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Cationic NHC–gold(I) complexes: Synthesis, isolation, and catalytic activity

Pierre de Frémont [a], Nicolas Marion [b], Steven P. Nolan [a,b,*]

[a] Chemistry Department, University of New Orleans, New Orleans, LA 70148, USA
[b] Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain

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ABSTRACT

The reaction of [(NHC)AuCl] complexes (NHC = N-heterocyclic carbene) with a chloride abstractor of the type AgX, where X is a non-coordinating anion, led, in the presence of a neutral coordinating solvent S, to a series of cationic gold(I) complexes of formulae [(NHC)Au(S)]X. Hence, different cationic NHC–gold(I) species bound to acetonitrile, pyridine, 2-Br-pyridine, 3-Br-pyridine, norbornadiene, and THF could be synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopies. Among these, the results of X-ray diffraction studies for [(IPr)Au(NCMe)]SbF_6, [(IAd)Au(NCMe)]PF_6, [(IPr)Au(pyr)]PF_6, [(IPr)Au(2-Br-pyr)]PF_6, [(IPr)Au(3-Br-pyr)]PF_6 are discussed. As special feature, the structure of [(IPr)Au(2-Br-pyr)]PF_6 presented a secondary interaction between the gold and bromine atoms. Additionally, while attempting to obtain crystals of [(IPr)Au(nbd)]PF_6, we crystallized a decomposition product featuring a very rare PF_4^- anion as bridging ligand with formulae [(μ-PF_4)((IPr)Au)$_2$]PF_4. The observation of a possible P–F bond activation has important implications for cationic Au-based homogeneous catalysis. Finally, we compared the catalytic activities of the different cationic [(NHC)Au(S)]X complexes in the allylic acetate rearrangement reaction and notably observed the inertness of pyridine-based catalysts.

1. Introduction

As part of an ongoing program aimed at examining the role of N-heterocyclic carbenes (NHCs) in transition metal-mediated reactions, we have recently studied the stabilizing effects of NHCs surrounding unsaturated and "reactive" metal centers. Since the isolation of the first stable "free" NHC, bearing two sterically demanding adamantyl groups on the nitrogens of an imidazolyl framework, by Arduengo [1], sterically encumbering NHCs have allowed for the isolation of a great variety of unusual organometallic species [2]. In view of their highly interesting steric and electronic properties [3], NHCs have also been employed to prepare efficient and robust catalysts for a wide array of organic transformations [4].

We recently reported the synthesis and isolation of a series of well-defined NHC–gold(I) complexes [5]. The first NHC–gold(I) complexes were reported in 1989 [6] and these usually bore two strongly bound ligands arranged in a linear fashion around a gold cation. They can be neutral or cationic and present the [(NHC)AuX] or [(NHC)$_2$Au]X composition [7]. Until recently, catalytic organogold chemistry appeared to have been somewhat forgotten. The "noble" character of the metal was possibly at the origin of the misconception that it would perform poorly in catalysis. This misconception has now been shattered, as numerous examples of phosphine– and NHC–gold mediated transformations have recently appeared [8,9]; gold(I) halide complexes being especially efficient at activating alkyne moieties toward nucleophilic addition under mild reaction conditions. The use of silver salts, with an accompanying non-coordinating anion, is usually required to generate the active catalyst. It is commonly accepted that silver assists in halide abstraction from the gold center generating a highly electrophilic monoligated cationic gold complex [10]. Nevertheless, such complexes have proven difficult to isolate. Notably, attempts to synthesize or isolate [(ItBu)Au]BF_4 by Baker [11] (ItBu = 1,3-di-*tert*-butylimidazol-2-ylidene) and [(Ph_3P)Au]X (X = BF_4, PF_6, SbF_6) by Gagosz [12] have so far failed due to rapid decomposition of these complexes to colloidal gold(0). To prevent such decomposition, we thought of using a coordinating solvent, and consequently reported the acetonitrile adduct of a cationic gold(I) complex [(IPr)Au(NCMe)]PF_6 (**1**) (Fig. 1, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) [13], bearing a bulky NHC ligand, that proved to be active in the enyne cycloisomerization reaction [14]. Similarly, Echavarren reported the isolation of [(Ph_3P)Au(NCMe)]PF_6 [15], highlighting the importance of the non-coordinating anion as well as the neutral coordinating molecule in the stabilization of such species. In the same report, acetonitrile and arene adducts of monoligated cationic gold(I) complexes such as **2** and **3** (Fig. 1), bearing very bulky *ortho*-diphenylphosphine ligands, could also be isolated. Recently, the use of CAAC ligand (CAAC = cyclic alkyl amino carbene) by Bertrand, led to further advances in gold(I)

* Corresponding author. Address: Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain.
E-mail address: snolan@iciq.es (S.P. Nolan).

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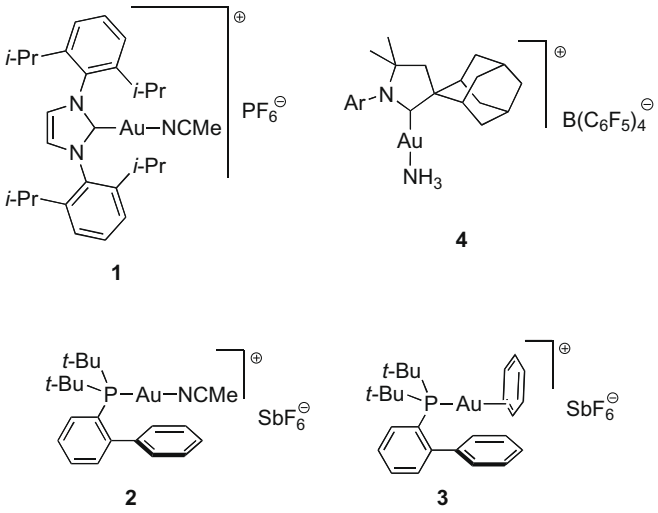


Fig. 1. Structures of selected cationic gold(I) complexes.

coordination chemistry, with the isolation of both arene- [16] and ammonia-adducts [17] of cationic gold(I) complexes, such as **4**.

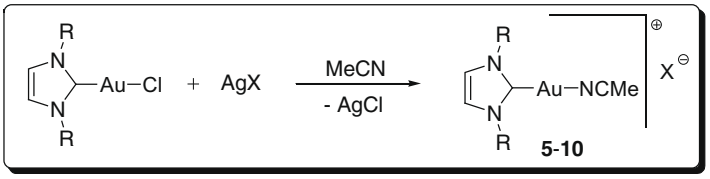
Herein, we present the continuation of our work on NHC-based cationic gold(I) species, including the isolation and characterization of such complexes by using a NHC ligand of sufficient bulk and a weakly coordinating solvent such as acetonitrile or THF leading to relatively stable yet reactive cationic gold(I) complexes.

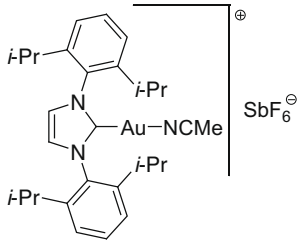
2. Results and discussion

2.1. Acetonitrile-containing cationic NHC–gold(I) complexes

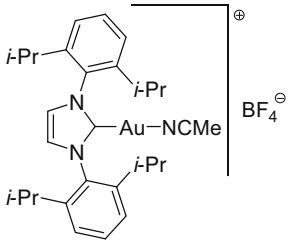
The previously reported [(IPr)AuCl] [5], [(IMes)AuCl] [5] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), [(ItBu)AuCl] [11] and [(IAd)AuCl] [5] (IAd = 1,3-diadamantylimidazol-2-ylidene) were dissolved in acetonitrile and $AgPF_6$, $AgSbF_6$, $AgBF_4$, or $AgB(C_6F_5)_4$ was added in slight excess, leading to the rapid formation of a precipitate (AgCl). After stirring the solutions for one minute, the suspensions were filtered through a plug of Celite affording acetonitrile solutions of [(NHC)Au(NCMe)]X complexes **5–10** (Scheme 1).

Attempts to obtain solid materials for all complexes by simply removing the solvent under vacuum led to a white powder turning grey with the appearance of colloidal silver(0). To remove the excess of silver, complexes were dissolved in cold DCM and filtered over a plug of silicagel. All complexes are stable in air and can be stored as a white powder indefinitely in a freezer. They are stable in acetonitrile and chlorinated solvents at room temperature for several days, with the exception of [(IMes)Au(NCMe)]PF_6 (**10**) and [(ItBu)Au(NCMe)]PF_6 (**9**), which both rearrange into [$(NHC)_2$Au(PF_6)] and [$Au(NCMe)_4$]PF_6. Interestingly, in these cases no formation of gold(0) was observed.

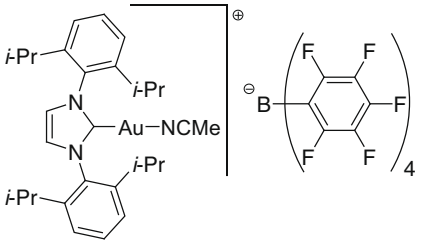




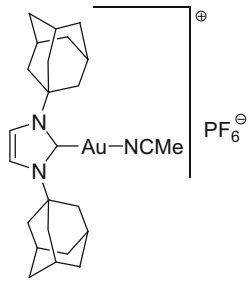
5, [(IPr)Au(NCMe)]SbF_6



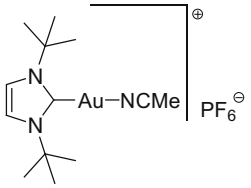
6, [(IPr)Au(NCMe)]BF_4



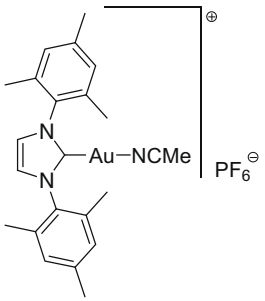
7, [(IPr)Au(NCMe)][$B(C_6F_5)_4$]



8, [(IAd)Au(NCMe)]PF_6



9, [(ItBu)Au(NCMe)]PF_6



10, [(IMes)Au(NCMe)]PF_6

Scheme 1. Synthesis of cationic [(NHC)Au(NCMe)]X complexes **5–10**.

Table 1
^{13}C NMR data for [(NHC)AuCl] and [(NHC)Au(NCMe)]X complexes.

[(NHC)AuCl]	Solvent	δc Au–C (ppm)	[(NHC)Au(NCMe)]X	Solvent	δc Au–C (ppm)
[(IPr)AuCl]	$CDCl_3$	175.1	[(IPr)Au(NCMe)]PF_6 (**1**)	$CDCl_3$	166.1
			[(IPr)Au(NCMe)]SbF_6 (**5**)	$CDCl_3$	166.0
			[(IPr)Au(NCMe)]BF_4 (**6**)	$CDCl_3$	165.9
			[(IPr)Au(NCMe)]$B(C_6F_5)_4$ (**7**)	$CDCl_3$	166.1
[(IAd)AuCl]	$CDCl_3$	166.3	[(IAd)Au(NCMe)]PF_6 (**8**)	$CDCl_3$	157.7
[(ItBu)AuCl]	$CDCl_3$	168.2	[(ItBu)Au(NCMe)]PF_6 (**9**)	CD_3CN	159.7
[(IMes)AuCl]	$CDCl_3$	173.4	[(IMes)Au(NCMe)]PF_6 (**10**)	CD_3CN	165.3

^1H and ^{13}C NMR spectra of the neutral precursors and the novel cationic complexes were recorded. While the pattern of the ^1H NMR spectra remained the same with no trace of decomposition products between neutral and cationic gold(I) complexes, we observed a slight downfield shift for the backbone protons of the imidazole fragment. We attribute this change to a loss of electronic density in the heterocyclic system, due a delocalization of the π-electrons toward the more acidic gold center. The ^{13}C NMR spectra present signals for the carbenic carbons that are significantly shifted upfield for all complexes (Table 1).

Once again, this observation confirmed a more acidic gold center. Both ^1H and ^{13}C NMR studies support the presence of an electron deficient gold center, confirming the very likely presence of monoligated gold(I) complexes.

To unambiguously establish the solid state structure of these complexes, suitable X-ray quality crystals for single crystal diffraction studies were grown from saturated acetonitrile solutions of [(IPr)Au(NCMe)]SbF_6 (**5**) and [(IAd)Au(NCMe)]PF_6 (**8**). For **6**, **7**, **9** and **10**, no suitable crystals could be obtained for X-ray diffraction. Results from the diffraction studies confirmed the structure determined by NMR and, notably, the coordination of one acetonitrile molecule to the gold center (Figs. 2 and 3).

Both structures, as the one of [(IPr)Au(NCMe)]PF_6 that we reported earlier [13], revealed a nearly linear (NHC)–Au–(NCMe) arrangement with a C–Au–N angle close to 180°. The C–Au bond lengths range between 1.952(2) and 1.990(2) Å; they are similar to those found for the neutral corresponding [(NHC)AuCl]. The N–Au bond lengths range between 2.008(2) Å and 2.022(2) Å, which is in the range of reported gold complexes with nitrogen donor ligands [18], but slightly longer than known gold(I) complexes with coordinated acetonitrile such as [$Au(NCMe)_2$]X [19] with a Au–N length bond equal to 1.96 Å.

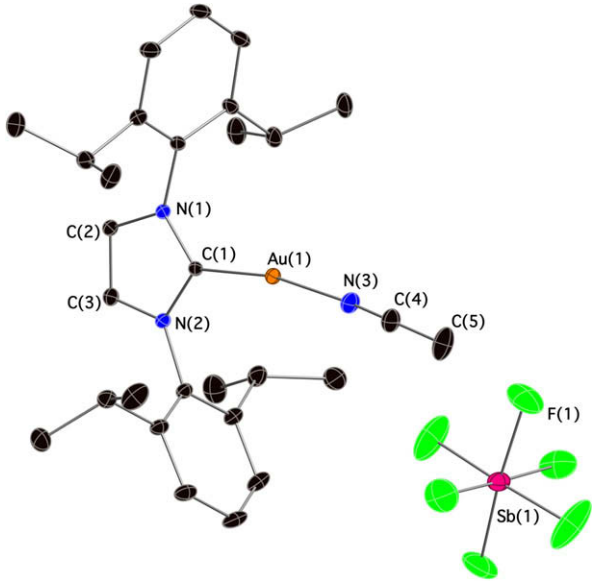


Fig. 2. Crystal structure of [(IPr)Au(NCMe)]SbF_6 (**5**) (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Au(1)–C(1) 1.974(2); Au(1)–N(3) 2.013(3); C(1)–N(1) 1.344(3); C(1)–N(2) 1.353(3); N(3)–C(4) 1.137(4); Sb(1)–F(1) 1.865(3). Selected angles (°): C(1)–Au(1)–N(3) 175.57(10); Au(1)–N(3)–C(4) 173.5(3); N(1)–C(1)–Au(1) 130.94(17); N(1)–C(1)–N(2) 105.4(2). Selected torsion angles (°): N(1)–C(2)–C(3)–N(2) 0.9(3).

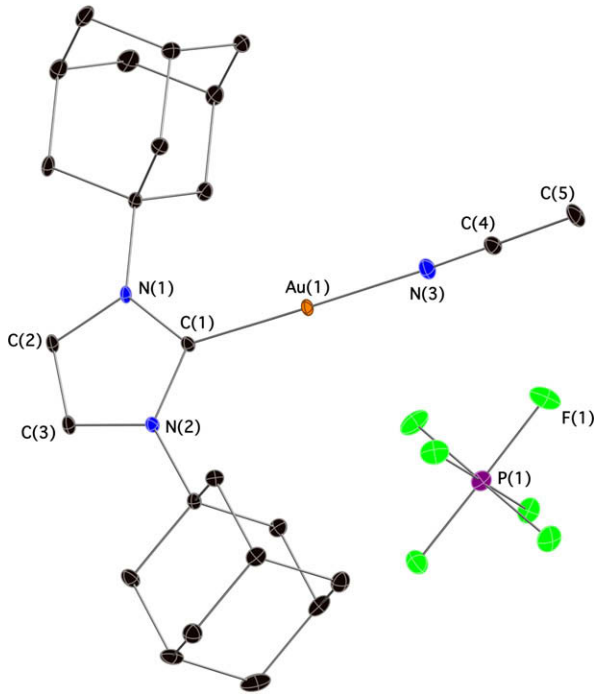


Fig. 3. Crystal structure of [(IAd)Au(NCMe)]PF_6 (**8**) (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Au(1)–C(1) 1.990(2); Au(1)–N(3) 2.008(2); C(1)–N(1) 1.359(3); C(1)–N(2) 1.358(3); N(3)–C(4) 1.139(3); P(1)–F(1) 1.605(2). Selected angles (°): C(1)–Au(1)–N(3) 178.75(10); Au(1)–N(3)–C(4) 176.2(2); N(1)–C(1)–Au(1) 127.02(16); N(1)–C(1)–N(2) 106.1(2). Selected torsion angles (°): N(1)–C(2)–C(3)–N(2) 0.4(3).

2.2. Cationic [(NHC)Au(L)]X complexes (X = THF, nbd, pyr, 2-Br-pyr, 3-Br-pyr)

We were interested in further testing the stability of such complexes. Attempts to synthesize a cationic gold(I) complex in dry dichloromethane or dry chloroform with silver salts led to the rapid appearance of large amounts of colloidal gold(0). The ^1H NMR spectra of these products indicated the existence of two different NHC environments attributed to at least two NHC–gold species in solution. Nevertheless, these species decomposed rapidly and we were not able to obtain further characterization. It should be noted that in most cases we observed very broad NMR signals in the ^1H spectrum, indicating the possibility of a polymeric structure, which also decomposed rapidly before full characterization. We confirmed in this manner the necessity of a coordinating solvent to stabilize the cationic gold center.

Tetrahydrofuran (THF) was then employed as an alternative to acetonitrile to generate [(IPr)Au(S)]PF_6 (S = coordinating solvent). In THF, no decomposition was observed, as long as an excess of THF was maintained (i.e. at least a three fold excess to the gold complex), even after subjecting the THF solution to air for 24 h. Surprisingly, a gel was obtained, attributed to the ring-opening polymerization of THF [20]. On the other hand, any attempt to dry the sample led to decomposition of [(IPr)Au(THF)]PF_6 (**11**).

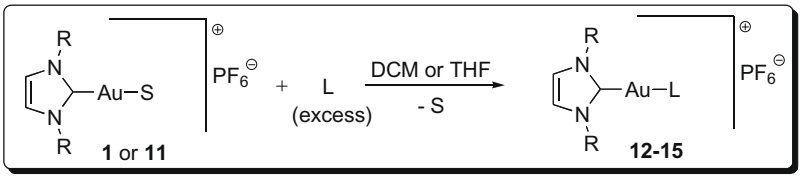
The ^{13}C NMR spectrum indicated a gold species in THF that is even more acidic than in acetonitrile with a carbenic carbon appearing at a more upfield resonance (δ = 159.7 ppm versus 167.6 ppm in THF-d_8). The complex in THF also displayed a second, more downfield, signal with a low intensity (after few hours) for the deuterated THF that confirmed the formation of poly-THF [21]. It is noteworthy that the cationic polymerization of THF by ring-opening, in the presence of a Lewis acids such as $FeCl_3$ or the trityl cation is well known [21]. In the present case, this polymerization behavior confirms the presence of a cationic gold centered complex capable of acting as a Lewis acid for polymerization reactions; an interesting reaction profile that we have recently examined [22]. We also noticed that adding [(IPr)Au(NCMe)]PF_6 (**1**), synthesized from acetonitrile, into THF led to THF polymerization. Since the acetonitrile needs to be displaced from the gold center by THF to initiate the polymerization, this result shows that in solution the molecules of solvent are weakly bound, labile and can be easily displaced from gold.

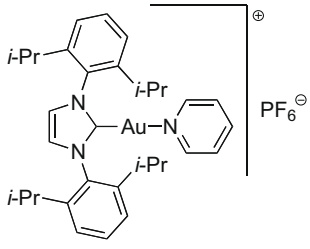
To broaden the range of available cationic NHC–gold(I) complexes, different pyridines, and norbornadiene were employed to generate respectively the following new complexes [(IPr)Au(pyr)]PF_6 (**12**), [(IPr)Au(2-Br-pyr)]PF_6 (**13**), [(IPr)Au(3-Br-pyr)]PF_6 (**14**) and [(IPr)Au(nbd)]PF_6 (**15**). These new cationic gold(I) compounds were obtained in high yields from [(IPr)Au(NCMe)]PF_6 (**1**) and [(IPr)Au(THF)]PF_6 (**11**) by substitution of acetonitrile or THF bound to gold. In the case of **15** a large excess of norbornadiene and a longer reaction time were required (Scheme 2).

Complexes **12–14** are stable in air and can be stored as a white powder indefinitely in a freezer. They are also stable in acetonitrile, THF, and chlorinated solvents, at room temperature. They display similar ^1H and ^{13}C NMR signals pattern. The carbenic carbons resonate between 166.0 and 167.1 ppm. The bromide group does not appear to noticeably influence the electronic properties of the pyridine ligands.

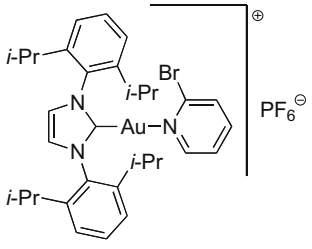
X-ray quality crystals suitable for single crystal diffraction studies were grown from saturated DCM solutions of [(IPr)Au(pyr)]PF_6 (**12**), [(IPr)Au(2-Br-pyr)]PF_6 (**13**), and [(IPr)Au(3-Br-pyr)]PF_6 (**14**) (Figs. 4–6). The structures present a classical linear arrangement around the gold(I) center with only slight variation of the Au–(pyridine) and Au–(NHC) bond lengths. As special feature, we observed in complex **13** a secondary interaction between the bromine of the 2-bromopyridine and the gold center (d(Au–Br) = 3.34 Å versus $\sum r_{vdw}$ = 3.54 Å). Interestingly, this secondary interaction forces the pyridine plane to be coplanar with the imidazole plane, whereas they are almost perpendicular in complexes **12** and **14** (see Figs. 4–6).

[(IPr)Au(nbd)]PF_6 (**15**) is stable in air, on the contrary to other olefin–gold(I) complexes previously described [23]. It can be kept as a white powder in the freezer but slowly decomposes in THF or DCM. After a few days in solution, the ^1H NMR spectrum of **15** presents the same aspect while the characteristic septuplet of PF_6^- at −141.3 ppm on the ^{31}P NMP spectrum disappears to be replaced by a broad triplet at −11.5 ppm. From both spectra, it can be assumed that **15** is degraded by decoordination of norbornadiene from the $[(IPr)Au]^+$ fragment, which would further interact with PF_6^-. ^1H and ^{13}C NMR spectra of **15** exhibit a norbornadiene ligand with two non-equivalent olefin sides characterized by two different sets of broad signals. One set exhibits the chemical shift of free norbornadiene while the second one is slightly upfield. Such NMR spectra are characteristic of a gold(I) center possessing a norborna-

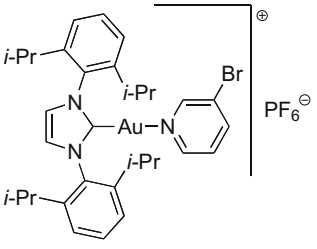




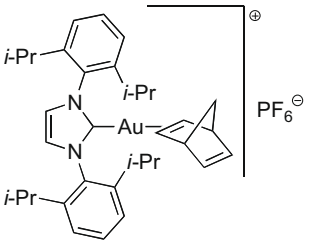
12, [(IPr)Au(pyr)]PF_6



13, [(IPr)Au(2-Br-pyr)]PF_6



14, [(IPr)Au(3-Br-pyr)]PF_6



15, [(IPr)Au(nbd)]PF_6

Scheme 2. Synthesis of cationic [(NHC)Au(L)]PF_6 complexes.

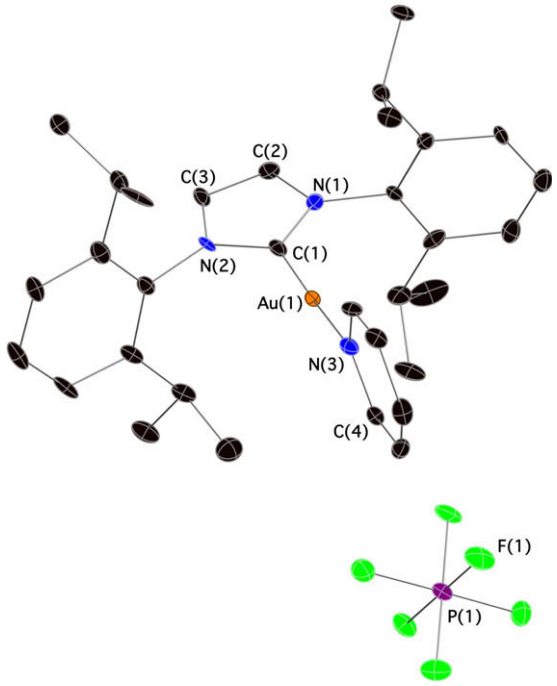


Fig. 4. Crystal structure of $[(IPr)Au(pyr)]PF_6$ (**12**) (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Au(1)–C(1) 1.961(7); Au(1)–N(3) 2.049(6); C(1)–N(1) 1.344(8); C(1)–N(2) 1.369(8); P(1)–F(1) 1.597(5). Selected angles (°): C(1)–Au(1)–N(3) 177.1(3); N(1)–C(1)–Au(1) 128.4(5); N(1)–C(1)–N(2) 103.9(5). Selected torsion angles (°): N(2)–C(1)–N(3)–C(4) 94.54(9); N(1)–C(2)–C(3)–N(2) 0.1(8).

diene bound by only one double bond. The slight upfield shift observed for the olefin signals indicates that the olefin is acting almost as a pure electron donor with negligible back-bonding from the gold(I) center [24].

Repeated attempts to crystallize **15** in a saturated solution of dried THF/octane, gave white crystals suitable for X-ray diffraction study. Nevertheless, the structure of **15** was not confirmed and the complex $[(\mu\text{-}PF_4)((IPr)Au)_2]PF_4$ (**16**) was observed instead (see

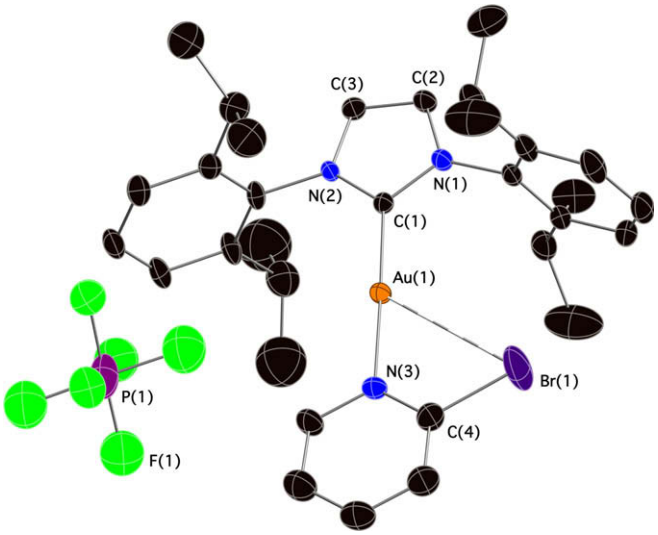


Fig. 5. Crystal structure of $[(IPr)Au(2\text{-}Br\text{-}pyr)]PF_6$ (**13**) (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Au(1)–C(1) 1.976(5); Au(1)–N(3) 2.069(5); Au(1)–Br(1) 3.344; C(1)–N(1) 1.352(7); C(1)–N(2) 1.339(6); N(3)–C(4) 1.338(9); C(4)–Br(1) 1.853(8); P(1)–F(1) 1.488(14). Selected angles (°): C(1)–Au(1)–N(3) 178.5(2); Au(1)–N(3)–C(4) 124.2(5); N(1)–C(1)–Au(1) 126.0(4); N(1)–C(1)–N(2) 105.2(4). Selected torsion angles (°): N(1)–C(1)–N(3)–C(4) 0.05(7); N(1)–C(2)–C(3)–N(2) 0.0(0).

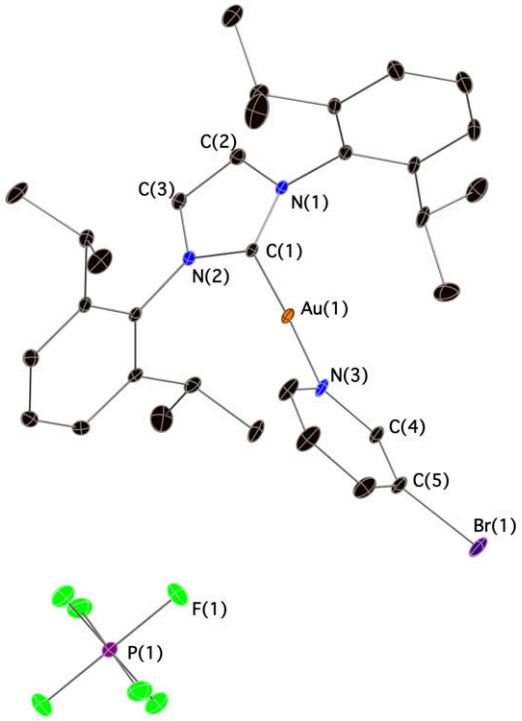


Fig. 6. Crystal structure of $[(IPr)Au(3\text{-}Br\text{-}pyr)]PF_6$ (**14**) (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Au(1)–C(1) 1.974(3); Au(1)–N(3) 2.055(3); C(1)–N(1) 1.355(3); C(1)–N(2) 1.349(5); C(5)–Br(1) 1.879(3); P(1)–F(1) 1.604(2). Selected angles (°): C(1)–Au(1)–N(3) 175.54(10); Au(1)–N(3)–C(4) 120.3(2); N(1)–C(1)–Au(1) 129.2(2); N(1)–C(1)–N(2) 104.9(2). Selected torsion angles (°): N(1)–C(2)–C(3)–N(2) 0.3(4); N(1)–C(1)–N(3)–C(4) 76.65(4).

Fig. 7). Such complex can be seen as an intermediate in the decomposition pathway of **15**. It is worthy to note that structures featuring a PF_4^- anion are extremely scarce [25] and unknown in gold chemistry [26]. The formation of this decomposition product from an unsaturated cationic gold(I) species probably occurred via P–F bond activation with pre-coordination of the PF_6 anion to the gold center of the type $Au\cdots F\text{–}PF_5$. Even though the mechanistic details for the formation of **16** remain elusive, this observation is of importance in the context of cationic gold(I) catalysis since the most utilized weakly coordinating counteranions are all perfluoro anions (i.e. BF_4, PF_6, SbF_6). Finally, it is noteworthy that decomposition of the cationic gold complexes never occurred through the cleavage of the Au–(NHC) bond.

2.3. Comparative study of [(NHC)Au(L)]X complexes in the rearrangement of allylic acetates

Having in hands the cationic NHC–gold(I) complexes described above, we were interested in testing their catalytic activity, notably in order to obtain further information on the nature of the bonding between gold and the different neutral coordinating molecules used [27]. We decided to carry out preliminary investigations on the rearrangement of allylic acetates [28], a reaction that we recently reported using an *in situ* protocol for the formation of the active cationic gold(I) catalyst [29]. Results are reported in Table 2.

Several conclusions can be drawn from these preliminary results. The principal one is that pyridine-containing complexes **12–14** did not catalyze the conversion of allylic acetate **17** into its isomer **18** (Entries 10–12). We believe that this is mainly due to the strong affinity of pyridine derivatives for the cationic gold(I) center, as demonstrated by the stability of numerous isolated pyridine–gold(I) adducts [30–31]. Remarkably, even the presence

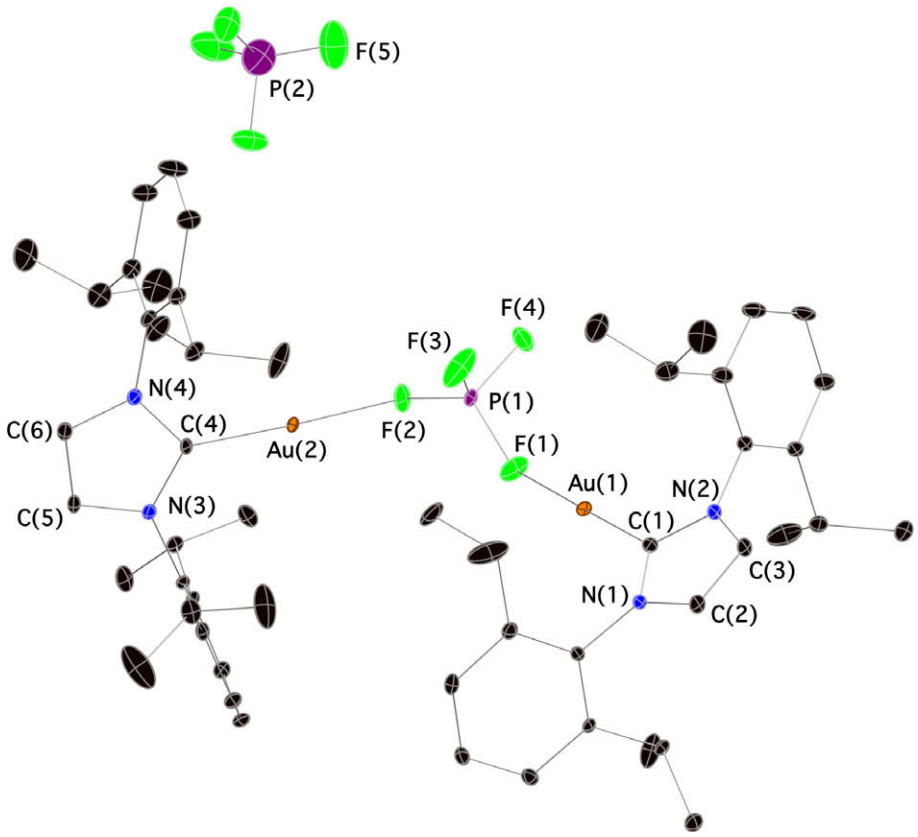


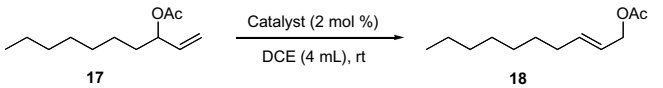
Fig. 7. Crystal structure of $[(\mu\text{-}PF_4)((IPr)Au)_2]PF_4$ (**16**) (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Au(1)–C(1) 1.956(5); Au(1)–F(1) 2.055(4); C(1)–N(1) 1.351(6); C(1)–N(2) 1.345(6); P(1)–F(1) 1.482(4); P(1)–F(2) 1.489(4); P(1)–F(3) 1.527(6); P(1)–F(4) 1.553(5); Au(2)–F(2) 2.042(4); Au(2)–C(4) 1.962(5); C(4)–N(3) 1.349(7); C(4)–N(4) 1.352(6); P(2)–F(5) 1.353(8). Selected angles (°): F(1)–P(1)–F(2) 115.5(3); F(3)–P(1)–F(4) 105.0(4); C(1)–Au(1)–F(1) 179.04(18); Au(1)–F(1)–P(1) 128.3(3); C(4)–Au(2)–F(2) 177.40(18); Au(2)–F(2)–P(1) 132.3(3); N(1)–C(1)–N(2) 105.2(4); N(3)–C(4)–N(4) 105.7(4). Selected torsion angles (°): N(1)–C(2)–C(3)–N(2) 0.3(6); N(3)–C(5)–C(6)–N(4) 0.5(7).

of a bulky bromine atom in *ortho*-position did not lead to a more facile decoordination from the cationic center (Entry 11).

While the whole series of acetonitrile-containing [(NHC)Au(NCMe)]X complexes allowed for good yields in the formation of **18** (Entries 5–9), it should be noted that prolonged reaction times (48 h) were required when compared to the *in situ* prepared cationic gold(I) catalyst (Entry 4). This can be explained by the necessity for the olefin substrate to displace a coordinating molecule of acetonitrile from the gold center. In the case of the *in situ* generated NHC–gold(I) catalyst, the cationic metal center can be considered as "bare" since the reaction is performed in a non-coordinating solvent (DCE), leading to enhance catalytic activity. The catalytic activity of the norbornadiene gold complex **15** can be considered intermediate between that of the acetonitrile and pyridine adducts. Indeed, only moderate conversion was observed after prolonged reaction time (Entry 13).

Finally, to further demonstrate the importance of an available coordination site on the gold center, and the role of subtrate/solvent binding equilibrium, we carried out two reactions using the *in situ* procedure in coordinating solvents, as depicted in Eqs. (1) and (2). Hence, the formation of **18** was greatly slowed down in acetonitrile (Eq. (1)) and required several days in order to reach a similar conversion as the one previously observed in DCE. As expected, the use of pyridine proved detrimental to the rearrangement of **17** into **18**, and even after several days, no formation of internal alkene was observed (Eq. (2)). It should be noted that, in both cases, no precipitation of colloidal gold was observed, highlighting the stability of both the acetonitrile and the pyridine adducts of NHC–gold(I) complexes.

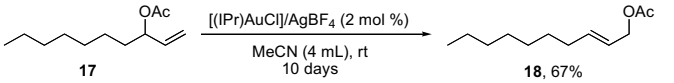
Table 2
[(NHC)Au(L)]X-Catalyzed rearrangement of allylic acetate.



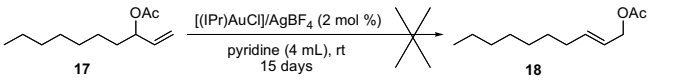
17 **18**

Entry	Catalyst (2 mol%)	Time	**18** (GC conversion) (%)[a]
1	None	10 d	NR
2	$AgBF_4$	10 d	NR
3	$[PdCl_2(PhCN)_2]$	6 h	70
4	$[(IPr)AuCl]/AgBF_4$	10 h	69
5	$[(IPr)Au(NCMe)]PF_6$ (**1**)	48 h	69
6	$[(IPr)Au(NCMe)]SbF_6$ (**5**)	48 h	67
7	$[(IPr)Au(NCMe)]BF_4$ (**6**)	48 h	73
8	$[(IPr)Au(NCMe)]B(C_6F_5)_4$ (**7**)	48 h	68
9	$[(ItBu)Au(NCMe)]PF_6$ (**9**)	48 h	67
10	$[(IPr)Au(pyr)]PF_6$ (**12**)	10 d	NR
11	$[(IPr)Au(2\text{-}Br\text{-}pyr)]PF_6$ (**13**)	10 d	NR
12	$[(IPr)Au(3\text{-}Br\text{-}pyr)]PF_6$ (**14**)	10 d	NR
13	$[(IPr)Au(nbd)]PF_6$ (**15**)	5 d	50

[a] GC conversions are the average of at least 2 runs. NR = no reaction; pyr = pyridine; nbd = norbornadiene.



(1)



(2)

3. Conclusion

We have isolated and characterized by NMR spectroscopy and X-ray diffraction study several well-defined cationic [(NHC)Au(L)]X complexes, which are postulated as the active catalysts in numerous gold mediated organic transformations. A comparative study of their catalytic activity showed that acetonitrile-based complexes are best suited for potential applications in catalysis while pyridine-based compounds proved to be inactive in the rearrangement of allylic acetates. Studies aimed at exploring this relative stability/activity issue are presently ongoing in our laboratories.

4. Experimental

4.1. General information

All reactions were carried out open to air unless indicated otherwise. All NHCs were synthesized according to literature procedures.[32] Anhydrous pentane was used as purchased. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian-400, Bruker-400 or Bruker-500 MHz spectrometer at ambient temperature in $CDCl_3$, THF-d_8 and CD_3CN containing tetramethylsilane (Cambridge Isotope Laboratories, Inc).

4.2. Synthesis of cationic gold(I) complexes

4.2.1. [(IPr)Au(NCMe)]SbF_6 (**5**)

In a scintillation vial, [(IPr)AuCl] (250 mg, 1 equiv., 0.40 mmol) was dissolved in dried acetonitrile (2 mL) and $AgSbF_6$ (152 mg, 1.05 equiv., 0.43 mmol) was added. The solution was stirred for 1 min. Acetonitrile was removed under vacuum and DCM (2 mL) was added. Filtration over a plug of silicagel gave a clear greenish solution. After removal of the DCM under vacuum, the desired complex was obtained as a white powder. Yield: 310 mg (90%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.57 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.36 (s, 2H, $CH^{imidazole}$), 7.34 (d, J = 8.0 Hz, 4H, CH^{Ar}), 2.45 (septuplet, J = 7.0 Hz, 4H, $CH(CH_3)_2$), 2.31 (s, 3H, N≡C–CH_3), 1.28 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.23 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 166.0 ($C^{carbene}$), 145.7 (C^{Ar}), 133.1 (C^{Ar}), 131.5 (CH^{Ar}), 125.0 (CH^{Ar}), 124.6 ($CH^{imidazole}$), 120.5 (N≡C), 28.9 (CH, $CH(CH_3)_2$), 24.8 (CH_3, $CH(CH_3)_2$), 24.1 (CH_3, $CH(CH_3)_2$), 2.6 (CH_3, N≡C–CH_3). ^{19}F NMR ($CDCl_3$): No signals visible, due to the antimony nucleus (I = 7/2).

4.2.2. [(IPr)Au(NCMe)]BF_4 (**6**)

In a scintillation vial, [(IPr)AuCl] (300 mg, 1 equiv., 0.48 mmol) was dissolved in dry acetonitrile (2 mL) and $AgBF_4$ (94 mg, 1 equiv., 0.48 mmol) was added in the dark. The solution was stirred for 1 min. Acetonitrile was removed under vacuum and DCM (2 mL) was added. Filtration over a plug of silicagel gave a colorless solution. After removal of the DCM under vacuum, the desired complex was obtained as a white powder. Yield: 328 mg (96%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.56 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.41 (s, 2H, $CH^{imidazole}$), 7.32 (d, J = 8.0 Hz, 4H, CH^{Ar}), 2.43 (septuplet, J = 7.0 Hz, 4H, $CH(CH_3)_2$), 2.37 (s, 3H, N≡C–CH_3), 1.27 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.23 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 165.9 (C, $C^{carbene}$), 145.6 (C, C^{Ar}), 133.2 (C, C^{Ar}), 131.4 (CH, CH^{Ar}), 125.1 (CH, CH^{Ar}), 124.6 (CH, $CH^{imidazole}$), 121.0 (C, N≡C), 28.9 (CH, $CH(CH_3)_2$), 24.8 (CH_3, $CH(CH_3)_2$), 24.1 (CH_3, $CH(CH_3)_2$), 2.6 (CH_3, N≡C–CH_3). ^{11}B NMR ($CDCl_3$): δ (ppm) = −1.1 (s, BF_4^-). ^{19}F NMR ($CDCl_3$): δ (ppm) = −153.7 (s, BF_4^-).

4.2.3. [(IPr)Au(NCMe)][$B(C_6F_5)_4$] (**7**)

In a scintillation vial, [(IPr)AuCl] (150 mg, 1 equiv., 0.24 mmol) was dissolved in dry acetonitrile (2 mL) and $AgB(C_6F_5)_4 \cdot 0.5$ toluene (246 mg, 1.05 equiv., 0.25 mmol) was added. The solution was stirred for 1 min. Acetonitrile was removed under vacuum and DCM (2 mL) added. Filtration over a plug of silicagel gave a clear greenish solution. After removal of the DCM under vacuum, the desired complex was obtained as a white powder. Yield: 307 mg (98%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.56 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.36 (d, J = 8.0 Hz, 4H, CH^{Ar}), 7.32 (s, 2H, $CH^{imidazole}$), 2.47 (septuplet, J = 7.0 Hz, 4H, $CH(CH_3)_2$), 2.22 (s, 3H, N≡C–CH_3), 1.29 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.25 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 166.1 (C, $C^{carbene}$), 148.3 (d, J = 246 Hz, C, C^{Ar}–F), 145.7 (C, C^{Ar}), 139.5 (broad s, C, C^{Ar}–B), 137.6 (broad s, C, C^{Ar}–F), 137.0 (broad s, C, C^{Ar}–F), 133.0 (C, C^{Ar}), 131.5 (CH, CH^{Ar}), 124.7 (CH, CH^{Ar}), 124.7 (CH, $CH^{imidazole}$), 119.6 (C, N≡C), 29.0 (CH, $CH(CH_3)_2$), 24.6 (CH_3, $CH(CH_3)_2$), 23.9 (CH_3, $CH(CH_3)_2$), 2.4 (CH_3, N≡C–CH_3). ^{11}B NMR ($CDCl_3$): δ (ppm) = −16.7 (s, $B(C_6F_5)_4^-$). ^{19}F NMR ($CDCl_3$): δ (ppm) = −132.7 (s, o-C^{Ar}–F), −163.3 (t, $J^3(^{19}F–^{19}F)$ = 21.0 Hz, p-C^{Ar}–F), −167.0 (broad t, $J^3(^{19}F–^{19}F)$ = 21.0 Hz, m-C^{Ar}–F).

4.2.4. [(IAd)Au(NCMe)]PF_6 (**8**)

In a scintillation vial, [(IAd)AuCl] (100 mg, 1 equiv., 0.18 mmol) was partially dissolved in dry acetonitrile (2 mL) and $AgPF_6$ (47 mg, 1.05 equiv., 0.18 mmol) was added. The solution was stirred for one minute. Acetonitrile was removed under vacuum and DCM (2 mL) was added. Filtration over a plug of silicagel gave a clear greenish solution. After removal of the DCM under vacuum, the desired complex was obtained as a white powder. Yield: 113 mg (88%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.35 (s, 2H, $CH^{imidazole}$), 2.47 (m, 14H, CH_2), 2.25 (s, 6H, CH_2), 2.18 (s, 3H, N≡C–CH_3), 1.77 (m, 10H, CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 157.7 (C, $C^{carbene}$), 120.4 (C, N≡C), 118.6 (CH, $CH^{imidazole}$), 60.5 (CH, N–$CH^{adamantyl}$), 45.3 (CH_2), 36.4 (CH_2), 31.0 (CH_2), 2.8 (CH_3, N≡C–CH_3). ^{31}P NMR ($CDCl_3$): δ (ppm) = −141.3 (septuplet, $J^1(^{31}P–^{19}F)$ = 712.0 Hz, PF_6^-). ^{19}F NMR ($CDCl_3$): δ (ppm) = −74.0 (d, $J^1(^{19}F–^{31}P)$ = 712.0 Hz, PF_6^-).

4.2.5. [(ItBu)Au(NCMe)]PF_6 (**9**)

In a scintillation vial, [(ItBu)AuCl] (50 mg, 1 equiv., 0.12 mmol) was dissolved in acetonitrile (2 mL) and $AgPF_6$ (31 mg, 1 equiv., 0.12 mmol) was added. The solution was stirred one minute and filtered over Celite to give a colorless solution. After removal of acetonitrile under vacuum, a white powder was isolated. ^{1}H NMR (CD_3CN) δ (ppm) = 7.38 (s, 2H, $CH^{imidazole}$), 1.83 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (CD_3CN) δ (ppm) = 159.7 (C, $C^{carbene}$), 60.6 (C, $C(CH_3)_3$), 32.7 (CH_3, $C(CH_3)_3$).

4.2.6. [(IMes)Au(NCMe)]PF_6 (**10**)

In a scintillation vial, [(IMes)AuCl] (50 mg, 1 equiv., 0.09 mmol) was dissolved in acetonitrile (2 mL) and $AgPF_6$ (24 mg, 1 equiv., 0.09 mmol) was added. The solution was stirred one minute and filtered over Celite to give a colorless solution. After removal of acetonitrile in vacuum, a white powder is isolated which decomposes in air, turning purple after few hours. ^{1}H NMR (CD_3CN) δ (ppm) = 7.50 (s, 2H, $CH^{imidazole}$), 7.15 (s, 4H, CH^{Ar}), 2.38 (s, 6H, CH_3), 1.31 (s, 12H, CH_3). ^{13}C NMR (CD_3CN) δ (ppm) = 165.3 (C, $C^{carbene}$), 141.9 (C, C^{Ar}), 136.4 (C, C^{Ar}), 135.6 (C, C^{Ar}), 130.0 (CH, CH^{Ar}), 125.6 (CH, $CH^{imidazole}$), 21.5 (CH_3), 18.2 (CH_3). NB: It should be noted that after one day in acetonitrile, 10 showed extra signals in the ^{13}C NMR spectrum that were attributed to [$(IMes)_2Au^+$][PF_6^-].

4.2.7. [(IPr)Au(THF)]PF_6 (**11**)

In a scintillation vial, [(IPr)AuCl] (200 mg, 1 equiv., 0.32 mmol) was dissolved in THF (2 mL) and $AgPF_6$ (81 mg, 1 equiv., 0.32 mmol) was added. The solution was stirred one minute and filtered over Celite to give a colorless solution. Overnight, the THF becomes a gel and two extra signals appear for the residual protons of the deuterated THF at 2.7 and 1.0 ppm downfield from the two normal THF signals. Appearance of colloidal gold(0) was

observed after 3 days. After removal of THF under vacuum, a white powder was isolated and decomposed after a few hours, turning grey. ^{1}H NMR (THF-d_8) δ (ppm) = 7.82 (s, 2H, CH^{imidazole}), 7.59 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.42 (d, J = 8.0 Hz, 2H, CH^{Ar}), 2.57 (sept, J = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.33 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (THF-*d8*) δ (ppm) = 159.7 (C, C^{carbene}), 146.7 (C, C^{Ar}), 134.8 (C, C^{Ar}), 131.7 (CH, CH^{Ar}), 126.3 (CH, CH^{Ar}), 125.1 (CH, CH^{imidazole}), 29.7 (CH, *C*H(CH$_3$)$_2$), 25.8 (CH$_3$, CH(*C*H$_3$)$_2$), 24.7 (CH$_3$, CH (*C*H$_3$)$_2$).

*4.2.8. [(IPr)Au(pyr)]PF$_6$ (**12**)*

In a scintillation vial, [(IPr)Au(NCMe)]PF$_6$ (**1**) (100 mg, 1 equiv., 0.13 mmol) was partially dissolved in dry DCM (2 mL) and pyridine (12 µl, 1.1 equiv., 1.44 mmol) was added. The solution was stirred for six hours. DCM and the excess pyridine were removed under vacuum. The desired complex was obtained as a white powder. Yield: 91 mg (91%). ^{1}H NMR (CDCl$_3$): δ (ppm) = 8.05–7.80 (broad m, 3H, CH^{pyr}), 7.58–7.52 (broad m, 2H, CH^{pyr}), 7.55 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.46 (s, 2H, CH^{imidazole}), 7.33 (d, J = 8.0 Hz, 4H, CH^{Ar}), 2.53 (septuplet, J = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 1.30 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.24 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ (ppm) = 167.1 (C, C^{carbene}), 150.6 (CH, CH^{pyr}), 145.8 (C, C^{Ar}), 133.2 (C, C^{Ar}), 131.3 (CH, CH^{Ar}), 127.7 (broad s, CH, CH^{pyr}), 126.8 (CH, CH^{pyr}), 125.0 (CH, CH^{Ar}), 124.7 (CH, CH^{imidazole}), 29.0 (CH, *C*H(CH$_3$)$_2$), 24.5 (CH$_3$, CH(*C*H$_3$)$_2$), 23.8 (CH$_3$, CH(*C*H$_3$)$_2$). ^{31}P NMR (CDCl$_3$): δ (ppm) = −141.4 (septuplet, J^1(^{31}P–^{19}F) = 711.0 Hz, PF$_6^-$). ^{19}F NMR (CDCl$_3$): δ (ppm) = −74.2 (d, J^1(^{19}F–^{31}P) = 711.0 Hz, PF$_6^-$).

*4.2.9. [(IPr)Au(2-Br-pyr)]PF$_6$ (**13**)*

In a scintillation vial, [(IPr)Au(NCMe)]PF$_6$ **1** (200 mg, 1 equiv., 0.26 mmol) was partially dissolved in dry DCM (2 mL) and 2-bromopyridine (26 µl, 1.05 equiv., 0.27 mmol) was added. The solution was stirred for 6 h and the DCM was removed under vacuum. The remaining solid was washed with pentane. The desired complex was obtained as a white powder. Yield: 192 mg (82%). ^{1}H NMR (CDCl$_3$): δ (ppm) = 7.95 (broad m, 1H, CH^{pyr}), 7.71 (broad m, 2H, CH^{pyr}), 7.65 (broad m, 1H, CH^{pyr}), 7.57 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.45 (s, 2H, CH^{imidazole}), 7.35 (d, J = 8.0 Hz, 4H, CH^{Ar}), 2.53 (septuplet, J = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 1.31 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ (ppm) = 166.9 (C, C^{carbene}), 152.7 (C^{pyr}), 145.3 (C, C^{Ar}), 143.2 (C^{pyr}), 143.1 (C^{pyr}), 133.7 (C, C^{Ar}), 131.7 (C^{pyr}), 131.3 (CH, CH^{Ar}), 126.0 (C^{pyr}), 125.6 (CH, CH^{imidazole}), 124.9 (CH, CH^{Ar}), 29.0 (CH, *C*H(CH$_3$)$_2$), 24.7 (CH$_3$, CH(*C*H$_3$)$_2$), 24.2 (CH$_3$, CH(*C*H$_3$)$_2$). ^{31}P NMR (CDCl$_3$): δ (ppm) = −141.3 (septuplet, J^1(^{31}P–^{19}F) = 711.0 Hz, PF$_6^-$). ^{19}F NMR (CDCl$_3$): δ (ppm) = −74.2 (d, J^1(^{19}F–^{31}P) = 711.0 Hz, PF$_6^-$).

*4.2.10. [(IPr)Au(3-Br-pyr)]PF$_6$ (**14**)*

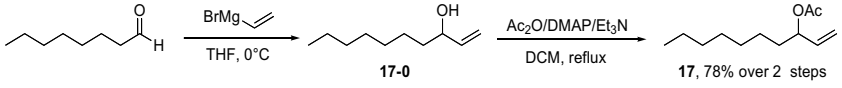
In a scintillation vial, [(IPr)Au(NCMe)]PF$_6$ **1** (200 mg, 1 equiv., 0.26 mmol) was partially dissolved in dry DCM (2 mL) and 3-bromopyridine (26 µl, 1.05 equiv., 0.27 mmol) was added. The solution was stirred for 6 h and the DCM was removed under vacuum. The remaining solid was washed with pentane. The desired complex was obtained as a white powder. Yield: 188 mg (80%). ^{1}H NMR (CDCl$_3$) δ (ppm) = 8.14 (broad m, 1H, CH^{pyr}), 7.91 (broad m, 2H, CH^{pyr}), 7.70 (broad m, 1H, CH^{pyr}), 7.59 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.45 (s, 2H, CH^{imidazole}), 7.36 (d, J = 8.0 Hz, 4H, CH^{Ar}), 2.53 (septuplet, J = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 1.32 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.27 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ (ppm) = δ 166.0 (C, C^{carbene}), 150.9 (C^{pyr}), 149.5 (broad s, C^{pyr}), 145.6 (C, C^{Ar}), 144.6 (broad s, C^{pyr}), 133.3 (C, C^{Ar}), 128.9 (broad s, C^{pyr}), 131.4 (CH, CH^{Ar}), 125.2 (CH, CH^{imidazole}), 124.6 (CH, CH^{Ar}), 122.9 (broad s, C^{pyr}), 28.9 (CH, *C*H(CH$_3$)$_2$), 24.8 (CH$_3$, CH(*C*H$_3$)$_2$), 24.0 (CH$_3$, CH(*C*H$_3$)$_2$). ^{31}P NMR (CDCl$_3$): δ (ppm) = −141.3 (septuplet, J^1(^{31}P–^{19}F) = 711.0 Hz, PF$_6^-$). ^{19}F NMR (CDCl$_3$): δ (ppm) = −73.5 (d, J^1(^{19}F–^{31}P) = 711.0 Hz, PF$_6^-$).

*4.2.11. [(IPr)Au(nbd)]PF$_6$ (**15**)*

In a scintillation vial, [(IPr)Au(NCMe)]PF$_6$ (**1**) (500 mg, 1 equiv., 0.66 mmol) was partially dissolved in dry DCM (5 mL) and norbornadiene (nbd) (612 mg, 0.68 mL, 10 equiv., 6.6 mmol) was added. The solution was stirred overnight. All the DCM and the excess norbonadiene was removed under vacuum and DCM (10 mL) was added. Filtration over a plug of silicagel gave a clear greenish solution. After removal of the DCM under vacuum, the desired complex was obtained as a white powder. Yield: 457 mg (84%). ^{1}H NMR (CDCl$_3$) δ (ppm) = 7.53 (t, J = 8.0 Hz, 2H, CH^{Ar}), 7.50 (s, 2H, CH^{imidazole}), 7.30 (d, J = 8.0 Hz, 4H, CH^{Ar}), 6.85 (s, 2H, CH^{nbd}), 6.52 (s, 2H, CH^{nbd}), 3.62 (s, 2H, CH^{nbd}), 2.40 (septuplet, J = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 1.40 (s, 2H, CH$_2^{nbd}$), 1.25 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.23 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ (ppm) = 182.0 (C, C^{carbene}), 145.7 (C, C^{Ar}), 143.2 (broad s, CH, CH^{nbd}), 134.4 (very broad s [only seen by HMQC sequence], CH, CH^{nbd}), 133.1 (C, C^{Ar}), 131.5 (CH, CH^{Ar}), 125.1 (CH, CH^{Ar}), 124.9 (CH, CH^{imidazole}), 52.2 (CH, CH^{nbd}), 30.3 (CH$_2$, CH$_2^{nbd}$), 28.9 (CH, *C*H(CH$_3$)$_2$), 25.0 (CH$_3$, CH(*C*H$_3$)$_2$), 24.0 (CH$_3$, CH(*C*H$_3$)$_2$). ^{31}P NMR (CDCl$_3$): δ (ppm) = −141.4 (septuplet, J^1(^{31}P–^{19}F) = 713.0 Hz, PF$_6^-$). ^{19}F NMR (CDCl$_3$): δ (ppm) = −73.7 (d, J^1(^{19}F–^{31}P) = 713.0 Hz, PF$_6^-$).

4.3. Cationic gold(I)-catalyzed rearrangement of allylic acetates

*4.3.1. Synthesis of allylic acetate (**17**)*



*4.3.1.1. Dec-1-en-3-ol **17-0**.* In an oven-dried round-bottom flask, a solution of the 1-octanal (4.70 mL, 30 mmol, 1 equiv.) in THF (70 mL) was stirred for 10 min under nitrogen at 0 °C. To the reaction mixture, allyl magnesiumbromide 1.6 M (22.5 mL, 36 mmol, 1.2 equiv.) was added and the reaction was stirred for 20 min. The reaction was then allowed to warm up to room temperature, quenched with a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and evaporated to give the crude allylic alcohol **17-0** that was engaged in the next step without further purification.

^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 5.86–5.77 (m, 1H, C*H*=CH$_2$), 5.16 (d, J = 17.2 Hz, 1H, CH=C*H*$_2$), 5.04 (d, J = 10.4 Hz, 1H, CH=C*H*$_2$), 4.03 (m, 1H, C*H*–OH), 2.65 (broad s, 1H, OH), 1.51–1.46 (m, 2H, C*H*$_2$–CH–OH), 1.32–1.18 (m, 10H, CH$_2$), 0.85 (t, J = 6.8 Hz, 3H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.4 (CH, *C*H=CH$_2$), 114.3 (CH$_2$, CH=*C*H$_2$), 73.1 (CH, CH–OH), 37.0 (CH$_2$), 31.8 (CH$_2$), 29.5 (CH$_2$), 29.2 (CH$_2$), 25.3 (CH$_2$), 22.6 (CH$_2$), 14.0 (CH$_3$).

*4.3.1.2. Dec-1-en-3-yl acetate (**17**).* Allylic alcohol **17-0** (10 mmol, 1 equiv.), dichloromethane (30 mL), 4-dimethylaminopyridine (DMAP) (0.360 g, 3.0 mmol, 0.3 equiv.), Et_3N (5.6 mL, 40 mmol, 4 equiv.), and Ac_2O (1.8 mL, 20 mmol, 2 equiv.) were added in turn in a round-bottom flask equipped with a condenser. The reaction mixture was heated overnight at reflux. The reaction was then

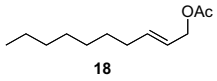
quenched with a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and evaporated to give a crude product that was purified by flash chromatography on silica gel (pentane/Et_2O 95/5), and yielded 1.55 g (78% over 2 steps) of dec-1-en-3-yl acetate (**17**).

^1H NMR (400 MHz, CDCl3): δ (ppm) = 5.78-5.70 (m, 1H, C*H*=CH_2), 5.22-5.16 (m, 2H, CH=C*H*$_2$), 5.13-5.10 (m, 1H, C*H*–OAc), 2.02 (s, 3H, OAc), 1.62-1.51 (m, 2H, C*H*$_2$–CH–OH), 1.34-1.17 (m, 10H, CH_2), 0.84 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1 (C, C=O), 136.6 (CH, *C*H=CH_2), 116.4 (CH_2, CH=*C*H$_2$), 74.7 (CH, CH–OH), 34.1 (CH_2), 31.7 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 25.0 (CH_2), 22.6 (CH_2), 21.1 (CH_3, OAc), 14.0 (CH_3). HMRS: Calc. for $C_{12}H_{22}O_2Na$ (M+Na): 198.1620. Found: 198.1624.

4.3.2. General procedure for the [(NHC)Au(L)]X-catalyzed rearrangement of allylic acetates

To a DCE solution (3 mL) of [(NHC)Au(L)]X (2 mol %) in a 5 mL vial, was added a DCE solution (1 mL) of allylic acetate 17 (0.25 mmol, 50 mg). The reaction mixture was stirred for the indicated time, while the conversion was being controlled by GC, and the resulting mixture was dissolved in pentane, filtered through Celite and evaporated. The crude product was purified by flash chromatography on silica gel.

4.3.2.1. (E)-Dec-2-enyl acetate (**18**)



18

^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.79–5.70 (m, 1H, CH=), 5.63–5.54 (m, 1H, CH=), 4.53 (dd, J = 6.8, 1.6 Hz, 2H, C*H*$_2$–OAc), 2.06 (s, 3H, OAc), 2.00–1.93 (m, 2H, C*H*$_2$–CH=), 1.32–1.20 (m, 10H, CH_2), 0.83 (t, J = 6.9 Hz, 3H, CH_3).

Supplementary material

CCDC 692734, 692733, 692735, 692736, 692737 and 692738 contain the supplementary crystallographic data for ([(IPr)Au(NCMe)]SbF_6 **5**), ([(IAd)Au(NCMe)]PF_6 **8**), ([(IPr)Au(pyr)]PF_6 **12**), ([(IPr)Au(2-Br-pyr)]PF_6 **13**), ([(IPr)Au(3-Br-pyr)]PF_6 **14**), and ([(μ-PF_4)((IPr)Au)$_2$]PF_4 **16**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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