Å; Au-C31 of 2.091(9); C31-32 1.456(12) Å; C32-O32 of 1.230(11) Å.

Synthetic Methodologies for the Preparation of [Au(IPr)(acetonyl)] 2a

Once 2a was fully characterized, several synthetic approaches leading to its formation were investigated, including the use of various bases. The addition of KOH (6 equiv.) led to the isolation of 2a in 47% isolated yield after 48 h (route A, Scheme 3), while the addition of NEt₃ (6 equiv.) led to recover the chloride derivative 1a.

Once it was established that K₂CO₃ was the best base to promote the transformation, we studied the reaction using the well-defined [Au(IPr)(Cl)] (1a) rather than a·HCl. Treatment of 1a with 6 equiv. of K₂CO₃ in acetone at 60 °C gave full conversion to the acetonyl complex after 24 h (route B, Scheme 3). 2a was isolated in 84% yield and 81% overall yield from [Au(SMe₂)(Cl)] used in the preparation of [Au(IPr)(Cl)].[12]

Finally, the possibility of forming acetonyl complexes without an external base was investigated. Gratifyingly, [Au(IPr)(acetonyl)] was obtained in 90% yield using [Au(IPr)(OH)] (3a) by simply stirring 3a in acetone at room temperature for 4 h. This represents an 86% overall yield (based on the initial [Au(SMe₂)(Cl)] synthon) taking into account the preparation of [Au(IPr)(OH)] (route C, Scheme 3).[10, 34] It should be noted that all reactions were carried out under air and made use of technical grade solvents.

The formation of the acetonyl complex can be explained as follows (Scheme 4); in route A, [Au(IPr)(Cl)] is initially formed, as observed by ¹H NMR spectroscopy. From this point, route A and B proceed via the same mechanism. The large excess of base (K₂CO₃) would promote deprotonation of acetone generating the corresponding tautomer, that would then react with the soft electrophilic metal center in 1a, affording [Au(IPr)(CH₂CO₂H)] and KCl. This hypothesis was supported by the identification of 4-hydroxy-4-methyl-2-pentanone in the reaction mixture, the result of the base promoted aldol condensation of acetone.[35] Furthermore, it should be noted that the formation of 2a was not

Scheme 3. Synthetic routes to 2a. Total number of steps from a·HCl and overall yield are reported.

In route C, [Au(IPr)(OH)], which contains an internal base, is able to deprotonate acetone, affording 2a and releasing water as a side-product. The ability of 3a to deprotonate substrates with pKₐ<31 has been previously reported.[10]

Scheme 4. Proposed mechanism for the formation of 2a (route A and B).

Synthesis of [Au(NHC)(acetonyl)] Derivatives

The preparation of Au-acetonyl derivatives, bearing NHC ligands of different electronic and steric properties, was explored next (Table 1). To this end, route B (Scheme 3) appeared as the methodology of choice where the readily accessible and commercially available [Au(NHC)(Cl)] compounds were used as precursors. Following this route, the synthesis and isolation of [Au(NHC)(OH)] derivatives was not necessary, therefore reducing the number of synthetic steps in the process. In addition, the preparation of Au-acetonyl derivatives containing non-IPr based ligands was more accessible, as [Au(NHC)(Cl)] complexes are air and moisture stable,[12] while the corresponding [Au(NHC)(OH)] compounds must be prepared and stored under strictly inert conditions.[36]
The most characteristic feature was the presence of strong adsorption bands at ca. 1650 cm\(^{-1}\) corresponding to the C=O stretching frequency of the acetonyl moiety (Table 2).\(^{24}\)

\[\text{Table 2. NMR and IR spectroscopic data for 2a-g} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>(\delta\text{-CH}_2) (^{1}) (ppm)</th>
<th>(\delta\text{-CH}_3) (^{1}) (ppm)</th>
<th>(\delta\text{-C=CH}) (^{1}) (ppm)</th>
<th>(\nu\text{C=O}) (^{1}) (cm(^{-1}))</th>
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<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>2.06</td>
<td>1.53</td>
<td>193.06</td>
<td>1643</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>2.10</td>
<td>1.64</td>
<td>191.31</td>
<td>1643</td>
</tr>
<tr>
<td>3</td>
<td>2c</td>
<td>1.99</td>
<td>1.44</td>
<td>212.01</td>
<td>1643</td>
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<tr>
<td>4</td>
<td>2d</td>
<td>2.02</td>
<td>1.54</td>
<td>211.58</td>
<td>1645</td>
</tr>
<tr>
<td>5</td>
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<td>2.06</td>
<td>1.52</td>
<td>193.01</td>
<td>1651</td>
</tr>
<tr>
<td>6</td>
<td>2f</td>
<td>2.33</td>
<td>1.67</td>
<td>192.61</td>
<td>1651</td>
</tr>
<tr>
<td>7</td>
<td>2g</td>
<td>2.64</td>
<td>2.21</td>
<td>186.55</td>
<td>1643</td>
</tr>
</tbody>
</table>

\(^{1}\)H NMR (CDCl\(_3\)); \(^{13}\)C\(^{1}\)H) dept NMR (CDCl\(_3\));\(^{\ddagger}\) FTIR (ATR).

The structures of complexes 2a-c and 2e-f were unambiguously characterized by X-ray diffraction analysis. Single crystals of the [Au(NHC)(CH\(_2\)COCH\(_2\))] derivatives were grown by slow diffusion of pentane into saturated DCM or THF solutions.\(^{14}\) Figure 3 shows crystallographic representations of 2a-c and 2e-g. Unfortunately, several attempts to obtain suitable single crystals of 2d were unsuccessful. A summary of the most relevant crystallographic data for the different Au-acetonyl complexes is given in Table 3.

\[\text{Table 3. Significant X-ray crystallographic data: angles (deg) and length (Å)} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>(\chi_{\text{C}_{\text{CH}}-\text{CH}_2}) (deg)</th>
<th>Au-CH(_2) (Å)</th>
<th>CH(_2)-CO (Å)</th>
<th>C=O (Å)</th>
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<tr>
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<td>175.7(3)</td>
<td>2.09(1)</td>
<td>1.456(12)</td>
<td>1.230(11)</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>176.2(8)</td>
<td>2.06(3)</td>
<td>1.453(12)</td>
<td>1.232(11)</td>
</tr>
<tr>
<td>3</td>
<td>2c</td>
<td>174.4(4)</td>
<td>2.054(10)</td>
<td>1.445(16)</td>
<td>1.183(16)</td>
</tr>
<tr>
<td>4</td>
<td>2e</td>
<td>176.3(3)</td>
<td>2.222(9)</td>
<td>1.497(16)</td>
<td>1.230(19)</td>
</tr>
<tr>
<td>5</td>
<td>2f</td>
<td>177.4(3)</td>
<td>2.096(9)</td>
<td>1.453(15)</td>
<td>1.202(14)</td>
</tr>
<tr>
<td>6</td>
<td>2g</td>
<td>178.62(17)</td>
<td>2.083(5)</td>
<td>1.467(6)</td>
<td>1.227(6)</td>
</tr>
</tbody>
</table>

\(^{\ddagger}\) Several molecules were found in the crystal lattice of these complexes: the range of distances and angles obtained is shown.

Following route B, the synthesis of [Au(NHC)(CH\(_2\)COCH\(_2\))] derivatives bearing IMes (2b), SiPr (2c), SiMes (2d), IPr\(^{[38]}\) (2e), IPr\(^{[39]}\) (2f) and IAd\(^{[39]}\) (2g) was accomplished. All complexes were obtained in good to excellent yields, ranging from 65-97\% (Table 1, entries 1-6) and fully characterized by NMR and IR spectroscopies and elemental analysis.

The most notable spectroscopic features of the [Au(NHC)(CH\(_2\)COCH\(_2\))] complexes are summarized in Table 2. The \(^{1}\)H NMR spectra of the complexes in CDCl\(_3\) showed two singlets corresponding to the -CH\(_2\) and -CH\(_3\) groups of the acetonyl moiety. In the case of complexes 2a-2f, bearing N-aryl substituted NHC ligands, these signals appeared in the range of 2.06-2.33 ppm for the -CH\(_2\) group, and 1.44-1.67 ppm for the -CH\(_3\) group (Table 2, entries 1-6). These resonances appeared significantly shifted downfield in the case of 2g (2.64 ppm for the -CH\(_2\) group; 2.21 ppm for -CH\(_3\) group), bearing an N-alkyl NHC ligand, the most electron-donating of this series of NHC derivatives (Table 2, entry 7).\(^{[36]}\) The downfield region of the \(^{13}\)C\(^{[1]}\)H NMR spectra of complexes 2a-2g showed the presence of two singlets. One of them corresponded to the carbenic carbon atom (186.55 – 212.01 ppm) while the other was assigned to the carbon of the carbonyl group (212.12 - 212.50 ppm).\(^{[24]}\) All complexes were characterized by FTIR (ATR) spectroscopy. The most characteristic feature was the presence of strong adsorption bands at ca. 1650 cm\(^{-1}\) corresponding to the C=O stretching frequency of the acetonyl moiety (Table 2).\(^{[24]}\)
Figure 4. Thermal ellipsoid representation of 2b, c and 2e-g showing 50% probability. Most of the H atoms were omitted for clarity. Two different molecules were found in the crystal lattice of 2b and 2f, while 4 different conformers were found in 2c. In these three cases, the thermal ellipsoid representation of one of the molecules is shown in the Figure. 2f presented a symmetry-induced disorder in the acetonyl region, due to a mismatch between the space group symmetry and the inherent symmetry of the complex.

Stoichiometric Reactivity of [Au(NHC)(acetonyl)] Complexes

The reactivity of 2a in term of its acid/base behavior was explored next. Protonolysis reactions of 2a with organic acids, of known pKₐ (DMSO) values,[42] were performed to gauge its basicity.[43] Thereby, free acetone would be released in the reaction medium and easily removed by evaporation.

Attempts to deprotonate C-H bonds of fluoroarenes, such as pentafluorobenzene and 1,3,5-trifluorobenzene, (pKₐ (DMSO) = 29-31.5), in toluene at 100 °C, to obtain [Au(IPr)(C₆F₅H₅)] (n=3, 5) were unsuccessful. However, phenylacetylene (pKₐ (DMSO) = 28.8) reacted successfully with 2a to give the corresponding complex 4a, which was isolated in 87% yield after heating the mixture at 80 °C for 24 h (Scheme 5).

With these results in hand, we tested other acidic species with lower pKₐ than phenylacetylene. 2a was reacted with phenol (pKₐ (DMSO) = 18) at 80 °C to synthesize the corresponding gold(I)-phenolate 5a derivative in 76% isolated yield. This reaction is an alternative protocol to the ones previously reported for the synthesis of gold-phenolates.[43]

Acetylacetone (acac-H) and dimethoxy malonate, with pKₐ (DMSO) values ~13-16, reacted with 2a at 80 °C to give 6a and 7a respectively in good yields (79-61% isolated yields).[44] Using more acidic substrates (pKₐ<10), a large number of organogold species were synthesized at room temperature. Indeed, 2a reacted with 4-mercaptopyridine, affording 8a in 88% isolated yield. This product is particularly interesting, as gold complexes bearing a similar moiety have proven to present anticancer properties.[44]

Gold(I)-carboxylates, 9a-12a, were easily obtained in good yields (72-88%) by treatment of 2a with the corresponding carboxylic acids; these compounds have been used as well-defined catalysts, and proposed as intermediates in carboxylation/decarboxylation reactions.[45]

Interestingly, 2a also provided access to the well-established catalyst [Au(IPr)(NTf₂)]₄[46] (13a) in good yield (89%) using trifluoromethanesulfonic acid (HTf₂).

Moreover, using an excess of pinacolborane, as a hydride source, [Au(IPr)(H)] (14a) was obtained in 80% yield.[49] This reaction was carried out under argon atmosphere due to the high reactivity of 14a.
Furthermore, suitable crystals for X-ray diffraction analysis of the new complexes 6a, 8a and 11a were obtained and their purity was confirmed by elemental analyses.\textsuperscript{[67]}

Scheme 5. Transformations involving 2a.

2a was reacted with t-BuPh$_3$SiCl, affording the stable complex 1a and the substituted silyloxy acetone, which were isolated in 99% and 72% yields, respectively (Scheme 6).

Scheme 6. Reactivity of 2a with a substituted silane.

In view of this reactivity, [Au(IPr)(CH$_3$COCH$_3$)] (2a) emerged as a powerful precursor for several organogold compounds, as well as an attractive alternative to the well-known [Au(IPr)(Cl)] and [Au(IPr)(OH)] synthons.\textsuperscript{[10, 12]}

In this context, the [Au(IMes)(acetonyl)] (2b) complex was of particular interest as IMes is one of the most common NHCs in gold chemistry. However, its reactivity has been less developed compared to IPr, presumably because of the lower stability of Au-IMes complexes. For example, while [Au(IPr)(OH)] can be prepared on a multi-gram scale and stored under air, the Au-IMes hydroxide analogue is air and moisture sensitive.\textsuperscript{[36]} In contrast to [Au(IMes)(OH)], the [Au(IMes)(acetonyl)] derivative (2b) is a stable complex, easily synthesized using technical grade solvents and handled under non-inert conditions. For these reasons, we explored the synthetic potential of 2b (Scheme 7).\textsuperscript{[48]}

The basicity of [Au(IMes)(CH$_3$COCH$_3$)] was evaluated by reacting it with different organic molecules bearing acidic protons; in contrast to 2a, 2b did not react with phenylacetylene (pK$_a$ (DMSO) = 28.8). This suggests that 2b is less basic than 2a. Therefore, more acidic substrates (pK$_a$ (DMSO) < 28.8) were required to obtain organogold derivatives.

Indeed, 2b reacted with phenol, forming the corresponding gold-phenolate complex (5b) in 86% yield. Reaction of 2b with acac-H and dimethoxy malonate, at 80 °C, afforded 6b and 7b in high yields (84% and 86% respectively). Furthermore, acetic acid was reacted with 2b to give 9b in 64% isolated yield.

Treatment of 2b with an excess of pinacol borane afforded [Au(IMes)(H)] (14b) which was isolated in high yield (83%).\textsuperscript{[49]} As is the case with 14a, this reaction required inert conditions to prevent decomposition of 14b.

Finally, 2b reacted smoothly with t-BuPh$_3$SiCl, affording 1b and the corresponding substituted silyl enol ether. The former was isolated in 99% yield and the latter in 68%.

Suitable crystals for X-ray diffraction analysis were obtained for the new complexes 5b, 7b and 9b, and elemental analyses confirmed their purities.\textsuperscript{[50]}

The observed reactivity makes [Au(IMes)(acetonyl)] a convenient precursor to synthesize a number of Au-IMes derivatives, which will enable further development of this chemistry.

Catalytic Reactivity of [Au(IPr)(acetonyl)] 2a

To further test the applicability of Au(NHC)-acetonyl complexes, we explored whether the newly synthesized derivatives could be used as precatalysts. As IPr is the most common NHC ligand in gold catalysis and its precursors are commercially available, we decided to use 2a as our reference catalyst.

We selected two well-defined gold(I)-catalyzed transformations: the hydration of alkynes to form ketones\textsuperscript{[51]} and the rearrangement of propargylic acetates to form substituted indenes.\textsuperscript{[52]} The active catalyst for these reactions is believed to be a [Au(NHC)]$^+$ species. We envisioned that this active catalyst could be formed \textit{in situ} by reacting 2a with a protic acid.\textsuperscript{[51-52]}

Therefore, the reactions can be performed without requiring the
use of expensive and hygroscopic silver salts AgX (X = OTf, BF₄, SbF₆, PF₆). Which are known to be active catalysts in a number of transformations. Benchmark substrates, usually employed in the development of these transformations, were used in order to permit a better comparison with the previously reported protocols.

**Gold(I)-Catalyzed Alkyne Hydration to Ketones**

A number of gold complexes have been demonstrated to effectively catalyze the hydration of alkynes. In order to test the catalytic activity of 2a in this transformation, we studied the hydration of diphenylacetylene (Table 4).

Neither 2a nor HBF₄·H₂O alone can catalyze the reaction (Table 4, entry 1 and 2). However, in the presence of a 1:1 ratio of 2a and HBF₄·H₂O, 1,2-diphenylethanone was obtained in 80% conversion after 2 h (Table 4, entry 3) and full conversion was reached after 4 h (Table 4, entry 4). When 2 equiv. of acid were used with respect to 2a, full conversion was obtained after 2 h (Table 4, entry 5). In agreement with previous findings using Au(I)-OH as precatalyst, a slight excess of acid was necessary to ensure the complete conversion of the precatalyst into the active species.

**Table 4** Hydration of alkynes

<table>
<thead>
<tr>
<th>Entry[c]</th>
<th>2a/HBF₄·H₂O</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
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<tr>
<td>1</td>
<td>1:0</td>
<td>2</td>
<td>n.r.[b]</td>
</tr>
<tr>
<td>2</td>
<td>0:1</td>
<td>2</td>
<td>n.r.[b]</td>
</tr>
<tr>
<td>3</td>
<td>1:1</td>
<td>2</td>
<td>80%[d]</td>
</tr>
<tr>
<td>4</td>
<td>1:1</td>
<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>1:2</td>
<td>2</td>
<td>&gt;99%[b]</td>
</tr>
</tbody>
</table>

*a Reaction conditions: diphenylacetylene (0.5 mmol), 1,4-dioxane/water (2:1, 1 mL); b GC conversions; c n.r. = no reaction*

**Gold(I)-catalyzed Synthesis of Substituted Indenes from Propargylic Acetates**

Cationic gold complexes have been shown to exhibit high catalytic activity in the intramolecular rearrangement-hydroarylation of propargylic acetates, affording different products depending on reaction conditions. Under anhydrous conditions, alkyne activation could lead to migration of the acetate group, producing allenes. These compounds are believed to be intermediates in the synthesis of indenes. Whereas, in the presence of water the reaction produced conjugated enones. Therefore, the catalytic behavior of 2a was tested in this transformation, using HBF₄·Et₂O to activate the Au-acetonyl derivative.

Reaction of propargylic acetate (15), in the presence of 2a and HBF₄·Et₂O (1:1.5), led to the formation of the alene (16) after 15 minutes (Table 5, entry 1). Conversion into a mixture (40:60) of the kinetic (17) and the thermodynamic (18) indenes was observed by GC analysis of the reaction mixture after 24 h (Table 5, entry 2). Longer reaction times (48 h) led to the exclusive formation of indene 18 (Table 5, entry 3). 2a was found to be less active compared to the closely related Au(I)-OH derivatives. However, the slower reactivity of the Au(I)-acetonyl complex permitted the addition of an extra control element to this transformation and allowed us to selectively obtain alene 16 and the thermodynamic indene 18.

**Table 5** Transformation of propargylic acetates into substituted allenes and indenes

<table>
<thead>
<tr>
<th>Entry[c]</th>
<th>Time</th>
<th>Conversion (%)</th>
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<tr>
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<tr>
<td>2</td>
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<td>3</td>
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</tbody>
</table>

*a Reaction conditions: propargylic alcohol (0.5 mmol), 2a (2 mol%), HBF₄·Et₂O (3 mol%), DCE (10 mL); b Conversion was calculated by 1H NMR using pivalaldehyde as internal standard (0.5 mmol); c Conversions and ratio between 17 and 18 were determined by GC analysis and confirmed by 1H NMR spectroscopy.*

**Conclusions**

The serendipitous discovery of the first Au(I)-NHC acetonyl complex is herein reported. This complex, first observed as a side-product, has been prepared by straightforward procedures from easily and commercially available precursors. A family of complexes has been synthesized. Their ease of preparation renders them attractive alternatives for the well-known [Au(NHC)(Cl)] or [Au(NHC)(OH)] complexes. Particular attention was focused on the complexes bearing the common IPr and IMes ligands where we have demonstrated that these species are versatile synthons, permitting access to a variety of organogold complexes. Our initial studies revealed that Au(IPr)-acetonyl is a useful precatalyst. Further studies to investigate new reactivities and properties of these intriguing Au-acetonyl complexes are currently ongoing.
Experimental Section

General considerations: Unless otherwise stated, all solvents and reagents were used as purchased and all reactions were performed under air. NMR spectra were recorded on 500 and 300 MHz spectrometers at room temperature in CDCl₃ or CD₆D. Chemical shifts (δ) are reported in ppm, relative to the solvent residual peak CDCl₃ (7.26 ppm for ¹H and 77.16 ppm for ¹³C). Data for ¹H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad signal, m = multiplet), coupling constants (J) in Hz and integration. For the assignment of the ¹H and ¹³C chemical shifts NMR spectra of gold complexes COSY, HSQC and HMBC experiments were also performed. Elemental analyses were carried out by the analytical services of London Metropolitan University. Crystals were grown by slow diffusion of pentane into a saturated DCM/THF/CDCl₃ solution. FTIR (ATR) spectra were recorded on a Shimadzu spectrophotometer. For full experimental data of all compounds, see supporting information.

Preparation of [Au(NHC)(CH₂COOH)] (2a-b), route A Scheme 3: A mixture of NHC-HCl (1 equiv.), [Au(SMe₂)(O)] (1 equiv.) and K₂CO₃ (6 equiv.) in acetone (2-3 mL) was stirred for 48-72 h at 60 °C. The solution was then filtered through a pad of Celite®, the solvent removed under vacuum. The resulting solid was dissolved in the minimum amount of CH₂Cl₂ (2-3 mL) and precipitated by addition of pentane (ca. 10 mL). The precipitate was collected by filtration, washed with pentane (3 x 2 mL) and dried under vacuum, affording the corresponding [Au(NHC)(CH₂COOH)] as a microcrystalline white solid.

Preparation of [Au(NHC)(CH₂COOH)] (2a-g), route B Scheme 3: A mixture of [Au(NHC)(Cl)] (1 equiv.) and K₂CO₃ (6 equiv.) in acetone (2 mL) was stirred at 60 °C for 24-72 h. The solution was then filtered through a pad of Celite®, the solvent removed under vacuum. The resulting solid was dissolved in the minimum amount of CH₂Cl₂ (2-3 mL) and precipitated by addition of pentane (ca. 10 mL). The precipitate was collected by filtration, washed with pentane (3 x 5 mL) and dried under vacuum, affording the corresponding [Au(NHC)(CH₂COOH)] as a microcrystalline white solid.

Preparation of [Au(Ipr)(CH₂COOH)] (2a), route C Scheme 3: [Au(Ipr)(Cl)] (400 mg, 0.66 mmol, 1 equiv.) was dissolved in acetone (5 mL) and stirred for 4 h at room temperature. The solvent was then removed under vacuum. The resulting solid was dissolved in the minimum amount of CH₂Cl₂ (2-3 mL) and precipitated by addition of pentane (ca. 10 mL). The precipitate was collected by filtration, washed with pentane (3 x 5 mL) and dried under vacuum, affording the corresponding [Au(Ipr)(CH₂COOH)] as a microcrystalline white solid in 90% yield.

[¹H NMR (CDCl₃)] (1,3-bis[2,6-diisopropylphenyl]-2,3-dihydro-1H-imidazol-2-yl)-2-oxopropanoylgold (2a): Complex 2a was synthesized following route A using piperidine (800 mg, 1.82 mmol, 1 equiv.), [Au(SMe₂)(O)] (554.37 mg, 1.82 mmol, 1 equiv.), K₂CO₃ (1.51 g, 10.92 mmol, 6 equiv.) in acetone (10 mL). The reaction was stirred for 48 h at 60 °C. The desired product was obtained as a white solid in 80% yield (968.52 mg, 1.51 mmol). Complex 2a was also synthesized following route B using [Au(Ipr)(Cl)] (500 mg, 1.82 mmol, 1 equiv.) and K₂CO₃ (1.51 g, 10.92 mmol, 6 equiv.) in acetone (5 mL). The reaction was stirred for 24 h at 60 °C. The desired product was obtained as a white solid in 84% yield (173.82 mg, 0.32 mmol). ¹H NMR (500 MHz, CDCl₃): δ = 7.49 (t, J = 7.8 Hz, 2H, CH₂), 7.28 (d, J = 7.8 Hz, 4H, CH aromatic ipr), 7.13 (s, 3H, CH imidazole ipr), 2.56 (sept, J = 6.9 Hz, 4H, CH(CH₂)₂), 2.06 (2H, CH₂), 1.53 (3H, CH₃), 1.32 (2H, 1H, CH(CH₂)₂), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₂)₃).
1 equiv.) and K₂CO₃ (120.2 mg, 0.870 mmol, 6 equiv.) in acetonitrile (2 mL). The reaction was stirred for 48 h at 60 °C. The desired product was obtained as a white solid in 81% yield (83.17 mg, 0.117 mmol). ¹H NMR (500 MHz, CDCl₃): δ = 7.54 (t, J = 7.7 Hz, 2H, CH aromatic IPr²), 7.31 (d, J = 7.8 Hz, 4H, CH aromatic IPr²), 2.46 (2.45 (sept, J=6.8, 4H, CH₂CH₂)), 2.06 (s, 2H, CH₂), 1.52 (s, 3H, CH₃), 1.34 (d, J = 6.8 Hz, 12H, CH₂(C₆H₅)₂), 1.25 (d, J = 6.9 Hz, 12H, CH₂(C₂H₅)), 1.07 (s, 3H, CH₃) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 212.13 (C=O), 192.71 (C carbene), 146.12 (CH aromatic IPr²), 126.12 (CH aromatic IPr²), 126.05 (CH aromatic IPr²), 124.00 (CH aromatic IPr²), 118.87 (CH aromatic IPr²), 39.85 (CH₂), 29.56 (CH₃), 29.24 (CH₂CH₂), 24.60 (CH₃CH₂), 23.61 (CH₃), elemental analysis calcd (%): C 50.46, H 5.53, N 6.94; found: C 49.42, H 5.47, N 6.93; FTIR (ATR) v = 1651 cm⁻¹.

\([\text{Au(IPr)}(\text{COCH₃})₂]\): δ = 212.74 (C=O), 193.64 (C carbene), 142.74 (CH aromatic IPr²), 127.80 (CH aromatic IPr²), 127.73 (CH aromatic IPr²), 126.73 (CH aromatic IPr²), 126.71 (CH aromatic IPr²), 123.80 (CH imidazole IPr²), 123.57 (CH imidazole IPr²), 123.98 (CH imidazole IPr²), 118.81 (CH aromatic IPr²), 118.79 (CH aromatic IPr²), 39.85 (CH₂), 29.56 (CH₃), 29.24 (CH₂CH₂), 24.60 (CH₃CH₂), 23.61 (CH₃), elemental analysis calcd (%): C 50.46, H 5.53, N 6.94; found: C 49.42, H 5.47, N 6.93; FTIR (ATR) v = 1651 cm⁻¹.

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Supporting Information: see Supporting Information.
A library of [Au(NHC)(acetonyl)] complexes has been easily synthesized. These complexes represent valuable synthetic precursors to a plethora of organogold species as well as active catalysts for gold(I)-catalyzed reactions.