CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201002607

[{Au(IPr)}$_2$(μ-OH)]X Complexes: Synthetic, Structural and Catalytic Studies

Rubén S. Ramón,[a] Sylvain Gaillard,[a] Albert Poater,[b, c] Luigi Cavallo,[b]
Alexandra M. Z. Slawin,[a] and Steven P. Nolan*[a]

Abstract: The synthesis of a series of dinuclear gold hydroxide complexes has been achieved. These complexes of type [{Au(IPr)}$_2$(μ-OH)]X (X = BF$_4$, NTf$_2$, OTf, FABA, SbF$_6$; IPr = 2,6-bis(disopropylphenyl)imidazol-2-ylidene; NTf$_2$ = bis(trifluoromethanesulfonyl)imidate; OTf = trifluoromethanesulfonate; FABA = tetrakis(pentafluorophenyl)borate) are easily formed in the presence of water and prove highly efficient in the catalytic hydration of nitriles. Their facile formation in aqueous media suggests they are of relevance in gold-catalyzed reactions involving water. Additionally, a series of [Au(IPr)(NCR)][BF$_4$] (R = alkyl, aryl) complexes was synthesized as they possibly occur as intermediates in the catalytic reaction mechanism. ^{1}H and ^{13}C NMR data as well as key bond lengths obtained by X-ray diffraction studies are compared and reveal an interesting structure–activity relationship. The collected data indicate a negligible effect of the nature of the nitrile on the reactivity of [Au(L)(NCR)][X] complexes in catalysis.

Keywords: gold · homogeneous catalysis · hydration · N-heterocyclic carbenes · nitriles

Introduction

The last decade has witnessed enormous activity in the area of homogenous gold catalysis allowing for significant developments in organic synthesis.[1] Earliest catalysts were simple gold salts such as AuCl$_3$, NaAuCl$_4$, and AuCl. More sophisticated organogold complexes bearing either phosphane or N-heterocyclic carbene (NHC)[2] ligands have gained popularity in recent years, but still require the use of a silver activator to enable catalysis.[3,4] The resulting active species is postulated to be a cationic Au^I complex.[4b] The first such species was isolated and characterized because of the stabilising effect imparted by the supporting NHC ligand.[5]

Recently, research into mechanistic aspects of gold catalysis has permitted useful synthetic insights. Isolating reactive intermediates involved in gold-based catalytic cycles is highly relevant to the development and evaluation of accurate mechanistic hypotheses.[6] In the course of investigations on gold-mediated transformations, some of which involved water, computational results suggested the viability of a [Au(IPr)(OH)] (**1**; IPr = 2,6 bis(disopropylphenyl)imidazol-2-ylidene) "intermediate".[7] Successes in catalytic transformations such as the Meyer–Schuster rearrangement of propargylic alcohols to conjugated enones[7a] and the hydration of nitriles to amides[8] made clear the next synthetic approach: the synthesis and isolation of **1**. This task was undertaken to hopefully permit these transformations in a more efficient way and with a catalytically more relevant entity, circumventing the need for silver co-catalysts. It would also address experimentally the hypothesis of the involvement of **1** as an intermediate in aqueous gold catalysis.

The synthesis and complete characterization of [Au(IPr)(OH)] (**1**) was achieved recently.[9] Complex **1** proved to be an excellent precursor to a plethora of new gold species, but exhibited only moderate catalytic efficacy in nitrile hydration and Meyer–Schuster rearrangement. In the course of recent NMR studies and upon acid activation of **1**, the gold complex [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2**) was isolated and its formation as a function of acid was investigated.[10] Encouraged by the reactivity of **2** in various gold-catalyzed transformations in terms of reactivity and stability, a series

---

[a] R. S. Ramón, Dr. S. Gaillard, Prof. Dr. A. M. Z. Slawin,
Prof. Dr. S. P. Nolan
EaStCHEM School of Chemistry
University of St Andrews, North Haugh
St Andrews, KY16 9ST (UK)
Fax: (+44) 01334463808
E-mail: snolan@st-andrews.ac.uk

[b] Dr. A. Poater, Prof. L. Cavallo
Dipartimento di Chimica, Università di Salerno
Via ponte don Melillo, 84084, Fisciano (SA) (Italy)

[c] Dr. A. Poater
Catalan Institute for Water Research (ICRA), H2O Building
Scientific and Technological Park of the University of Girona
Emili Grahit 101, 17003 Girona (Spain)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002607.

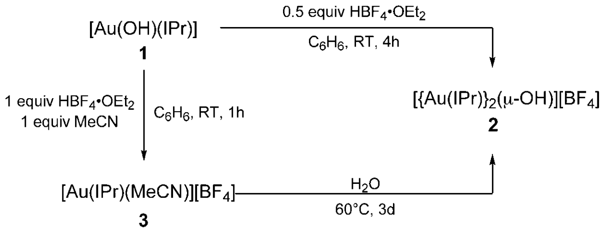
of [{Au(IPr)}$_2$(μ-OH)][X] (X = BF_4, NTf_2, OTf, FABA, and SbF_6; NTf_2 = bis(trifluoromethanesulfonyl)imidate; OTf = trifluoromethanesulfonate; FABA = tetrakis(pentafluorophenyl)borate) complexes was synthesized and applied to the hydration of nitriles in order to evaluate possible counteranion effects. The formation of [{Au(IPr)}$_2$(μ-OH)][X] and their stability/reactivity have been further investigated by DFT calculations and deactivation patterns in the nitrile hydration have been identified.

Results and Discussion

The synthesis of **2** can be achieved using a number of approaches (Scheme 1) that were revealed upon workup of the water-insoluble [Au(IPr)(CH_3CN)][BF_4] (**3**). In the initial synthetic route, stirring **3** in water at 60 °C for three days, in air, led to the formation of **2** in high yield.[11] Attempted extraction of **2** from the aqueous mother liquor with CH_2Cl_2 proved critical, as it re-converted **2** into **3** (see Supporting Information). However, washing the organic phase with water led to the isolation of pure **2**. A more economical (and practical) synthetic route[12] is to take advantage of the versatile synthon [Au(IPr)(OH)] (**1**) and its straightforward reaction with 0.5 equivalents $HBF_4 \cdot OEt_2$ in benzene at room temperature for 4 h to produce **3** in 90 % isolated yield.[13]

Interestingly, **1** can also function as a precursor to [Au(IPr)(CH_3CN)][BF_4] (**3**) under anhydrous conditions and without the use of costly light- and moisture-sensitive silver salts. Complex **1** reacts with one equivalent $HBF_4 \cdot OEt_2$ in the presence of one equivalent of acetonitrile to afford complete conversion into **3** (Scheme 1).[14] NMR studies on the acid activation of **1** are consistent with the sensitive equilibrium between these gold complexes determined by acid, water concentration, and the solvent used.[10]

To investigate the effect of the counteranion, a series of analogue complexes in which X = NTf_2 (**4**), OTf (**5**), FABA (**6**), and SbF_6 (**7**) was synthesized (for the solid state structures of **5**–**7**, see Figure 1). Of note, **4** has been recently reported and successfully applied in the Meyer–Schuster rearrangement.[15] Satisfyingly, all catalysts were obtained in good to excellent yields by using the synthetic protocol described to synthesize **2**. However, attempts to synthesize the PF_6 or succinimide analogues gave a mixture of products (X = PF_6) or a monogold complex (X = succinimide), respectively.



Scheme 1. Synthetic routes to [Au(IPr)(CH_3CN)][BF_4] **3** and [{Au(IPr)}$_2$(μ-OH)][BF_4] **2**.

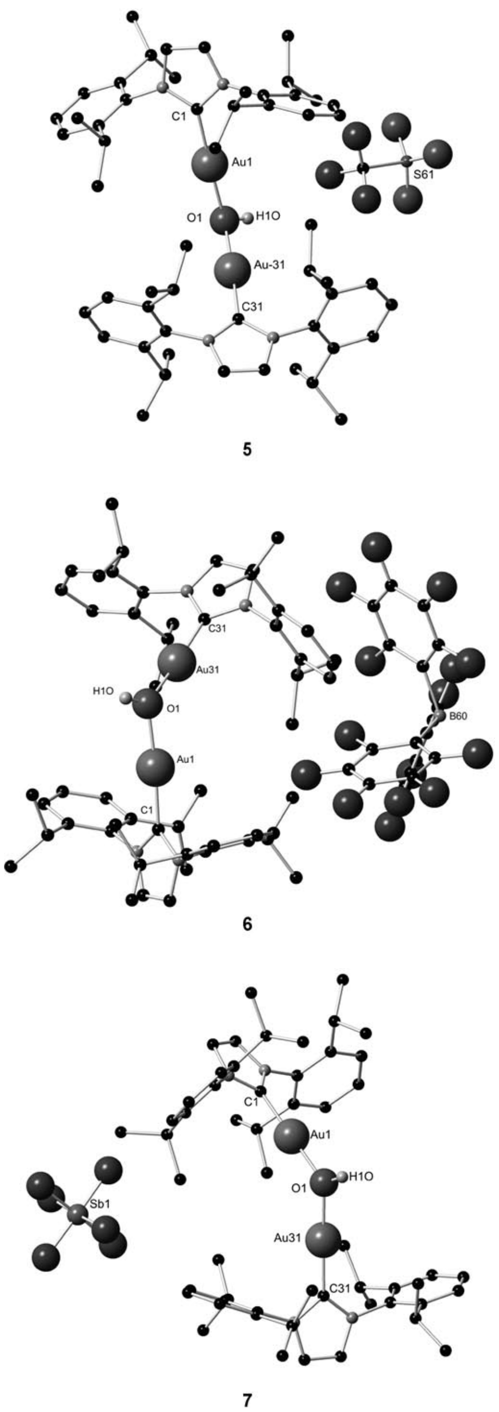


Figure 1. X-ray structures of (from left to right) [{Au(IPr)}$_2$(μ-OH)][X] (X = OTf (**5**), FABA (**6**), SbF_6 (**7**)). Selected bond lengths [Å] and angles [°] for **5**: Au1–O1 2.052(3), O1–Au31 2.042(4), Au1–C1 1.972(5), Au31–C31 1.961(5), Au31-O1-Au1 124.18(17), O1–H1O 0.95(2); for **6**: Au1–O1 2.040(4), O1–Au31 2.049(4), Au1–C1 1.961(6), Au31–C31 1.951(5), Au31-O1-Au1 118.5(2), O1–H1O 0.96(2); for **7**: Au1–O1 2.026(8), O1–Au31 2.055(8), Au1–C1 1.943(11), Au31–C31 1.957(11), Au31-O1-Au1 127.6(4), O1–H1O 0.9800.

Additionally, DFT calculations were used to shed light on the energetics of these transformations. Firstly, the binding of nitriles and water to $[Au(IPr)]^+$ is highly competitive (the bond dissociation energies (BDE) of MeCN, PhCN, and H_2O in CH_2Cl_2 are 31.0, 30.8 and 31.0 kcal mol^{-1}, respectively). This suggests that in aqueous solution, the large excess of water present should completely displace the nitrile in **3**. Secondly, the **1**→**3** transformation in Scheme 1 is favored by 14.7 kcal mol^{-1} in benzene. Thirdly, the **1**→**2** transformation in Scheme 1 is favored by 16.7 kcal mol^{-1} in benzene.

DFT calculations were also carried out on the structure and nature of **2**. The optimized computationally obtained structure of **2**[16] is in good agreement with its X-ray structure.[10] Focusing on a comparison between the DFT structures of **1** and **2**, the Au–O bond is slightly shorter in **1** (by 0.08 Å), whereas the O–H bond does not significantly vary (0.002 Å longer in **1**). These essentially unaltered distances suggest a similar bonding scheme is present in **1** and **2**. However, Mayer bond order (MBO)[17] within natural population analysis (NPA)[18] indicates remarkable changes. The MBO of the Au–O bonds in **2** (0.60) is almost half that found in **1** (1.16). In contrast, the MBO of the O–H bond is slightly reduced, from 0.92 in **1** to 0.86 in **2**. This indicates that dimer formation principally affects the Au–O bond rather than the O–H bond. Furthermore, a non-negligible MBO (0.14) is present between the Au centers, indicative of an interaction between the two [Au(IPr)] moieties. NPA decomposition indicates that donation occurs from each [Au(IPr)] σ-bond into an empty acceptor p_z MO on the other Au center (one of the interactions is illustrated in Figure 2). An estimate of this donor–acceptor interaction energy, in the framework of second-order perturbation theory, $E(2)$, amounts to 8.7 kcal mol^{-1}. This bimetallic cooperativity, together with the short Au···Au distance derived from the X-ray structure, indicates an intriguing deviation from the classical isolobal analogy between Au^+ and H_3O^+.

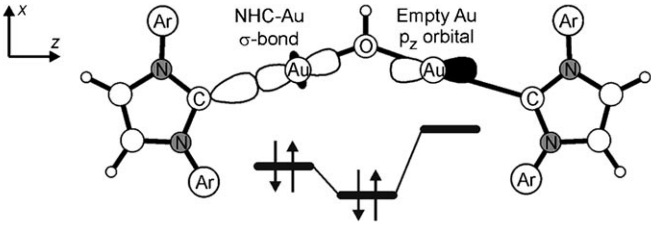


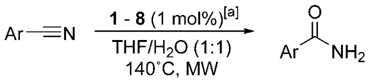
Figure 2. Schematic representation of the (IPr)Au··Au interactions and of the molecular orbitals involved.

The stability of **2** towards various dissociation pathways was examined next. Possible dissociation of **2** to **1**+[Au(IPr)][BF_4] is disfavored by 11.5 kcal mol^{-1} in benzene. Key to the stability of **2** is the weak coordinating ability of $[BF_4]^-$ in benzene, the BDE of BF_4^- to $[Au(IPr)]^+$ is 81.5 kcal mol^{-1} lower than that of OH^-. Furthermore, the stability of **2** towards water was examined. Aqueous dissociation of a Au fragment in **2** to **1**+$[Au(IPr)(OH_2)]^+ + [BF_4]^-$ is favored by 1.0 kcal mol^{-1}. In contrast, proton transfer from **2** to a water molecule to give $[\{Au(IPr)\}_2(\mu\text{-}O)] + H_3O^+$, is energetically disfavored by 47.0 kcal mol^{-1}, indicating that the weak links in **2** are the Au–O bonds.

The ease with which these transformations can be accomplished, and the calculated DFT energetic are suggestive of an equilibrium between $[Au(IPr)(CH_3CN)][BF_4]$ and $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ in aqueous media. Mechanistically, this implicates the direct involvement of a species such as **2** in catalysis involving water and cationic gold entities.[19]

With the series of catalysts in hand, their activity was tested in the hydration of nitriles. Recent investigations have determined $[Au(IPr)(NTf_2)]$[4a] (**8**) to be the most effective Au catalyst under optimized conditions (microwave heating).[8a,20] To adequately follow the reaction, the catalyst loading was lowered to 1 mol % gold and conversions were monitored by GC. Results of other relevant gold catalysts as well as in situ activated catalysts have been added to complete the screening (Table 1). No significant difference between the $[\{Au(IPr)\}_2(\mu\text{-}OH)][X]$ catalysts was observed. With the exception of **8**, which showed slightly poorer catalytic performance, and **1**, which afforded poor overall yields,[21] all catalysts showed comparable catalytic activity.[22] Using 10 % $HBF_4{\cdot}OEt_2$ in the absence of gold led to no conversion, even after 3 h. It is of interest that $[Au(IPr)(CH_3CN)][BF_4]$ (**3**) displays higher activity than **8**, as this is in contrast to the current results in nitrile hydration.[23] It was reasoned that under the reaction conditions (THF/H_2O 1:1), $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ (**2**) easily forms in situ from **3** to outperform **8**. The better coordinating NTf_2 ligand prevents the conversion of **8** to the corresponding $[\{Au(IPr)\}_2(\mu\text{-}OH)][NTf_2]$ (**4**) at ambient temperature.

Table 1. Conversions [%] of various gold systems in the hydration of nitrile.



Catalyst	Conv (0.25 h)	Conv (0.5 h)	Conv (0.75 h)	Conv (1 h)	Conv (2 h)	Conv (3 h)
$[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ **2**	37	44	54	61	79	89
$[\{Au(IPr)\}_2(\mu\text{-}OH)][OTf]$ **5**	37	48	57	62	80	88
$[\{Au(IPr)\}_2(\mu\text{-}OH)][SbF_6]$ **7**	37	51	62	70	87	93
$[\{Au(IPr)\}_2(\mu\text{-}OH)][FABA]$ **6**	39	52	61	71	85	94
$[\{Au(IPr)\}_2(\mu\text{-}OH)][NTf_2]$ **4**	38	53	60	68	83	90
[Au(OH)(IPr)] **1** + 0.5 HBF_4	31	43	52	59	75	84
[Au(OH)(IPr)] **1** + 1.5 HBF_4	36	50	59	66	84	91
$[Au(IPr)(CH_3CN)][BF_4]$ **3**	39	51	62	71	83	91
$[Au(NTf_2)(IPr)]$ **8**	19	28	44	58	74	87
[Au(OH)(IPr)] **1**	9	10	12	12	12	17
HBF_4	0	0	0	0	0	0

[a] Relative to the amount of gold used.

To support this hypothesis, the proposed equilibrium between complexes **3** and **2** in aqueous reaction media was examined.

When **3** is dissolved in CH_2Cl_2 and the resulting solution simply washed with water (3 times), **2** is formed in 96% yield. Since this reaction appears facile, the formation of **2** from [AuCl(IPr)] was also investigated. Chloride abstraction with $AgBF_4$ generates the putative $[Au(IPr)]^+[BF_4]^-$ species, and after removal of AgCl by filtration through Celite the organic phase was washed three times with water, in a similar manner as above. Recrystallization from CH_2Cl_2/pentane afforded **2** in 81% yield. The rapid and straightforward formation of **2** in aqueous media and similar conversion rates in nitrile hydration strongly support the conclusion that **2** is an important gold species in reactions containing water. To further support this hypothesis, [AuCl(IPr)] was dissolved in CD_2Cl_2 and activated with $AgBF_4$. After separating the precipitated AgCl, D_2O (50 μL) was added to the solution and a ^1H NMR sprectrum of the resulting solution was recorded. $[\{Au(IPr)\}_2(\mu\text{-}OD)][BF_4]$ was formed in 75% yield upon addition of D_2O. The remaining 25% appeared to be "bare" $[Au(IPr)]^+[BF_4]^-$. Additionally, we simulated reaction conditions in a ^1H NMR experiment using $[D_8]THF/D_2O$, confirming the formation of significant amounts of complex **2**. Interestingly, repeating the ^1H NMR experiment in coordinating $[D_6]DMSO$ yielded the $[D_6]DMSO$ complex quantitatively. The structure of the analogue $[Au(IPr)(dmso)][BF_4]$ (**9**) was confirmed by X-ray diffraction (see Figure 3). While these observations are not direct evidence for the active involvement of **2** in the catalytic cycle, it strongly suggests that **2** might be a relevant catalytic resting state in aqueous media. Furthermore, the excellent reactivity of $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ in catalysis excludes it as a deactivation intermediate, rather stating that this species might have a catalytically more active role appears more appropriate.

With the formation of **2** excluded as a deactivation route, possible alternatives were considered. Referring to the dramatically decreased reaction rate with increasing product formation, amido complexes have been considered as culprites. In a first approach, a 1:1 reaction of **4** and acetonitrile was conducted at 100 °C for 5 h in order to recover the catalyst at the end of the reaction. The corresponding ^1H NMR showed the formation of acetic acid and signals for two different and unknown [Au(IPr)] species. X-ray diffraction revealed the formation of $[\{Au(IPr)\}_2(MeCOO)][NTf_2]$ (**10**). For metal-catalyzed nitrile hydration, the unusual formation of carboxylic acid is rationalized by the stoichiometric amount of catalyst used. However, the formation of **10** strongly suggested to us the need to synthesize the amido complexes [Au(IPr)(NHCOPh)] (**11**) and $[\{Au(IPr)\}_2(PhCONH)][BF_4]$ (**12**). Using **1** and benzamide in stoichiometric amounts yielded **11** in 70% yield, as a 3:1 mixture of isomers. Under standard reaction conditions, **11** displayed very poor conversions in nitrile hydration, thus explaining the low reactivity of **1**. The most evident synthetic approach to **12**, namely the reaction of $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ with benzamide, led to the desired complex **12** in 81% yield.

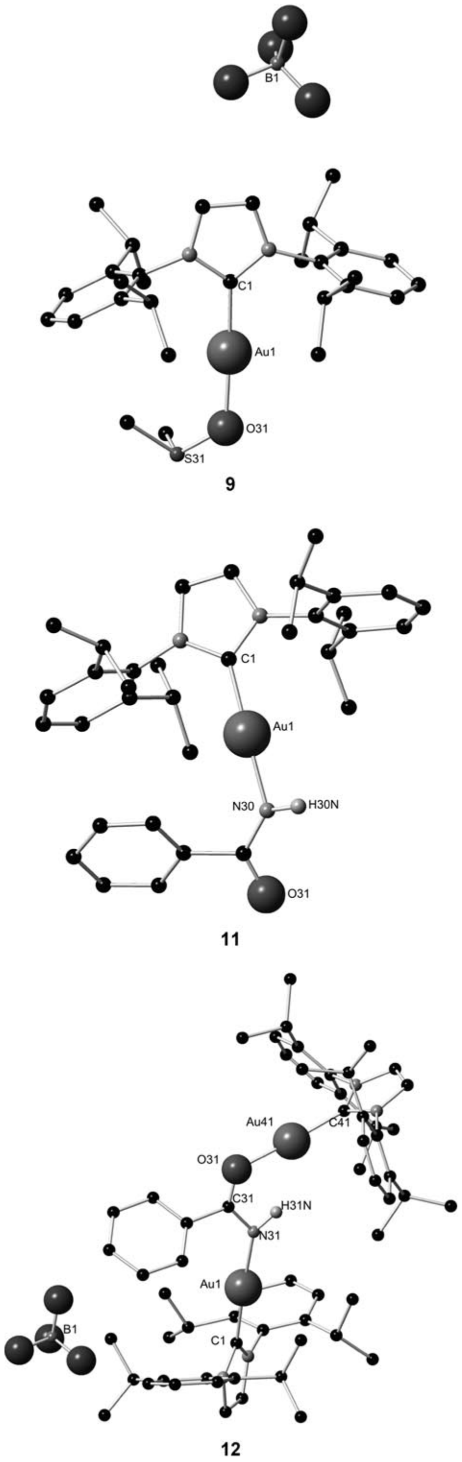
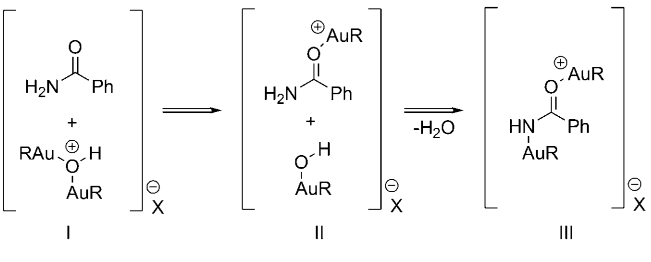


Figure 3. X-ray structures of (from left to right) $[Au(IPr)(DMSO)][BF_4]$ (**9**), [Au(NHCOPh)(IPr)] (**11**), and $[\{Au(IPr)\}_2(PhCONH)][BF_4]$ (**12**). Selected bond lengths [Å] and angles [°] for **9**: Au1−C1 1.951(4), Au1−O31 2.057(3), O31−S31 1.536(3), C1-Au1-O31 174.66(15), S31-O31-Au1 122.56(17); for **11**: Au1−C1 1.973(11), Au1−N30 2.015(10), N30−H30N 0.97(2), C1-Au1-N30 174.4(4), C31-N30-Au1 132.8(9), C31-N30-H30N 130(6), Au1-N30-H30N 97(6), O31-C31-N30 125.1(12); for **12**: Au1−C1 1.983(7), Au1−N31 2.030(6), N31−H31N 0.97(2), Au41−C41 1.965(7), O31−Au41 2.023(5), C1-Au1-N31 176.7(2), C31-N31-Au1 130.7(5), C31-N31-H31N 91(6), Au1-N31-H31N 138(7), O31-C31-N31 125.0(6), C41-Au41-O31 176.1(2), C31-O31-Au41 125.0(4).

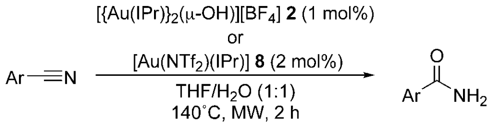
Interestingly, X-ray crystallographic studies on **11** and **12** revealed that the spatial location of the amido proton is significantly influenced by the gold centers (Figure 3). In **11**, the C31-N30-H30N angle is 130° and Au1-N30-H30N is 97°, whereas in **12** a strong orientation of the proton towards the oxo-coordinating gold center is observed (C31-N31-H31N, 91°, Au1-N31-H31N, 138°). Application of **12** in nitrile hydration as well as the addition of one equivalent of *p*-chlorobenzamide to a standard reaction using catalyst **2** resulted in very poor conversions. It appears plausible that the amide product poisons the reaction by trapping the active catalyst, resulting in a decreased reaction rate with progressing conversion. This fact appears to limit catalyst loadings to amounts above 1 mol% Au. Moreover, neither structure **11** or **12** can possibly act as an intermediate in the catalytic cycle. If so, a drop of reactivity should be noted after the very first cycle, but this is not the observed. In addition to acting in a deactivation manner, the formation of **12** from **2** presents another interesting aspect. While catalytic results does not correspond well with typical mechanistic approaches involving a metal hydroxide acting as a nucleophile,[24] it represents a rare example of a catalyst with dual reactivity. On the one hand, there is the [Au(IPr)(OH)] moiety acting as a base and deprotonating the amide, while the [Au(IPr)][BF$_4$] moiety coordinates through the oxygen atom. This is in fairly good agreement with a proposal by Toste et al. that deals with an equilibrium of tris[phosphinegold(I)]oxonium in the presence of allenynes in cycloisomerization.[25] A direct application of this proposal to reactions of digold complexes with amides would explain the observed formation of complex **12** (Scheme 2, I–III).

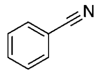
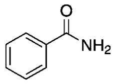
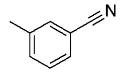
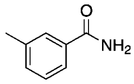
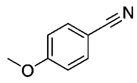
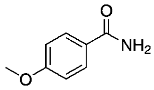
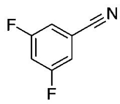
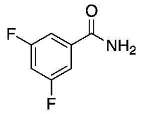
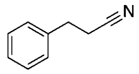
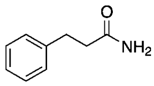
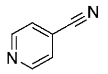
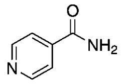
The excellent catalytic activity of **2** having been confirmed, a narrow reaction scope was examined with representative nitrile substrates. As shown in Table 2, good to excellent conversions were obtained for all substrates tested. Substrates that gave good conversions with **8** resulted in nearly quantitative conversion with **3** (Table 2, entries 1-4). Furthermore, substrates that proved problematic in reactions mediated by **8** were tested in order to gauge the efficacy of **3**. Using 3-phenylpropanenitrile, the corresponding amide (Table 2, entry 5) was obtained in excellent conversion (90%) compared to the previously obtained 30% when **8** was used. Moreover, with 2.5 mol% **2**, isonicotinonitrile (Table 2, entry 6) afforded 75% yield of the desired amide after 6 h, while using 5 mol% **8** only led to a low 31% conversion.



Scheme 2. Analogy for a proposal of Toste et al. for an equilibrium of tris[phosphinegold(I)]oxonium in the presence of allenynes in cycloisomerization with complexes **2**, **4–7** with amides.

Table 2. Scope of nitrile hydration using [{(Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2**) and [Au(NTf$_2$)(IPr)] (**8**).[8a]



	Substrate	Product	Conv [%] with **2**	Conv [%] with **8**
1			98	99
2			97	82
3			94	76
4			100	100
5			90[a]	30[b]
6			75[c]	31[d]

[a] 2.5 mol% **2** [b] 5 mol% **8** [c] 2.5 mol% **2**, 6 h [d] 5 mol% **8**, 6 h.

The nature of the substituents on a nitrile substrate, next to the nature of the metal center, influences the reactivity of the nitrile in hydrolysis.[26] Electron-acceptor groups improve the hydration on metal-bound nitriles.[27] This trend was also recognized for the gold catalysts.[8a] The synthesis of gold catalysts bearing nitrile ligands is well-known.[4c,5a,c] As these complexes can be considered intermediates in the hydration of nitrile mechanistic cycle, a series of ten representative [Au(IPr)(NCR)][X] complexes was synthesized in order to possibly correlate the reactivity of the nitrile with relevant ^{1}H and ^{13}C NMR shifts and bond length data obtained by X-ray diffraction (Table 3).

Of note, several attempts to synthesize benzonitrile complexes bearing strong electron-withdrawing substituents, such as NO$_2$, with the devloped procedures remained unsuccessful. As shown in Table 3, benzonitrile ligands bearing electron-donating substituents tend to lead to a slight downfield shift of the carbenic carbon resonance. The proton shift on the imidazolylidene backbone appears too minor for an adequate interpretation. By analogy, a comparison of the Au–N and N≡C bond lengths confirmed the lack of significant effects of the nitrile substituents. In the case of **21** and **22**, X-ray diffraction revealed, as expected, a preferred coordination of the gold center to the pyridine moiety[28] involving a decreased reactivity of those heterocycles in nitrile hydration. Interestingly, the Au–N distance is higher than in the complexes coordinating through a nitrile. The decrease

Table 3. Characteristic shifts and bond distances of complexes **13**–**22**.

	$[Au(IPr)(R)][BF_4]$		δ ($C_{carbene}$) [ppm]	δ ($H_{backbone}$) [ppm]	Au–N [Å]	N≡ [Å]
1	R=NCPh	**13**	165.5	7.48	2.018(7)[a]	1.141(10)[a]
2	$R=NCC_6H_4CH_3$	**14**	165.6	7.51	2.011(4)[a]	1.136(5)[a]
3	$R=NCC_6H_4N(CH_3)_2$	**15**	166.4	7.49	2.04(2)	1.15(3)
4	$R=NCC_6H_4OCH_3$	**16**	166.1	7.48	2.013(5)	1.146(7)
5	$R=NCC_6H_3(CH_3)_2$	**17**	165.4	7.57[b]	2.014(10)	1.147(14)
6	R=NCPhBr	**18**	165.6	7.46	2.015(3)	1.143(4)
7	$R=NCC_6H_4(COCH_3)$	**19**	165.3	7.46	n.d.[c]	n.d.[c]
8	$R=NCC(CH_3)_3$	**20**	165.3	7.47	2.023(7)	1.136(10)
9	R=2-cyanopyridine	**21**	166.0	7.43	2.064(3)[d]	1.136(5)[d]
10	R=4-cyanopyridine	**22**	166.2	7.42	2.056(5)[d]	1.142(8)[d]

[a] Bond length determined from one out two independent molecules. [b] Shift determined out of a multiplet. [c] Attempts to grow crystals remained unsuccessful. [d] 2- and 4-cyanopyridine are coordinated to the gold center through the pyridine moiety.

in reactivity is smaller for 2-cyanopyridine as the nitrile moiety is in direct proximity to the coordinated gold center, while in the case of 4-cyanopyridine the gold center is simply too remotely located. From a catalytic point of view, the choice of the nitrile ligand does not significantly influence catalytic reaction yields.[29] Therefore, other aspects, such as nitrile economic costs, toxicity, ease of preparation, and complex stability, should be key considerations in the preparation of [Au(L)(NCR)][X] complexes.

Conclusion

The high-yield synthesis of a dinuclear gold complex **2** has been achieved and this species has demonstrated high catalyst efficiency in the hydration of nitriles and also permitted an expansion of the reaction scope. Advantageously, this simple synthetic protocol makes use of the readily available synthon **1**. Using the air- and moisture stable **1**, a highly active catalytic species can be generated in situ and this methodology has proven exceedingly effective in the hydration of nitriles. The facile formation of **2** and **3** from **1** suggests a broader potential role of **1** and **2** as "pre-catalytic" species in gold-mediated transformations. Formation of **2** from **3** and $[AuCl(IPr)]/[AgBF_4]$ by simple addition of water strongly suggests **2** to be a reactive intermediate or relevant resting state in water-inclusive reactions. Mono- and di-gold complexes of benzamide have been isolated and proved ineffective in nitrile hydration. Finally, a series of $[Au(IPr)(NCR)][BF_4]$ complexes was synthesized in order to examine mechanistic arguments presented in the literature in the context of diverse reactivities involving nitrile substrates. data, as well as comparison of bond lengths obtained from X-ray diffraction studies do not clearly indicate any trend as to the optimum ligand to use; all appear equally competent. Reactivity involving heterocyclic nitriles such as cyanopyridines is clearly influenced by the coordination of the aromatic heteroatom to the gold center.

The simple use of a gold complex in conjunction with a protic acidic activator represents an attractive alternative to the use of gold halide complexes requiring a silver-based halide abstractor.

Experimental Section

If not otherwise stated, manipulations were performed under air. Solvents were of puriss grade and used as received. NMR spectra were collected on 400 MHz and 300 MHz spectrometers at ambient temperature in $CDCl_3$. Chemical shifts are given in parts per million (ppm) with respect to TMS. Chemical shifts of ^{19}F spectra are given in parts per million (ppm) with respect to $CFCl_3$.

Synthesis of $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ (3)

Route A: Complex **2** (2.0 g, 2.80 mmol) was suspended in water (3 mL, 167 mmol) and stirred at 60°C for 72 h in air. The reaction mixture was extracted with CH_2Cl_2 and the organic phase was washed four times with a large excess of water (20 mL) and dried over $MgSO_4$. The mixture was filtered and the volatiles were evaporated under reduced pressure. The resulting white crude product was recrystallized from CH_2Cl_2/pentane to give 1.71 g (96%) of a white microcrystalline solid.

Route B: Complex **1** (97 mg, 0.160 mmol) was dissolved in benzene (2 mL) and tetrafluoroboric acid/diethyl ether complex (11.0 μL, 0.080 mmol) was added by syringe. The reaction mixture was stirred 4 h at room temperature. Pentane was added to the reaction to precipitate the product as a white solid. The crude white product was recrystallized from CH_2Cl_2/pentane to give 92 mg (90%) of a white microcrystalline solid. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.50$ (t, $J=7.8$ Hz, 4H), 7.26 (s, 4H), 7.24 (d, $J=7.8$ Hz, 8H), 2.39 (sept, $J=6.9$ Hz, 8H), 1.19 (d, $J=6.9$ Hz, 24H), 1.11 ppm (d, $J=6.9$ Hz, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=162.6$, 145.4, 133.6, 130.7, 124.2, 124.1, 28.6, 24.4, 23.8 ppm; ^{19}F NMR (185 MHz, $CDCl_3$): $\delta=-154.90$, -154.85 ppm; elemental analysis calcd (%): C 50.87, H 5.77, N 4.39; found: C 51.06, H 5.27, N 4.36.

Synthesis of $[(Au(IPr)(CH_3CN)][BF_4]$ (2) from 1: Complex **1** (100 mg, 0.166 mmol) was dissolved in toluene (2 mL) and tetrafluoroboric acid/diethyl ether complex (0.023 mL, 0.166 mmol) was added by syringe. Then, acetonitrile (8.67 μL, 0.166 mmol) was added and the heterogeneous reaction mixture was stirred 2 h at room temperature. Pentane was added to precipitate 114 mg (96%) of a white microcrystalline solid the NMR data of which confirms the synthesis of **2**. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.58$ (t, $J=7.8$ Hz, 2H), 7.38 (s, 2H), 7.34 (d, $J=7.8$ Hz, 4H), 2.44 (sept, $J=6.9$ Hz, 4H), 2.39 (s, 3H), 1.29 (d, $J=6.9$ Hz, 12H), 1.24 ppm (d, $J=6.9$ Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=166.3$, 145.5, 133.0, 131.5, 124.8, 124.6, 121.0, 28.9, 24.7, 24.0, 2.7 ppm; ^{19}F NMR (185 MHz, $CDCl_3$): $\delta=-154.98$, -153.92 ppm.

Synthesis of $[\{Au(IPr)\}_2(\mu\text{-}OH)][NTf_2]$ (4): Trifluoromethanesulfonimide (73 mg, 0.260 mmol) was dissolved under N_2 in anhydrous toluene (2 mL) and complex **1** (313 mg, 0.519 mmol) was added. The reaction mixture was stirred overnight at room temperature. Pentane (10 mL) was added to the reaction to ensure complete precipitation of the product. The white solid was collected by filtration, washed with pentane (2×5 mL) and dried under vacuum to give 381 mg (100%) of a white microcrystalline solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.49$ (t, $J=7.8$ Hz, 4H), 7.26–7.20 (m, 12H), 2.37 (sept, $J=6.8$ Hz, 8H), 1.17 (d, $J=6.8$ Hz, 24H), 1.11 ppm (d, $J=6.8$ Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=162.9$, 145.6, 133.7, 130.9, 124.3, 124.2, 120.1 (q, $J=321.7$ Hz), 28.8, 24.6, 23.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-79.2$ ppm; elemental analysis calcd (%): C 45.81, H 5.01, N 4.77; found: C 45.78, H 4.92, N 4.57.

Synthesis of $[\{Au(IPr)\}_2(\mu\text{-}OH)][OTf]$ (5): Triflic acid (5.5 μL, 0.06 mmol) was added to anhydrous toluene (2 mL) and complex **1** (75 mg, 125 μmol) was added. The reaction mixture was stirred overnight at room temperature. Pentane (2 mL) was added to the reaction to ensure complete precipitation of the product. The white solid was collected by filtration, washed with pentane (2×5 mL) and dried under vacuum to give 71 mg (85 %) of a white microcrystalline solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.50 (t, J=7.9 Hz, 4H), 7.25 (s, 4H), 7.24 (d, J=7.9 Hz, 8H), 2.39 (sept, J=6.9 Hz, 8H), 1.19 (d, J=6.9 Hz, 24H), 1.12 ppm (d, J=6.9 Hz, 24H); ^{13}C NMR (101 MHz, CDCl$_3$): δ=162.8, 145.4, 133.6, 130.7, 124.2, 124.1, 28.7, 24.5, 23.9 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ=−78.6 ppm; elemental analysis calcd (%): C 49.40, H 5.50, N 4.19; found: C 49.95, H 5.88, N 3.91.

Synthesis of [{Au(IPr)}$_2$(μ-OH)][FABA] (6): *N,N* -dimethylanilinium tetrakis(pentafluorophenyl)borate (DAN FABA) (33 mg, 0.04 mmol) was dissolved in anhydrous toluene (2 mL) and complex **1** (50 mg, 0.08 mmol) was added. The reaction mixture was stirred overnight at room temperature. Pentane (2 mL) was added to the reaction to ensure complete precipitation of the product. The white solid was collected by filtration, washed with pentane (2×5 mL) and dried under vacuum to give 73 mg (94 %) of a white microcrystalline solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.49 (t, J=7.8 Hz, 4H), 7.24 (d, J=7.8 Hz, 8H), 7.14 (s, 4H), 2.37 (sept, J=6.8 Hz, 8H), 1.17 ppm (d, J=6.9 Hz, 24H), 1.11 (d, J=6.9 Hz, 24H); ^{13}C NMR (101 MHz, CDCl$_3$): δ=163.3, 145.4, 133.5, 130.9, 124.3, 123.8, 28.7, 24.4, 23.8 ppm; ^{19}F NMR (282 MHz, CDCl$_3$): δ=−133.06, −163.95, −167.54 ppm; elemental analysis calcd (%): C 50.17, H 3.94, N 3.00; found: C 50.25, H 4.10, N 3.01.

Synthesis of [{Au(IPr)}$_2$(μ-OH)][SbF$_6$] (7): 65 wt % aqueous HSbF$_6$ (31 mg, 85 μmol) was added to toluene (2 mL) and complex **1** (103 mg, 170 μmol) was added. The reaction mixture was stirred overnight at room temperature. Pentane (2 mL) was added to the reaction to ensure complete precipitation of the product. The white solid was collected by filtration, washed with pentane (2×5 mL) and dried under vacuum to give 101 mg (83 %) of a white microcrystalline solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.50 (t, J=7.8 Hz, 4H), 7.24 (d, J=7.8 Hz, 8H), 7.22 (s, 4H), 2.39 (sept, J=6.8 Hz, 8H), 1.19 (d, J=6.8 Hz, 24H), 1.11 ppm (d, J=6.8 Hz, 24H); ^{13}C NMR (101 MHz, CDCl$_3$): δ=162.6, 145.5, 133.6, 130.7, 124.2, 124.1, 28.6, 24.4, 23.8 ppm; elemental analysis calcd (%): C 45.55, H 5.17, N 3.40; found: C 45.49, H 5.18, N 3.40.

Synthesis of [Au(IPr)(dmso)][BF$_4$] (9): In a NMR tube complex **2** (20 mg, 0.028 mmol) was diluted in DMSO (500 μL). NMR spectroscopy showed immediate full conversion. Volatile compounds were separated under low pressure to obtain colorless microcrystalline solid in quantitative yield (21 mg, 99 %). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ=7.95 (s, 2H), 7.58 (t, J=7.9 Hz, 2H), 7.41 (d, J=7.9 Hz, 4H), 2.39 (sept, J=6.8 Hz, 4H), 1.22 (d, J=6.8 Hz, 12H), 1.17 ppm (d, J=6.8 Hz, 12H); ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ=160.9, 145.3, 133.5, 130.9, 125.4, 124.3, 28.4, 24.0, 23.6 ppm; ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ=−148.63, −148.68 ppm; elemental analysis calcd (%): C 46.04, H 5.64, N 3.70; found: C 45.71, H 5.50, N 3.53.

Synthesis of [Au(IPr)(NHCOPh)] (11): Complex **1** (50 mg, 0,083 mmol) was dispersed in toluene (2 mL) and benzamide (10 mg, 0,083 mmol) was added. The reaction mixture was stirred overnight at RT. Then, pentane (2 mL) was added and precipitate was collected by filtration, washed with pentane (3×5 mL), and dried under reduced pressure to obtain a colorless solid (51 %, 87 mg).

Synthesis of [{Au(IPr)}$_2$(PhCONH)][BF$_4$] (12): Complex **3** (25 mg, 0.02 mmol) was dispersed in toluene (3 mL) and benzamide (2.4 mg, 0.02 mmol) added. The reaction mixture was stirred overnight at RT. Then, pentane (2 mL) was added and the precipitate was collected via filtration, washed with pentane (3×5 mL) and dried under reduced pressure to obtain a colorless solid (81 %, 22 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.59 (t, J=7.9 Hz, 2H), 7.40 (s, 2H), 7.36 (t, J=7.9 Hz, 2H), 7.31 (d, J=7.9 Hz, 4H), 7.25 (s, 2H) 7.17 (d, J=7.9 Hz, 4H), 6.78 (t, J=7.9 Hz, 2H), 5.13 (s, 1H), 2.45 (m, 8H), 1.27–1.18 (m, J=6.8 Hz, 24H), 1.17–1.11 ppm (m, J=7.5 Hz, 24H); ^{13}C NMR (101 MHz, CDCl$_3$): δ=180.2, 172.1, 163.9, 145.7, 135.9, 134.1, 133.8, 131.1, 131.0, 130.5, 128.1, 127.2, 124.6, 124.5, 124.3, 28.9, 24.7, 24.5, 24.1, 24.0 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ=−154.92, −154.98 ppm; elemental analysis calcd (%): C 53.17, H 5.71, N 5.08; found: C 52.71, H 5.60, N 4.81.

Synthesis of [Au(IPr)(NCPh)][BF$_4$] (13): 48 wt % aqueous BF$_4$ (22 μL, 0.17 mmol) was added to a dispersion of complex **1** (100 mg, 0.17 mmol) and benzonitrile (24 μL, 0.18 mmol) in toluene (2 mL). The reaction mixture was stirred overnight at room temperature. Pentane (2 mL) was added to the reaction to ensure complete precipitation of the product. The white solid was collected by filtration, washed with pentane (2×5 mL), and dried under vacuum to give 123 mg (96 %) of a white microcrystalline solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.86–7.74 (m, 3H), 7.66–7.55 (m, 4H), 7.48 (s, 2H), 7.37 (d, J=7.7 Hz, 4H), 2.50 (sept, J=6.9 Hz, 4H), 1.33 (d, J=6.9 Hz, 12H), 1.27 ppm (d, J=6.9 Hz, 12H); ^{13}C NMR (101 MHz, CDCl$_3$): δ=165.5, 145.8, 136.8, 133.8, 133.2, 131.4, 130.2, 125.4, 124.7, 119.8, 106.4, 29.0, 24.9, 24.1 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ=−154.64, −154.69 ppm; elemental analysis calcd (%): C 52.66, H 5.33, N 5.42; found: 51.77, H 5.22, N 5.32.

Synthesis of [Au(IPr)(NCC$_6$H$_4$CH$_3$)][BF$_4$] (14): AgBF$_4$ (31 mg, 0.16 mmol) was placed under argon in a Schlenk tube wrapped with alumina foil. CH$_2$Cl$_2$ (4 mL) was added followed by 4-toluonitrile (19 mg, 0.16 mmol). Then, [AuCl(IPr)] (100 mg, 0.16 mmol) was added and the reaction mixture was stirred 30 min at RT. CH$_2$Cl$_2$ (5 mL) was added and the reaction mixture was filtered over a plug of silica. Volatile compounds were removed under reduced pressure to yield a colorless oil. Recrystallization with CH$_2$Cl$_2$/pentane and addition of some ether yielded a colorless solid (62 mg, 49 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.67 (d, J=8.2 Hz, 2H), 7.60 (t, J=7.9 Hz, 2H), 7.51 (s, 2H), 7.43–7.33 (m, 6H), 2.51 (sept, J=6.9 Hz, 4H), 2.45 (s, 3H), 1.33 (d, J=6.8 Hz, 12H), 1.27 ppm (d, J=6.8 Hz, 12H); ^{13}C NMR (101 MHz, CDCl$_3$): δ=165.6, 148.7, 145.7, 133.7, 133.3, 131.4, 130.9, 125.5, 124.6, 120.4, 103.0, 28.9, 24.9, 24.1, 22.4 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ=−154.66. −154.73 ppm; elemental analysis calcd (%): C 52.19, H 5.38, N 5.22; found: C 52.63, H 5.08, N 6.12.

Synthesis of [Au(IPr){NCC$_6$H$_4$N(CH$_3$)$_2$}][BF$_4$] (15): AgBF$_4$ (125 mg, 0.64 mmol) was placed under argon in a Schlenk tube wrapped with alumina foil. CH$_2$Cl$_2$ (14 mL) was added followed by 4-dimethylaminobenzonitrile (94 mg, 0.64 mmol). Then, [AuCl(IPr)] (400 mg, 0.64 mmol) was added and the reaction mixture was stirred 30 min at RT. CH$_2$Cl$_2$ (10 mL) was added and the reaction mixture was filtered over a plug of silica. Volatile compounds were removed under reduced pressure to yield a colorless oil. Recrystallization with CH$_2$Cl$_2$/pentane and addition of some ether yielded a colorless solid (179 mg, 34 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.57 (t, J=7.9 Hz, 2H), 7.49 (s, 2H), 7.44 (d, J=9.2 Hz, 2H), 7.34 (d, J=7.9 Hz, 4H), 6.64 (d, J=9.2 Hz, 2H), 3.06 (s, 6H), 2.49 (sept, J=6.8 Hz, 4H), 1.30 (d, J=6.8 Hz, 12H), 1.25 ppm (d, J=6.8 Hz, 12H); ^{13}C NMR (101 MHz, CDCl$_3$): δ=166.4, 154.5, 145.7, 134.9, 133.4, 131.3, 125.3, 124.6, 123.9, 111.9, 88.2, 40.0, 28.9, 24.8, 24.0 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ=−154.67, 154.73 ppm; elemental analysis calcd (%): C 52.88, H 5.66, N 6.84; found: C 53.65, H 5.89, N 6.28.

Synthesis of [Au(IPr)(NCC$_6$H$_4$OCH$_3$)][BF$_4$] (16): AgBF$_4$ (25 mg, 0.13 mmol) was placed under argon in a Schlenk tube wrapped with alumina foil. CH$_2$Cl$_2$ (4 mL) was added followed by anisonitrile (17 mg, 0.13 mmol). Then, [AuCl(IPr)] (79 mg, 0.13 mmol) was added and the reaction mixture was stirred 30 min at RT. CH$_2$Cl$_2$ (5 mL) was added and the reaction mixture was filtered over a plug of silica. Volatile compounds were removed under reduced pressure to yield a colorless oil. Recrystallization with CH$_2$Cl$_2$/pentane and addition of some ether yielded a colorless solid (72 mg, 70 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.70 (d, J=9.0 Hz, 2H), 7.60 (t, J=7.9 Hz, 2H), 7.48 (s, 2H), 7.37 (d, J=7.9 Hz, 4H), 7.08 (d, J=9.0 Hz, 2H), 3.90 (s, 3H), 2.50 (sept, J=6.8 Hz, 4H), 1.33 (d, J=6.8 Hz, 12H), 1.27 ppm (d, J=6.8 Hz, 12H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=166.1, 166.0, 145.7, 136.1, 133.3, 131.4, 125.4, 124.7, 121.2, 116.2, 96.7, 56.3, 29.0, 24.9, 24.1 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ=−154.57. −154.63 ppm; elemental analysis calcd (%): C 53.25, H 5.49, N 5.32; found: C 53.35, H 5.23, N 6.13.

Synthesis of [Au(IPr){NCC$_6$H$_3$(CH$_3$)$_2$}][BF$_4$] (17): AgBF$_4$ (31 mg, 0.16 mmol) was placed under argon in a Schlenk tube wrapped with alumina foil. CH$_2$Cl$_2$ (4 mL) was added followed by 2,6-dimethylbenzonitrile (21 mg, 0.16 mmol). Then, [AuCl(IPr)] (100 mg, 0.16 mmol) was added and the reaction mixture was stirred 30 min at RT. CH$_2$Cl$_2$ (5 mL) was added and the reaction mixture was filtered over a plug of silica. Volatile compounds were removed under reduced pressure to yield a colorless oil. Recrystallization with CH_2Cl_2/pentane and addition of some ether yielded a colorless solid (74 mg, 57 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.66$–7.48 (m, 5 H), 7.36 (d, $J = 7.7$ Hz, 4 H), 7.20 (d, $J = 7.5$ Hz, 2 H), 2.52 (sept, $J = 6.7$ Hz, 4 H), 2.36 (s, 6 H), 1.31 (d, $J = 6.7$ Hz, 12 H), 1.28 ppm (d, $J = 6.7$ Hz, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 165.4$, 145.7, 144.6, 136.1, 133.3, 131.3, 128.5, 125.6, 124.6, 119.7, 107.6, 28.9, 24.8, 24.1, 20.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -154.58$. −154.63 ppm; elemental analysis calcd (%): C 53.81, H 5.64, N 5.23; found: C 53.3, H 5.55, N 5.82.

Synthesis of [Au(IPr)(NCPhBr)][BF$_4$] (18): 48 wt % aqueous BF_4 (11 μL, 0.08 mmol) was added to a dispersion of complex **1** (50 mg, 0.08 mmol) and benzonitrile (17 μL, 0.09 mmol) in toluene (2 mL). The reaction mixture was stirred overnight at room temperature. Pentane (2 mL) was added to the reaction to ensure complete precipitation of the product. The white solid was collected by filtration, washed with pentane (2 × 5 mL) and dried under vacuum to give 62 mg (87 %) of a white microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.81$–7.66 (m, 4 H), 7.60 (t, $J = 7.9$ Hz, 2 H), 7.46 (s, 2 H), 7.37 (d, $J = 7.9$ Hz, 4 H), 2.49 (sept, $J = 6.8$ Hz, 4 H), 1.33 (d, $J = 6.8$ Hz, 12 H), 1.27 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 165.6$, 145.7, 135.1, 133.8, 133.2, 132.7, 131.5, 124.7, 119.3, 105.3, 29.0, 24.9, 24.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -154.20$, −154.25 ppm; elemental analysis calcd (%): C 47.80, H 4.72, N 4.92; found: C 48.06, H 4.68, N 4.64.

Synthesis of [Au(IPr)(NCC$_6$H$_4$(COCH$_3$))][BF$_4$] (19): $AgBF_4$ (48 mg, 0.25 mmol) was placed under argon in a Schlenk tube wrapped with alumina foil. CH_2Cl_2 (6 mL) was added followed by 3-acetobenzonitrile (35 mg, 0.24 mmol). Then, [AuCl(IPr)] (150 mg, 0.24 mmol) was added and the reaction mixture was stirred 30 min at RT. CH_2Cl_2 (5 mL) was added and the reaction mixture was filtered over a plug of silica. Volatile compounds were removed under reduced pressure to yield a colorless oil. Recrystallization with CH_2Cl_2/pentane and addition of some ether yielded a colorless solid (195 mg, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.43–8.30 (m, 2 H), 8.11–7.99 (m, 1 H), 7.89–7.77 (m, 1 H), 7.66–7.55 (m, 2 H), 7.46 (s, 2 H), 7.38 (d, $J = 7.7$ Hz, 4 H), 2.64 (s, 3 H), 2.50 (sept, $J = 6.8$ Hz, 4 H), 1.35 (d, $J = 6.8$ Hz, 12 H), 1.27 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 195.8$, 165.3, 145.6, 137.8, 137.3, 136.1, 133.1, 131.4, 125.4, 124.6, 118.7, 107.3, 28.8, 26.7, 24.8, 24.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -154.08$. −154.13 ppm; elemental analysis calcd (%): C 52.89, H 5.30, N 5.14; found: C 52.99, H 4.44, N 4.81.

Synthesis of [Au(IPr)(NCC(CH$_3$)$_3$)][BF$_4$] (20): $HBF_4 \cdot OEt_2$ (11 μL, 0.08 mmol) was added to a dispersion of complex **1** (50 mg, 0.08 mmol) and pivalonitrile (18 μL, 0.08 mmol) in toluene (2 mL). The reaction mixture was stirred 3 h at room temperature. Pentane (2 mL) was added to the reaction to ensure complete precipitation of the product. The white solid was collected by filtration, washed with pentane (2 × 5 mL) and dried under vacuum to give 52 mg (83 %) of a white microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.60$ (t, $J = 7.7$ Hz, 2 H), 7.47 (s, 2 H), 7.36 (d, $J = 7.7$ Hz, 4 H), 2.47 (sept, $J = 6.8$ Hz, 4 H), 1.42 (s, 9 H), 1.29 (d, $J = 6.8$ Hz, 12 H), 1.26 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 165.3$, 145.7, 133.3, 131.3, 125.5, 124.7, 29.5, 28.9, 27.3, 24.8, 24.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -154.14$, −154.19 ppm; elemental analysis calcd (%): C 50.87, H 6.00, N 5.56; found: C 49.58, H 5.79, N 4.93.

Synthesis of [Au(IPr)(2-cyanopyridine)][BF$_4$] (21): $AgBF_4$ (31 mg, 0.16 mmol) was placed under argon in a Schlenk tube wrapped with alumina foil. CH_2Cl_2 (5 mL) was added followed by 2-cyanopyridine (17 mg, 0.16 mmol). Then, [AuCl(IPr)] (100 mg, 0.16 mmol) was added and the reaction mixture was stirred 30 min at RT. CH_2Cl_2 (5 mL) was added and the reaction mixture was filtered over a plug of silica. Volatile compounds were removed under reduced pressure to yield a colorless oil. Recrystallization with CH_2Cl_2/pentane a colorless solid (122 mg, 98 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.43$–8.28 (m, 1 H), 8.22–8.10 (m, 2 H), 7.91 (d, $J = 7.3$ Hz, 1 H), 7.58 (t, $J = 7.9$ Hz, 2 H), 7.43 (s, 2 H), 7.36 (d, $J = 7.9$ Hz, 4 H), 2.54 (sept, $J = 6.8$ Hz, 4 H), 1.36 (d, $J = 6.8$ Hz, 12 H), 1.27 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 166.0$, 153.6, 145.6, 143.7, 133.3, 133.2, 132.2, 132.0, 131.6, 125.1, 124.7, 114.3, 29.1, 24.8, 24.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -153.40$, −153.46 ppm; elemental analysis calcd (%): C 51.05, H 5.19, N 7.22; found: C 49.12, H 5.08, N 6.67.

Synthesis of [Au(IPr)(4-cyanopyridine)][BF$_4$] (22): $AgBF_4$ (75 mg, 0.39 mmol) was placed under argon in a Schlenk tube wrapped with alumina foil. CH_2Cl_2 (10 mL) was added followed by 4-cyanopyridine (40 mg, 0.39 mmol). Then, [AuCl(IPr)] (240 mg, 0.39 mmol) was added and the reaction mixture was stirred 30 min at RT. CH_2Cl_2 (10 mL) was added and the reaction mixture was filtered over a plug of silica. Volatile compounds were removed under reduced pressure to yield a crude solid. Recrystallization with CH_2Cl_2/pentane a colorless solid (213 mg, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.26$ (d, $J = 5.8$ Hz, 2 H), 7.92 (d, $J = 5.8$ Hz, 2 H), 7.58 (t, $J = 7.8$ Hz, 2 H), 7.42 (s, 2 H), 7.36 (d, $J = 7.8$ Hz, 4 H), 2.52 (sept, $J = 6.8$ Hz, 4 H), 1.34 (d, $J = 6.8$ Hz, 12 H), 1.27 ppm (d, $J = 6.8$ Hz, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 166.2$, 152.3, 145.6, 133.2, 131.5, 129.6, 125.0, 125.0, 124.7, 114.5, 28.9, 24.9, 24.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -154.55$. −154.60 ppm; elemental analysis calcd (%): C 51.05, H 5.19, N 7.22; found: C 51.55, H 5.38, N 7.15.

General procedure for the nitrile hydration: In a typical reaction, [Au(NTf$_2$)(IPr)] (13 mg, 20 μmol, 2 mol %) or [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (17 mg, 10 μmol, 1 mol %) was added to THF (0.5 mL) in a 2 mL microwave vial in air. Benzonitrile (103 mg, 1 mmol) was added, followed by distilled H_2O (500 μL). The vial was sealed and heated in the microwave for 2 h at 140 °C (7 bar). The conversion was determined by gas chromatography.

Computational details: The BP86[30] calculations were performed with the Gaussian 03 package. The SVP basis set was used for main group atoms,[31] while the relativistic SDD effective core potential in combination with a triple-ζ basis set was used for Au.[32] Solvent effects were included through single-point calculations, on the gas-phase optimized geometries, with the PCM approach.[33]

Acknowledgements

The ERC (Advanced Investigator Award-FUNCAT to S.P.N.) and the EPSRC are gratefully acknowledged for support of this work. Syngenta is thanked for a CASE studentship award. L.C. thanks the ENEA-CRESCO for support and access to computational resources. We thank Drs. Pierre de Frémont and Nicolas Marion for helpful discussions and preliminary synthetic contributions. S.P.N. is a Royal Society-Wolfson Research Merit Award holder.

---

[1] a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; b) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; c) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; d) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1782; e) A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360–5369; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241.

[2] S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676.

[3] Of note, there are as well examples for gold catalysis without silver agents, whereas these complexes were mostly synthesized via a silver substrate.

[4] a) L. Ricard, F. Gagosz, *Organometallics* **2007**, *26*, 4704–4707; b) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem.* **1998**, *110*, 1475–1478; *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1418; c) C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677–1693.

[5] a) P. de Frémont, E. D. Stevens, M. R. Fructos, M. M. Díaz-Requejo, P. J. Pérez, S. P. Nolan, *Chem. Commun.* **2006**, 2045–2047; b) P. de Frémont, N. M. Scott, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 2411–2418; c) C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, *J. Org. Chem.* **2008**, *73*, 7721–7730; d) P. de Frémont, N. Marion, S. P. Nolan, *J. Organomet. Chem.* **2009**, *694*, 551–560; e) Y. Harrak, A. Simonneau, M. Malacria, V. Gandon, L. Fensterbank, *Chem. Commun.* **2010**, *46*,

865–867; f) N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815–1828; g) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378.

[6] a) A. S. K. Hashmi, A. M. Schuster, F. Rominger, *Angew. Chem.* **2009**, *121*, 8396–8398; *Angew. Chem. Int. Ed.* **2009**, *48*, 8247–8249; b) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642–17643; c) L.-P. Liu, G. B. Hammond, *Chem. Asian J.* **2009**, *4*, 1230–1236; d) D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem.* **2009**, *121*, 5843–5846; *Angew. Chem. Int. Ed.* **2009**, *48*, 5733–5736; e) D. Weber, M. R. Gagne', *Org. Lett.* **2009**, *11*, 4962–4965; f) T. J. Brown, M. G. Dickens, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2009**, *131*, 6350–6351.

[7] a) R. S. Ramón, N. Marion, S. P. Nolan, *Tetrahedron* **2009**, *65*, 1767–1773; b) N. Marion, P. Carlqvist, R. Gealageas, P. de Frémont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437–6451.

[8] a) R. S. Ramón, N. Marion, S. P. Nolan, *Chem. Eur. J.* **2009**, *15*, 8695–8697; b) For more references on metal catalyzed nitrile hydration, see ref. 8. See also: c) R. Garci'a-A'lvarez, J. Di'ez, P. Crochet, V. Cadierno, *Organometallics* **2010**, *29*, 3955–3965; d) T. J. Ahmed, S. M. M. Knapp, D. R. Tyler, *Coord. Chem. Rev.*, DOI:10.1016/j.ccr.2010.08.018.

[9] S. Gaillard, A. M. Slawin, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 2742–2744.

[10] S. Gaillard, J. Bosson, R. S. Ramón, P. Nun, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2010**, *16*, 13729–13740.

[11] The same reaction in was done in THF in order to obtain the THF analogues complex. Unfortunately, these efforts remained unsuccessful.

[12] In contrast to cationic nitrile complexes, the synthesis of [Au(OH)(IPr)] is realized without the use of any silver salts.

[13] Reactions conducted with aqueous HBF_4 in toluene lead to identical isolated yields.

[14] Washing the organic phase with brine resulted in full conversion into [AuCl(IPr)].

[15] R. S. Ramón, S. Gaillard, A. M. S. Slawin, A. Porta, A. D'Alfonso, G. Zanoni, S. P. Nolan, *Organometallics* **2010**, *29*, 3665–3668.

[16] DFT values for **2**: Au–Au 3.886; Au–O 2.081; Au–C 1.974; O–H 0.976 Å; Au-O-Au 137.9; Au-O-H 109.7°.

[17] a) I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270–274; b) I. Mayer, *Int. J. Quantum Chem.* **1984**, *26*, 151–154.

[18] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[19] We suspect at this stage that **3** could be a reservoir for the catalytically active mononuclear cationic gold species.

[20] A rudimentary test proofed **2** active in nitrile hydration. See reference [10].

[21] This conversion is poor but the presence of any activity of **1** under neutral condition is worthy of further investigation.

[22] Of note, Bayler-Schmidtbaur complexes proofed already active in catalysis. For recent examples, see: a) A. S. K. Hashmi, M. C. Blanco, E. Kurpejovic, W. Frey, J. W. Bats, *Adv. Synth. Catal.* **2006**, *348*, 709–713; b) A. S. K. Hashmi, M. Hamzić, F. Rominger, Jan W. Bats, *Chem. Eur. J.* **2009**, *15*, 13318–13322; also $[R_3Au_3O][X]$ complexes have been used successfully in catalysis: see: c) W. Li, W. Yuan, S. Pindi, M. Shi, G. Li, *Org. Lett.* **2010**, *12*, 920–923; d) P. Mauleón, J. L. Krinsky, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 4513–4520.

[23] The initial catalyst screening was performed with 2 mol % catalyst in a 1 M solution of dioxane/H_2O 2:1 at 100 °C and showed **4** to be the best catalyst. In order to compare **3** to all other catalysts tested, we subjected it to these same reaction conditions to seek the highest conversion rate among all catalysts. Since the optimizations in reference [8] revealed the importance of the amount of water used, we suggest that a lower conversion of [AuCl(IPr)]/$AgBF_4$ and $[Au(IPr)(CH_3CN)]BF_4$ into **3** occurs under these reaction conditions and result in lower conversions than when using **4** under these "unoptimized" conditions.

[24] In fact, mixing equimolar amounts of $[Au(IPr)(CH_3CN)]BF_4$ and [Au(OH)(IPr)] in CH_2Cl_2 results in full conversion into catalyst **2**.

[25] P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 4517–4526.

[26] V. Y. Kukushkin, A. J. L. Pombeiro, *Inorg. Chim. Acta* **2005**, *358*, 1–21.

[27] R. L. de La Vega, W. R. Ellis, W. L. Purcell, *Inorg. Chim. Acta* **1983**, *68*, 97–101.

[28] a) J. Y. Z. Chiou, S. C. Luo, W. C. You, A. Bhattacharyya, C. S. Vasam, C. H. Huang, I. J. B. Lin, *Eur. J. Inorg. Chem.* **2009**, 1950–1959; b) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Pérez, M. Rodríguez-Castillo, *Gold Bull.* **2007**, *40*, 172–183.

[29] A comparison of for example, $[Au(IPr)(CH_3CN)]PF_6$ and $[Au(IPr)(PhCN)]PF_6$ in nitrile hydration resulted in identical conversions.

[30] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) J. B. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[31] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.

[32] T. Leininger, A. Nicklass, H. Stoll, M. Dolg, P. Schwerdtfeger, *J. Chem. Phys.* **1996**, *105*, 1052–1059.

[33] M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327–335.

Received: September 9, 2010