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 synthons for the preparation of numerous organogold complexes. Moreover, they have proven to be precatalysts in common gold(I)-catalyzed reactions.

Introduction

The interest in gold chemistry has grown exponentially in the last decades.[1] Gold species have been found to be highly active catalysts for both homogeneous and heterogeneous transformations.[2] Moreover, organogold complexes present luminescent and biological properties, which make them attractive for the synthesis of new materials and for biomedical applications.[3]

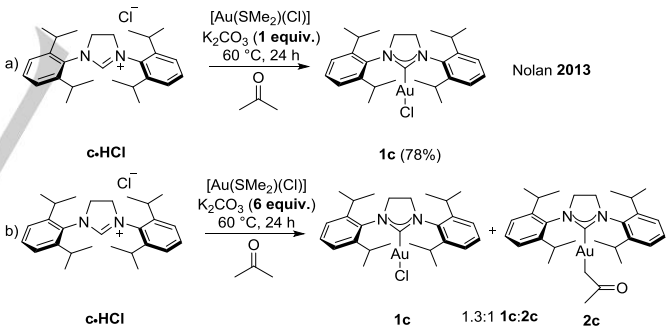
Initially, the use of simple gold salts as catalysts, such as AuCl, $AuCl_3$ or $NaAuCl_4$, was ubiquitous in gold catalysis. More recently, particular attention has been focused on the development of well-defined Au(I) and Au(III) complexes bearing ancillary ligands in order to examine whether or not enhanced catalytic activity could be achieved.[1a, 2a, 4]

N-heterocyclic carbene (NHC) species have appeared as excellent ligands for the synthesis of a wide range of organometallic complexes.[5] Their strong σ-donating ability and steric hindrance allow for strong metal-ligand bonds and prevent complex decomposition.[6] The use of NHC ligands in gold chemistry has allowed for the synthesis of a plethora of organogold complexes.[7] Indeed, highly unstable species have been isolated due to the unique properties of such ligands, e.g. the first Au(I)-*tert*-butoxide[8], Au(I)-fluoride[8] and Au(I)-hydride[9] species reported by the group of Sadighi, as well as the Au(I)-hydroxide[10] and Au(I)-alkylperoxo[11] complexes synthesized by Nolan and co-workers.

Among these complexes, [Au(NHC)(Cl)] compounds have been recognized as valuable precursors for several organogold complexes.[7c] An improved protocol for their synthesis has recently been developed.[12] This straightforward synthetic procedure allows for the preparation of [Au(NHC)(Cl)] complexes by reacting the corresponding imidazol(idin)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)][13] (**1a**) and [Au(IMes)(Cl)][14] (**1b**) were obtained in 1 h and 3 h respectively, the synthesis of [Au(SIPr)(Cl)][15] (**1c**) or [Au(SIMes)(Cl)][16] (**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. ^1H and $^{13}C\{^1H\}$ NMR analysis of the mixture allowed the characterization of the desired Au-Cl complex and of a new species identified as the acetonyl complex [Au(SIPr)(CH_2COCH_3)] (**2c**) (eq. b, Scheme 1).



Scheme 1. Formation of Au-chloride complex **1c** and Au-acetonyl complex **2c**.

Intrigued by the formation of this acetonyl complex, we decided to explore whether this derivative was also formed using the unsaturated and commercially available IPr·HCl salt (**a·HCl**). Therefore, a mixture of IPr·HCl and [Au(SMe_2)(Cl)] in equimolar amounts was stirred in acetone at 60 °C in the presence of 6 equivalents of K_2CO_3. After 48 h, full conversion to [Au(IPr)(CH_2COCH_3)] (**2a**) was obtained and the product was isolated in 80% yield (Scheme 2).

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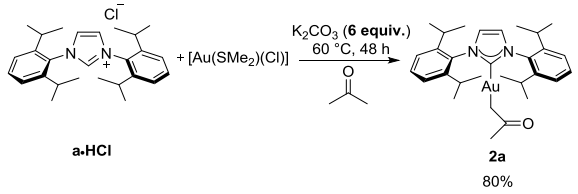


Scheme 2. Conversion of **a·HCl** and [Au(SMe$_2$)(Cl)] into **2a**.

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**), η^3-oxoallyl-M (**II**) and 2-oxoalkyl-M complexes (**III**) (Figure 1).[17]

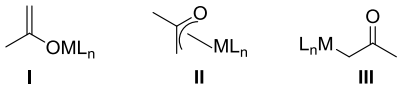


Figure 1. Different types of Metal-enolate bonding.

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 α-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_2O, 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, Ito synthesized and fully characterized stable Au(I)(PPh_3) -ketonyl and -homoketonyl complexes by adding sylilated 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]

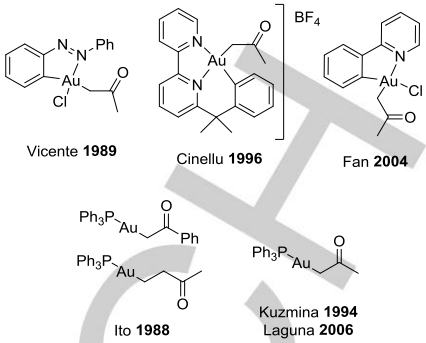


Figure 2. Some examples of reported Au(I) and Au(III)-ketonyl complexes

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 acetonyl 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_2CO_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 $^{13}C\{^1H\}$ 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 (νCO), in agreement with previously reported Au-acetonyl compounds.[28c] 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 $C_{carbene}$-Au-CH_2 angle of 175.7(3)°.[31a] The Au-$C_{carbene}$ distance of 2.024(7) Å lies in the typical range for gold(I)-NHC species.[7c, 31a] Other relevant distances are Au-CH_2 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]

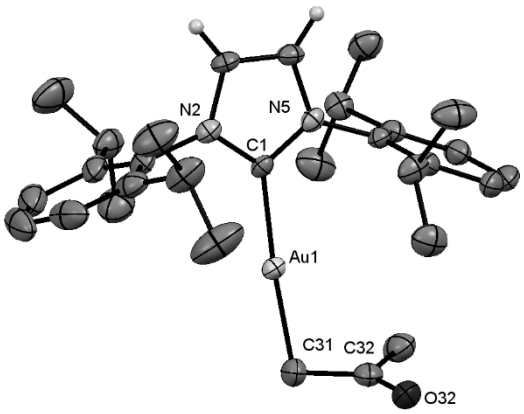


Figure 3. Thermal ellipsoid representation of **2a** showing 50% probability. Most of the H atoms were omitted for clarity. Selected bond angles (deg) and lengths (Å): C1-Au-C31 175.7(3)°; Au-C1 2.024(7) Å; Au-C31 of 2.091(9) Å; C31-32 1.456(12) Å, C32-O32 of 1.230(11) Å.

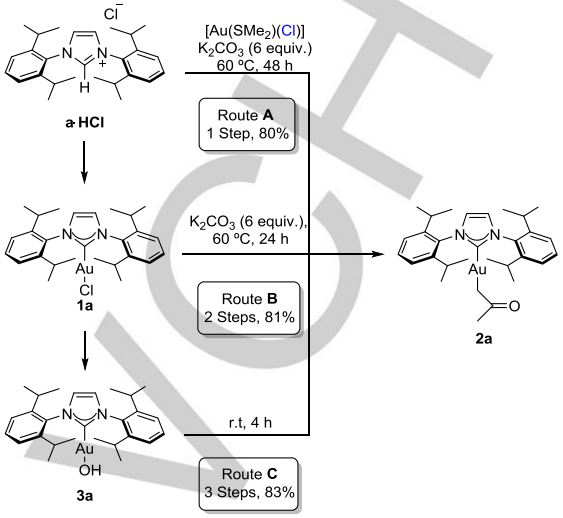
Synthetic Methodologies for the Preparation of [Au(IPr)(acetonyl)] 2a

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 NEt_3 (6 equiv.) led to recover the chloride derivative **1a**.

Once it was established that K_2CO_3 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 K_2CO_3 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(SMe_2)(Cl)] used in the preparation of [Au(IPr)(Cl)].[12]

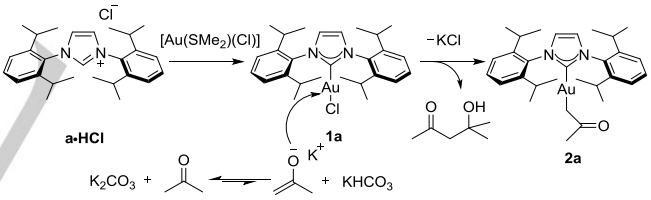
Finally, the possibility of forming acetonyl complexes without an external base was investigated. Gratifyingly, [Au(IPr)(acetonyl)] was obtained in 90% yield using [Au(IPr)(OH)] (**3a**) by simply stirring **3a** in acetone at room temperature for 4 h. This represents an 86% overall yield (based on the initial [Au(SMe_2)(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 ^{1}H NMR spectroscopy. From this point, route **A** and **B** proceed *via* the same mechanism. The large excess of base (K_2CO_3) would promote deprotonation of acetone generating the corresponding tautomer, that would then react with the soft electrophilic metal center in **1a**, affording [Au(IPr)(CH_2COCH_3)] 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 observed when NEt_3 was used as base, suggesting that the precipitation of KCl is the driving force of the reaction.



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 pK_a<31 has been previously reported.[10]

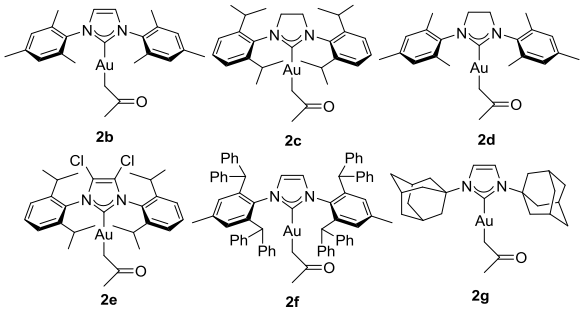


Scheme 4. Proposed mechanism for the formation of **2a** (route **A** and **B**).

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)][34] 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,[7c, 12] while the corresponding [Au(NHC)(OH)] compounds must be prepared and stored under strictly inert conditions.[36]

Table 1 Library of Au(NHC)-acetonyl complexes prepared in this study



Entry[a]	NHC ligands	Complex	Time (h)	Yield (%)
1	IMes	**2b**	72	71
2	SIPr	**2c**	72	97
3	SIMes	**2d**	72	73
4	IPr^{Cl}	**2e**	48	92
5	IPr*	**2f**	72	81
6	IAd	**2g**	72	65

[a] Reaction conditions: route **B** K_2CO_3 (6 equiv.), acetone, 60 °C.

Following route **B**, the synthesis of [Au(NHC)(CH_2COCH_3)] derivatives bearing IMes (**2b**), SIPr (**2c**), SIMes (**2d**), IPr^{Cl}[37] (**2e**), IPr*[38] (**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_2COCH_3)] 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 1.99-2.33 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).[5d] The downfield region of the $^{13}C\{^1H\}$ 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).[40] 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).[28c]

Table 2. NMR and IR spectroscopic data for **2a**-**g**

Entry	Complex	δ(-CH_2)[a] (ppm)	δ(-CH_3)[a] (ppm)	δ(-$C_{carb.}$)[b] (ppm)	νCO[c] (cm^{-1})
1	**2a**	2.06	1.53	193.06	1643
2	**2b**	2.10	1.64	191.31	1643
3	**2c**	1.99	1.44	212.01	1643
4	**2d**	2.02	1.54	211.58	1645
5	**2e**	2.06	1.52	193.01	1651
6	**2f**	2.33	1.67	192.61	1651
7	**2g**	2.64	2.21	186.55	1643

[a] ^{1}H NMR ($CDCl_3$); [b] $^{13}C\{^1H\}$ deptq NMR ($CDCl_3$); [c] 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_2COCH_3)] derivatives were grown by slow diffusion of pentane into saturated DCM or THF solutions.[41] 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.

Table 3. Significant X-ray crystallographic data: angles (deg) and length (Å)

Entry	Complex	C_{carb}-Au-CH_2 (deg)	Au-CH_2 (Å)	CH_2-CO (Å)	C=O (Å)
1	**2a**	175.7(3)°	2.091(9)	1.456(12)	1.230(11)
2[a]	**2b**	176.2(8)-177.3(9)°	2.06(3)-2.10(3)	1.45(3)-1.38(4)	1.32(4)-1.24(5)
3[a]	**2c**	174.4(4)-179.4(4)°	2.054(10)-2.111(12)	1.445(16)-1.531(18)	1.18(3) - 1.246(16)
4	**2e**	176.3(3)°	2.222(9)	1.497(16)	1.230(19)
5[a]	**2f**	177.4(3)-179.4(3)°	2.096(9)	1.453(15)-1.464(14)	1.20(2)-1.26(2)
6	**2g**	178.62(17)°	2.083(5)	1.467(6)	1.227(6)

[a] Several molecules were found in the crystal lattice of these complexes: the range of distances and angles obtained is shown.

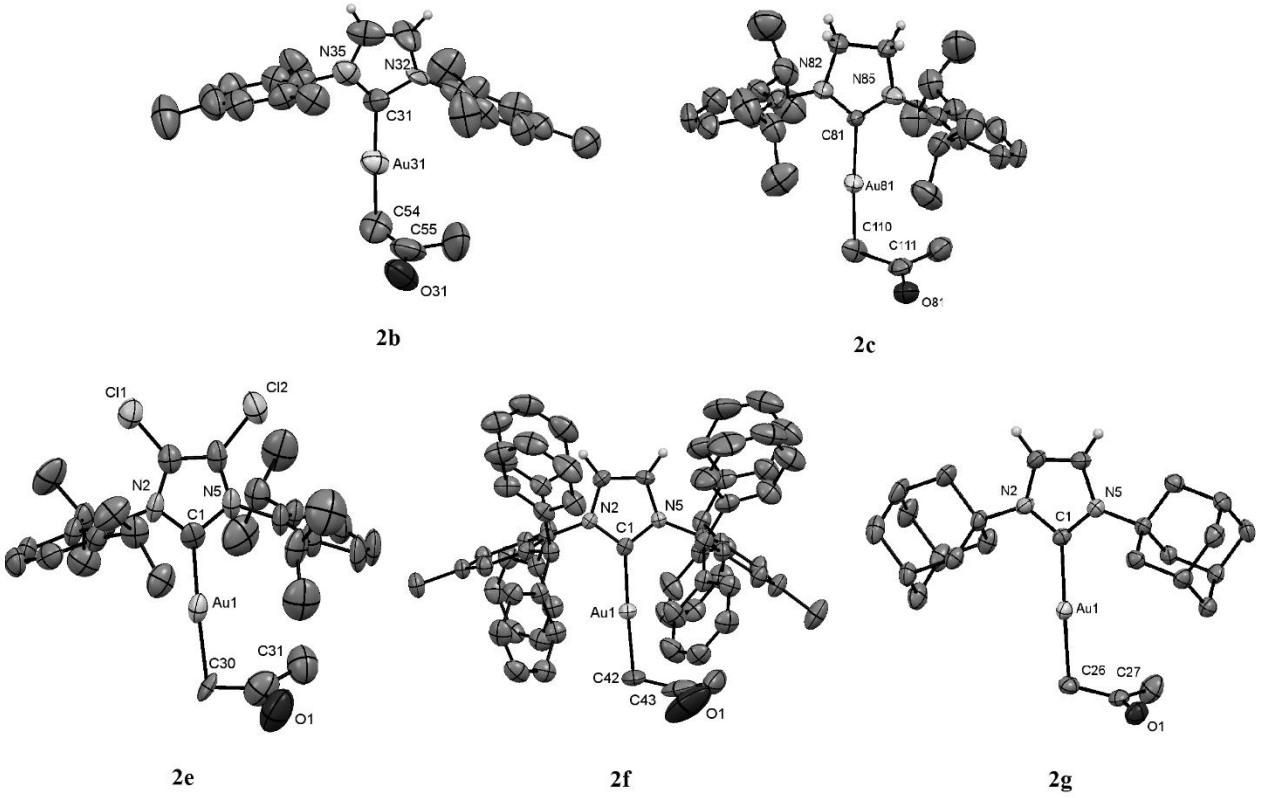


Figure 4. Thermal ellipsoid representation of **2b**, **c** and **2e-g** showing 50% probability. Most of the H atoms were omitted for clarity. Two different molecules were found in the crystal lattice of **2b** and **2f**; while 4 different conformers were found in **2c**. In these three cases, the 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 pK_a (DMSO) values,[42] were performed to gauge its basicity.[10] 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, (pK_a (DMSO) = 29-31.5), in toluene at 100 °C, to obtain [Au(IPr)($C_6F_nH_{5-n}$)] (n=3, 5) were unsuccessful. However, phenylacetylene (pK_a (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 pK_a than phenylacetylene. **2a** was reacted with phenol (pK_a (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 pK_a (DMSO) values ~13-16, reacted with **2a** at 80 °C to give **6a** and **7a** respectively in good yields (79-61% isolated yields).[10]

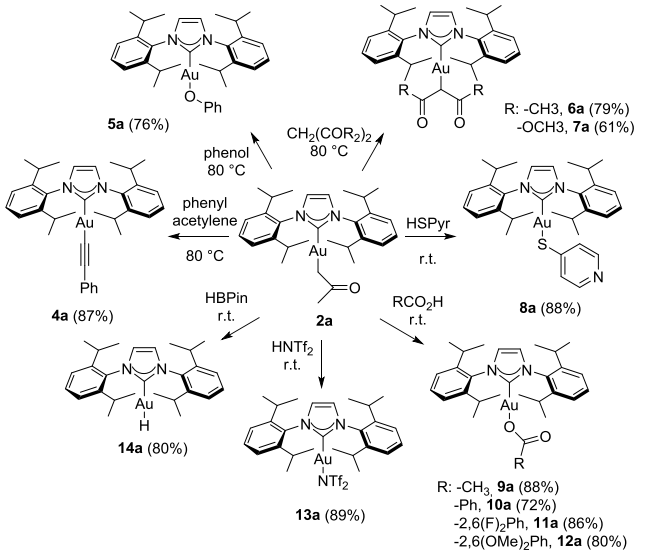
Using more acidic substrates (pK_a<10), a large number of organogold species were synthesized at room temperature. Indeed, **2a** reacted with 4-mercaptopyridine, affording **8a** in 88% isolated yield. This product is particularly interesting, as gold complexes bearing a similar moiety have proven to 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)(NTf_2)][46] (**13a**) in good yield (89%) using trifluoromethanesulfonic acid ($HNTf_2$).

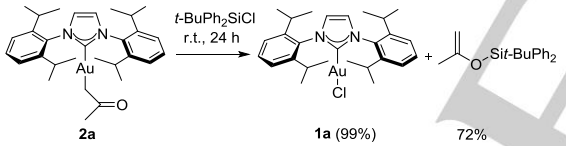
Moreover, using an excess of pinacolborane, as a hydride source, [Au(IPr)(H)] (**14a**) was obtained in 80% yield.[9] This reaction was carried out under argon atmosphere due to the high reactivity of **14a**.

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.[47]



Scheme 5. Transformations involving **2a**.

2a was reacted with *t*-BuPh$_2$SiCl, affording the stable complex **1a** and the substituted silyloxy acetone, which were isolated in 99% and 72% yields, respectively (Scheme 6).

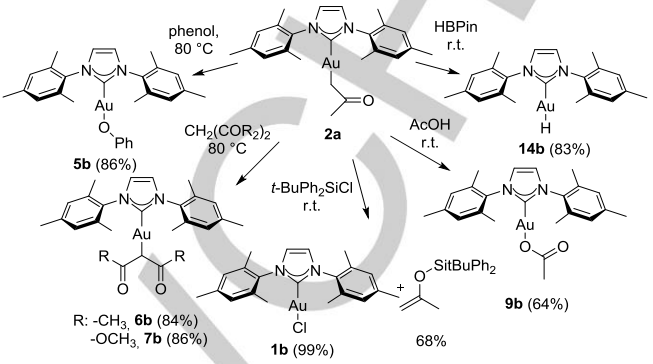


Scheme 6. Reactivity of **2a** with a substituted silane.

In view of this reactivity, [Au(IPr)(CH$_2$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.[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.[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).[48]

The basicity of [Au(IMes)(CH$_2$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.



Scheme 7. Reactivity of **2b**.

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%).[49] As is the case with **14a**, this reaction required inert conditions to prevent decomposition of **14b**.

Finally, **2b** reacted smoothly with *t*-BuPh$_2$SiCl, affording **1b** and the corresponding substituted sylil 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.[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.

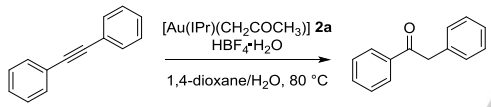
We selected two well-defined gold(I)-catalyzed transformations: the hydration of alkynes to form ketones[51] and the rearrangement of propargylic acetates to form substituted indenes.[52] The active catalyst for these reactions is believed to be a [Au(NHC)]$^+$ species. We envisioned that this active catalyst could be formed *in situ* by reacting **2a** with a protic acid.[51-52] Therefore, the reactions can be performed without requiring the

use of expensive and hygroscopic silver salts AgX (X = OTf, BF_4, SbF_6, PF_6),[53] which are known to be active catalysts in a number of transformations.[54]
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.[55] In order to test the catalytic activity of **2a** in this transformation, we studied the hydration of diphenylacetylene (Table 4).
Neither **2a** nor $HBF_4 \cdot H_2O$ alone can catalyze the reaction (Table 4, entry 1 and 2). However, in the presence of a 1:1 ratio of **2a** and $HBF_4 \cdot H_2O$, 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).[51, 55d] In agreement with previous findings using Au(I)-OH as precatalyst, [55d] a slight excess of acid was necessary to ensure the complete conversion of the precatalyst into the active species.

Table 4 Hydration of alkynes



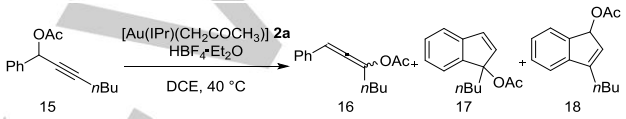
Entry[a]	**2a**:$HBF_4 \cdot H_2O$	Time (h)	Conversion (%)
1	1:0	2	n.r.[c]
2	0:1	2	n.r.[c]
3	1:1	2	80 [b]
4	1:1	4	>99 [b]
5	1:2	2	>99 [b]

[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.[52] Whereas, in the presence of water the reaction produced conjugated enones.[56] Therefore, the catalytic behavior of **2a** was tested in this transformation, using $HBF_4 \cdot Et_2O$ to activate the Au-acetonyl derivative.
Reaction of propargylic acetate (**15**), in the presence of **2a** and $HBF_4 \cdot Et_2O$ (1:1.5), led to the formation of the allene (**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.[56c] 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 allene **16** and the thermodynamic indene **18**.

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



Entry[a]	Time	**16**:**17**:**18**	Conversion (%)
1	15 min	1:0:0	**16** >99 [b]
2	24 h	0:0.6:1	**17** 40: **18** 60 [c]
3	48 h	0:0:1	**18** >99 [c]

[a] Reaction conditions: propargylic alcohol (0.5 mmol), **2a** (2 mol%), $HBF_4 \cdot Et_2O$ (3 mol%), DCE (10 mL); [b] Coversion was calculated by ^{1}H NMR using pivaladehyde as internal standard (0.5 mmol).[c] Conversions and ratio between **17** and **18** were determined by GC analysis and confirmed by ^{1}H 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 $CDCl_3$ or C_6D_6. Chemical shifts (δ) are reported in ppm, relative to the solvent residual peak $CDCl_3$ (7.26 ppm for ^1H and 77.16 ppm for ^{13}C) and C_6D_6 (7.16 ppm for ^1H and 128.06 ppm for ^{13}C). 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 $^{13}C\{^1H\}$ deptq 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/$CDCl_3$ solution. FTIR (ATR) spectra were recorded on a Shimadzu spectrophotometer. For full experimental data of all compounds, see supporting information.

Preparation of [Au(NHC)(CH_2COCH_3)] (2a-b), route A Scheme 3: A mixture of NHC·HCl (1 equiv.), [Au(SMe_2)(Cl)] (1 equiv.) and K_2CO_3 (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 CH_2Cl_2 (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)(CH_2COCH_3)] as a microcrystalline white solid.

Preparation of [Au(NHC)(CH_2COCH_3)] (2a-g), route B Scheme 3: A mixture of [Au(NHC)(Cl)] (1 equiv.) and K_2CO_3 (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 CH_2Cl_2 (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)(CH_2COCH_3)] as a microcrystalline white solid.

Preparation of [Au(IPr)(CH_2COCH_3)] (2a), route C Scheme 3: [Au(IPr)(OH)] (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 CH_2Cl_2 (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)(CH_2COCH_3)] as a microcrystalline white solid in 90% yield.

[Au(IPr)(CH_2COCH_3)] (1,3-bis(2,6-di*iso*propylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(2-oxopropyl)gold (2a): Complex **2a** was synthesized following **route A** using IPr·HCl (800 mg, 1.82 mmol, 1 equiv.), [Au(SMe_2)(Cl)] (554.37 mg, 1.82 mmol, 1 equiv.), K_2CO_3 (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)] (200 mg, 1.82 mmol, 1 equiv.) and K_2CO_3 (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, $CDCl_3$): δ = 7.49 (t, *J* = 7.8 Hz, 2H, CH aromatic IPr), 7.28 (d, *J* = 7.8 Hz, 4H, CH aromatic IPr), 7.13 (s, 2H, CH imidazole IPr), 2.56 (sept, *J* = 6.9 Hz, 4H, C<u>H</u>$(CH_3)_2$), 2.06 (s, 2H, CH_2), 1.53 (s, 3H, CH_3), 1.32 (d, *J* = 6.9 Hz, 12H, CH($C\underline{H}_3$)$_2$), 1.21 (d, *J* = 6.9 Hz, 12H, CH($C\underline{H}_3$)$_2$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 212.12 (C=O), 193.06 (C carbene), 145.83 (CH aromatic IPr), 134.42 (CH aromatic IPr), 130.47 (CH aromatic IPr), 124.41 (CH aromatic IPr), 124.15 (CH aromatic IPr), 122.81 (CH imidazole IPr), 40.71 (CH_2), 29.54 (CH_3), 28.88 ($\underline{C}H(CH_3)_2$), 24.53 (CH($\underline{C}H_3$)$_2$), 24.11 (CH($\underline{C}H_3$)$_2$); elemental analysis calcd (%): C 55.98 H 6.58, N 4.35; found: C 55.97, H 6.38, N 4.37; FTIR (ATR) ν = 1643 (C=O) cm^{-1}.

[Au(IMes)(CH_2COCH_3)] (1,3-dimesityl-2,3-dihydro-1H-imidazol-2-yl)(2-oxopropyl)gold (2b): Complex **2b** was synthesized following using IMes·HCl (800 mg, 2.34 mmol, 1 equiv.), [Au(SMe_2)(Cl)] (172.8 mg, 0.58 mmol, 1 equiv.), K_2CO_3 (1.95 g, 3.52 mmol, 6 equiv.) in acetone (10 mL). The reaction was stirred for 72 h at 60 °C. The desired product was obtained as a white solid in 68% yield (891.31 mg, 1.59 mmol). Complex **2b** was also synthesized following **route B** using [Au(IMes)(Cl)] (200 mg, 0.373 mmol, 1 equiv.) and K_2CO_3 (g, 3.52 mmol, 6 equiv.) in acetone (2 mL). The reaction was stirred for 72 h at 60 °C. The desired product was obtained as a white solid in 73% yield (151.62 mg, 0.27 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.04 (s, 2H, CH imidazole IMes), 7.00 (s, 4H, CH aromatic IMes), 2.34 (s, 6H, CH_3 *p*-phenyl IMes), 2.10 (s, 12H, CH_3 IMes), 2.09 (s, 3H, CH_2) 1.64 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 212.50 (C=O), 191.31 (C carbene), 139.47 (CH aromatic IMes), 134.92 (CH aromatic IMes), 129.34 (CH aromatic IMes), 41.13 (CH_2), 29.44 (CH_3), 21.26 (CH_3 *p*-phenyl IMes), 17.99 (CH_3 aromatic IMes); elemental analysis calcd (%): C 51.60, H 5.16, N 5.16; found: C 51.62, H 5.23, N 5.02; FTIR (ATR) ν = 1643 (C=O), cm^{-1}.

[Au(SIPr)(CH_2COCH_3)] 1,3-bis(2,6-di*iso*propylphenyl)imidazolidin-2-yl)(2-oxopropyl)gold (2c): Complex **2c** was synthesized following **route B** using [Au(SIPr)(Cl)] (100 mg, 0.16 mmol, 1 equiv.) and K_2CO_3 (138.88 mg, 3.52 mmol, 6 equiv.) in acetone (2 mL). The reaction was stirred for 72 h at 60 °C. The desired product was obtained as a white solid in 97% yield (100 mg, 0.156 mmol). ^1H NMR (300 MHz,$CDCl_3$) δ = 7.40 (dd, *J* = 8.3 Hz, 7.2 Hz, 2H, CH aromatic SIPr), 7.23 (d, *J* = 7.7 Hz, 4H, CH aromatic SIPr), 4.00 (s, 4H, CH imidazole SIPr), 3.06 (sept, *J* = 6.9 Hz, 4H, C<u>H</u>$(CH_3)_2$), 1.99 (q, *J* = 0.9 Hz, 2H, CH_2), 1.44 (d, *J* = 0.9 Hz, 12H, CH_3), 1.39 (d, *J* = 6.8 Hz, 12H, CH($C\underline{H}_3$)$_2$), 1.33 (d, *J* = 7.0 Hz, 12H, CH($C\underline{H}_3$)$_2$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 212.39 (C=O), 212.01 (C carbene), 146.83 (CH aromatic SIPr), 134.49 (CH aromatic SIPr), 129.75 (CH aromatic SIPr), 124.50 (CH aromatic SIPr), 53.72 (CH_2 imidazole SIPr), 41.00 (CH_2), 29.42 ($C\underline{H}(CH_3)_2$), 29.06 (CH_3), 25.11 (CH_3), 24.25 (CH_3); elemental analysis calcd (%): C 55.88, H 6.79, N 4.42; found: C 55.90, H 6.72, N 4.35; FTIR (ATR) ν = 1643 (C=O) cm^{-1}.

[Au(SIMes)(CH_2COCH_3)] 1,3-dimesitylimidazolidin-2-yl)(2-oxopropyl)gold (2d): Complex **2d** was synthesized following **route B** using [Au(SIMes)(Cl)] (100 mg, 0.58 mmol, 1 equiv.) and K_2CO_3 (486.51 mg, 3.52 mmol, 6 equiv.) in acetone (2 mL). The reaction was stirred for 72 h at 60 °C. The desired product was obtained as a white solid in 73% yield (75.76 mg, 0.13 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.95 (s, 4H, CH aromatic SIMes), 3.92 (s, 4H, CH_2 imidazole SIMes), 2.31 (s, 12H, CH_3 aromatic SIMes), 2.29 (s, 6H, CH_3 *p*-phenyl SIMes), 2.02 (d, *J* = 0.8 Hz, 2H, CH_2), 1.54 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 212.49 (C=O), 211.58 (C carbene), 138.66 (CH aromatic SIMes), 135.81 (CH aromatic SIMes), 135.09 (CH aromatic SIMes), 129.61 (CH aromatic SIMes), 50.86 (CH_2 imidazole SIMes), 41.41 (CH_2), 29.30 (CH_3), 21.18 (CH_3 *p*-phenyl SIMes), 18.17 (CH_3 aromatic SIMes); elemental analysis calcd (%): C 51.43, H 5.58, N 5.00; found: C 51.35, H 5.71, N 4.97; FTIR (ATR) ν = 1645 (C=O) cm^{-1}.

[Au(IPr^{Cl})(CH_2COCH_3)] 4,5-dichloro-1,3-bis(2,6-di*iso*propylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(2-oxopropyl)gold (2e): Complex **2e** was synthesized following **route B** using [Au(IPr^{Cl})(Cl)] (100 mg, 0.145 mmol,

1 equiv.) and K_2CO_3 (120.2 mg, 0.870 mmol, 6 equiv.) in acetone (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).^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (t, *J* = 7.7 Hz, 2H, CH aromatic IPr^{Cl}), 7.31 (d, *J* = 7.8 Hz, 4H, CH aromatic IPr^{Cl}), 2.46 (2.45 (sept, *J*=6.8, 4H, C<u>H</u>$(CH_3)_2$), 2.06 (s, 2H, CH_2), 1.52 (s, 3H, CH_3), 1.32 (d, *J* = 6.8 Hz, 12H, CH(C<u>H</u>$_3)_2$), 1.25 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 212.13 (C=O), 193.01 (C carbene), 146.29 (CH aromatic IPr^{Cl}), 131.37 (CH aromatic IPr^{Cl}), 124.47 (CH aromatic IPr^{Cl}), 118.87 (CH aromatic IPr^{Cl}), 39.85 (CH_2), 29.56 (CH_3), 29.24 (C<u>H</u>$(CH_3)_2$), 24.60 (CH(C<u>H</u>$_3)_2$), 23.61 (CH(C<u>H</u>$_3)_2$); elemental analysis calcd (%): C 50.64, H 5.53, N 3.94; found: C 50.52, H 5.47, N 3.99; FTIR (ATR) ν = 1651 (C=O) cm^{-1}.

[Au(IPr*)(CH$_2$COCH$_3$)] 1,3-bis(2,6-dibenzhydryl-4-methylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(2-oxopropyl)gold (2f): Complex **2f** was synthesized following **route B** using [Au(IPr*)(Cl)] (50 mg, 0.044 mmol, 1 equiv.) and K_2CO_3 (36.2 mg, 0.262 mmol, 6 equiv.) in acetone (2 mL). The reaction was stirred for 72 h at 60 °C. The desired product was obtained as a white solid in 92% yield (43.5 mg, 0.037 mmol).^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25 – 7.09 (m, 26H, Ph groups IPr*), 6.91 – 6.84 (m, 14H), 5.77 (s, 2H, CH imidazole IPr*), 5.32 (s, 4H, C<u>H</u>$(Ph)_2$), 2.33 (s, 2H, CH_2), 2.23 (s, 6H, CH_3 *p*-phenyl IPr*), 1.67 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 212.49 (C=O), 192.61 (C carbene), 142.84 (CH aromatic IPr*), 141.09 (CH aromatic IPr*), 139.91 (CH aromatic IPr*), 134.11 (CH aromatic IPr*), 130.13 (CH aromatic IPr*), 129.83 (CH aromatic IPr*), 129.46 (CH aromatic IPr*), 128.56 (CH aromatic IPr*), 128.45 (CH aromatic IPr*), 126.73 (CH aromatic IPr*), 126.71 (CH aromatic IPr*), 123.09 (CH imidazole IPr*), 51.29 (C<u>H</u>$(Ph)_2$), 41.37 (CH_2), 29.89 (CH_3), 21.98 (CH_3 *p*-phenyl IPr*); elemental analysis calcd (%): C 74.09, H 5.27, N 2.40; found: C 73.97, H 5.22, N 2.47. FTIR (ATR) ν = 1651 (C=O) cm^{-1}.

[Au(IAd)(CH$_2$COCH$_3$)] 1,3-di(adamantan-1-yl)-2,3-dihydro-1H-imidazol-2-yl)(2-oxopropyl)gold (2g): Complex **2g** was synthesized following **route B** using [Au(IAd)(Cl)] (50 mg, 0.088 mmol, 1 equiv.) and K_2CO_3 (72.9 mg, 0.527 mmol, 6 equiv.) in acetone (2 mL). The reaction was stirred for 72 h at 60 °C. The desired product was obtained as a white solid in 84% yield (43.26 mg, 0.073 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.02 (s, 2H, CH imidazole IAd), 2.64 (s, 2H, CH_2), 2.53 (d, *J* = 3.0 Hz, 13H. CH IAd), 2.25 (s, 6H, CH_2 IAd), 2.21 (s, 3H, CH_3), 1.76 (d, *J* = 3.2 Hz, 14H, CH IAd). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 213.09 (C=O), 186.55 (C carbene), 115.08 (CH imidazole IAd), 58.89 (CH IAd), 44.38 (CH IAd), 39.47 (CH IAd), 38.10 (CH_2), 36.04 (CH IAd), 30.06 (CH_2 IAd), 29.59 (CH_3); elemental analysis calcd (%): C 52.88, H 6.32, N 4.74; found: C 52.78, H 6.27, N 4.63; FTIR (ATR) ν = 1643 (C=O) cm^{-1}.

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[13] IPr = *N*, *N*'-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene;

[14] IMes = *N*, *N*'-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene;

[15] SIPr = *N*, *N*'-bis-(2,6-di*iso*propylphenyl)imidazolin-2-ylidene;

[16] SIMes = *N*, *N*'-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene.

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[38] IPr* = *N*, *N'*-1,3-bis(2,6-dibenzhydryl-4-methylphenyl)imidazol-2-ylidene;

[39] IAd = *N*, *N'*-diadamantylimidazol-2-ylidene;

[40] The assignements of the carbonyl groups of **2a-g** were made through HSQC and HMBC experiments.

[41] CCDC = CCDC 1039060 (**2b**), CCDC 1039061 (**2c**), CCDC 1039062 (**2e**), CCDC 1039063 (**2f**) and CCDC 1039064 (**2g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data%5Frequest/cif;

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Entry for the Table of Contents (Please choose one layout)

Layout 2:

FULL PAPER

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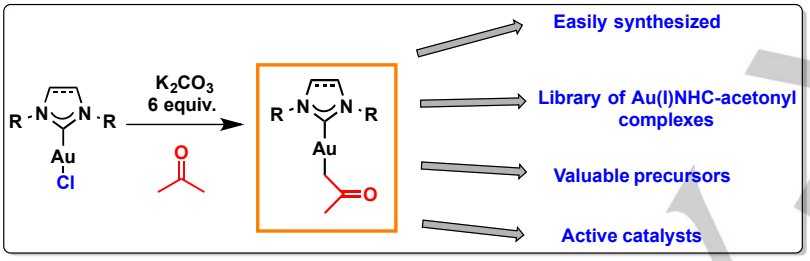
Page No. – Page No.

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



A library of [Au(NHC)(acetony l)] 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.