Synthesis, isolation and characterization of cationic gold(I) *N*-heterocyclic carbene (NHC) complexes†

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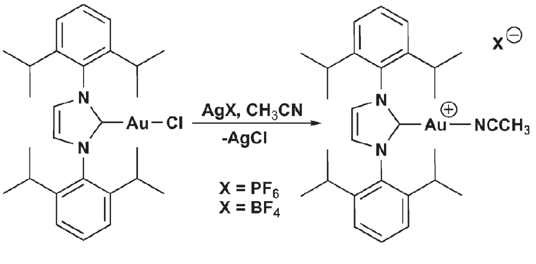
A number of cationic gold(I) complexes have been synthesized and found to be stabilized by the use of *N*-heterocyclic carbene ligands. These species are often employed as *in situ*-generated reactive intermediates in gold catalyzed organic transformations. An isolated, well-defined species was tested in gold-mediated carbene transfer reactions from ethyl diazoacetate.

As part of an ongoing program aimed at examining the role of *N*-heterocyclic carbenes (NHC) 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 free stable NHC, bearing two sterically demanding adamantyl groups on the nitrogens of an imidazolyl framework, by Arduengo *et al.*,[1] sterically encumbering NHCs have allowed the isolation of unusual three-coordinate (NHC)Ni(CO)$_2$ complexes,[2] highly unsaturated 14 electron Ir(I) species,[3] a number of orthometalated ruthenium[4] and iridium[5] species, well-defined monomeric copper(I) species[6] and formally 16 electron second generation ruthenium-based olefin metathesis catalysts.[7] In view of the steric and electronic properties of this ligand class, NHCs have been employed to prepare efficient and robust catalysts for transformations such as palladium-catalyzed cross-coupling reactions,[8] platinum-mediated hydrosilylation,[9] palladium telomerization of butadiene and methanol,[10] copper-catalyzed hydrosilylation[11] and ruthenium-based olefin metathesis,[12] to name a few.

We recently became involved in the synthesis and isolation of well-defined NHC–gold(I) complexes.[13] The first NHC–gold(I) complexes were reported in 1989,[14] and these usually bore two strongly bound ligands arranged in a linear fashion around a gold cation. These can be neutral or cationic and have either [(NHC)AuX][13] or [(NHC)$_2$Au$^+$][X$^-$][15] composition. Until recently, catalytic organogold chemistry appeared to have been somewhat forgotten. The "noble" character of the metal was possibly the origin of the misconception that it would perform poorly in catalysis. This misconception has now been shattered, as numerous examples of gold–phosphines[16] and gold–NHC[17]-mediated transformations have recently appeared. Gold(I) halide complexes are especially efficient at activating alkyne moieties towards nucleophilic addition under mild reaction conditions.[16,17] A recent example by He *et al.* also shows these complexes to be excellent co-catalysts in the intra- and intermolecular hydroamination of unsaturated olefins.[18] 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.[19] While Ferrer and Echavarren have reported the isolation of a monoligated complex, with a very bulky phosphine, [(2-(di-*tert*-butylphosphino)biphenyl) Au$^+$(NCMe)][SbF$_6$$^-$], as an active catalyst for cycloisomerization,[19] attempts to synthesize or isolate I^{t}BuAuBF$_4$ by Baker *et al.*[20] and PPh$_3$AuPF$_6$ by Gagosz *et al.*[21] have so far failed, due to the rapid decomposition of these complexes into colloidal gold(0). In this communication, we report the isolation and characterization of such complexes by using a NHC ligand of sufficient bulk and a weakly coordinating solvent, such as acetonitrile or tetrahydrofuran (THF), leading to relatively stable yet reactive cationic gold(I) complexes.

The previously reported IPrAuCl[13] (IPr = 1,3-bis(di-*iso*-propylphenyl)imidazol-2-ylidene), IMesAuCl[13] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and I^{t}BuAuCl[20] (I^{t}Bu = 1,3-di-*tert*-butylimidazol-2-ylidene) were dissolved in acetonitrile, and AgPF$_6$ or AgBF$_4$ was added in stoichiometric amounts, leading to the rapid formation of a precipitate (AgCl). After stirring the solutions for one minute, the suspensions were filtered through Celite to give the novel complexes in solution (Scheme 1).[22] The appearance of colloidal gold(0) was noticeable after a few hours for all solutions. Attempts to obtain solid materials for all complexes by simply removing the solvent under vacuum only led to rapid decomposition of the materials, obvious as the white material turns to a greyish powder. Carrying out these



Scheme 1 Synthesis route to cationic NHC–Au(I) complexes.

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reactions in the presence or absence of oxygen neither improved nor decreased the stability of the complexes.

Under these synthetic conditions, ^1H and ^{13}C NMR spectra of both the neutral precursors and novel products were recorded. While the pattern of the ^1H NMR spectra remained the same, with no trace of decomposition products between neutral and expected complexes, we observed a slight downfield shift for the backbone protons of the imidazole fragment. We attribute this change to a loss of electron density in the aromatic heterocyclic system, due a delocalization of the π-electrons towards the more acidic gold centre. Moreover, the ^{13}C NMR spectra present signals for the carbenic carbons that are significantly shifted upfield for all complexes. Once again, this observation confirms a more acidic gold center.[20] Both ^1H and ^{13}C NMR studies support the presence of an electron deficient gold centre, confirming the very likely presence of monoligated gold(I) complexes.

We were interested in further testing the stability of such complexes. Attempts to synthesize the complexes in dichloromethane (DCM) or chloroform lead to the rapid appearance of large amounts of colloidal gold. The ^1H NMR spectra of these reactions indicate the existence of two different NHC environments, attributed to at least two NHC–gold species in solution. We confirmed in this manner the necessity of a coordinating solvent to stabilize the cationic gold centre. Ample precedent exists for coordinating solvent stabilization of Pt and Pd complexes.[23,24] THF was employed as an alternative to acetonitrile to generate IPrAu(S)PF_6 (S = coordinating solvent). In THF, no decomposition was observed, even after 24 hours in solution in air, but surprisingly a gel was obtained, attributed to the ring opening polymerization of THF.[25] 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 position (159.7 *vs.* 167.6 ppm in CD_3CN). The complex in THF also displayed a second, more downfield signal of low intensity (after a few hours) for the deuterated THF, which confirmed the formation of poly-THF.[25] It is worthy to note that the cationic polymerization of THF by ring opening in the presence of a Lewis acid, such as $FeCl_3$ or the trityl cation, is well known.[26] In the present case, this polymerization behaviour confirms the presence of a cationic gold-centered complex that is capable of acting as a Lewis acid, an interesting reaction profile which we are presently examining. We also noticed that adding IPrAu(S)PF_6, synthesized from acetonitrile, into THF led to THF polymerization. While the acetonitrile needs to be displaced by the THF to initiate its polymerization, this result shows that, in solution, the molecules of solvent are weakly bound, labile and can easily be displaced from the gold.

To unambiguously establish the solid state structure of one of these complexes, X-ray quality crystals suitable for single crystal diffraction studies were grown from a saturated acetonitrile solution of IPrAu(NCMe)PF_6 (**1**).[27] While the complex slowly decomposes over several hours in solution with appearance of colloidal gold(0), suitable X-ray quality crystals could be grown in this manner. It is noteworthy that the appearance of decomposition in solution or the solid state for these complexes is related to the nature of the carbene and counterion used. Complex **1** is the most stable complex observed so far.

Results from the diffraction study confirm the NMR determined structure and the coordination of one acetonitrile to the gold centre. (Fig. 1). The metrical parameters reveal a nearly linear NHC–Au–$NCCH_3$ arrangement, with a C–Au–N angle of 177.9(78)°. The C–Au bond distance (1.952(2) Å) is similar to that found for IPrAuCl.[13] The N–Au bond distance of 2.022(2) Å is in the range of reported gold complexes with nitrogen donor ligands,[28] but slightly longer than known gold(I) complexes with coordinated acetonitrile such as $[Au^+(NCMe)_2][X^-]$,[29] with an Au–N bond distance equal to 1.96 Å. Finally, the N≡C bond distances between coordinated and non-coordinated molecules of acetonitrile remain the same, with a value of 1.12(3) Å,[30] explaining the observed lability of the bound acetonitrile molecule.

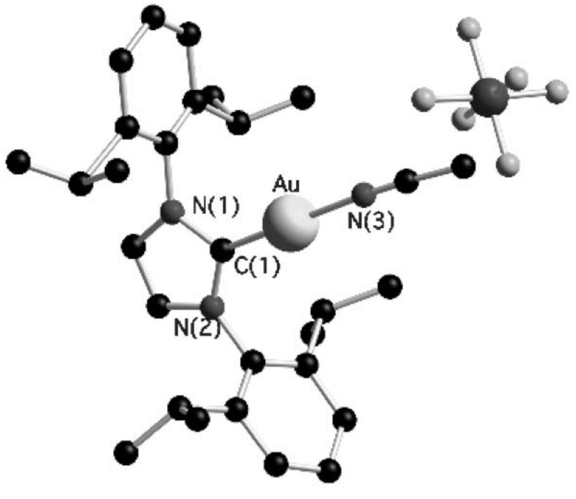

Fig. 1 Ball-and-stick representations of $[IPrAu^+(NCMe)][PF_6^-]$ (**1**). Hydrogens are omitted for clarity. Selected bond lengths (Å) and angle (°): C1–Au = 1.952(2), N1–C1 = 1.38(2), N2–C1 = 1.34(2), Au–N3 = 2.022(2) Å; C1–Au–N3 = 177.9(8).

Previous work from our laboratories has shown a very interesting catalytic behaviour of IPrAuCl in the presence of $NaBAr_4$ (BAr_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) for the decomposition of ethyl diazoacetate (N_2=$CHCO_2Et$, EDA) and subsequent transfer of the :$CHCO_2Et$ unit to organic substrates.[17] This procedure has led to the functionalization of aromatic sp^2 and primary sp^3 C–H bonds of alkanes in moderate to high yields, in a process that requires the assistance of a halide scavenger. Attempts to fully characterize a well-defined complex with a BAr_4 counterion has proven so far unsuccessful. Therefore, the availability of **1**, in solution or as an isolated solid, now allows for the study of its catalytic properties in this transformation. In reactions with catalytic amounts of **1**, ethyl diazoacetate was reacted with several substrates (Table 1). In the case of good

Table 1 Reaction of ethyl diazoacetate and several substrates in the presence of IPrAu(NCMe)PF_6 (**1**) as catalyst

Substrate	Product	Time/h	Yield (%)[a]
Methanol	$CH_3OCH_2CO_2Et$	0.2	>99
Ethanol	$CH_3CH_2OCH_2CO_2Et$	0.2	>99
Aniline	$PhN(H)CH_2CO_2Et$	24	>99
tert-Butylamine	t-$BuN(H)CH_2CO_2Et$	24	55
Styrene	Cyclopropanes	20	>99
Benzene	No reaction[b]	120	—
2,3-dimethylbutane	No reaction[b]	120	—

[a] Determined by GC, diethyl fumarate and maleate accounted for the remaining of the mass balance. [b] EDA not consumed.

nucleophiles such as alcohols, quantitative conversion was obtained within minutes. Longer times were required for aniline, whereas for *tert*-butylamine, incomplete conversion was observed even after 24 hours. A similar result was found with styrene, for which three days were required for complete conversion into cyclopropanes. This trend could be attributed to the ease of replacement of the coordinated acetonitrile in **1** by the substrate. In accordance with this, the use of more weakly coordinating molecules such benzene or 2,3-dimethylbenzene has led to undetectable yields; only very minor amounts of diethyl fumarate and maleate were detected by GC after several days, with most of the initial EDA remaining in solution. However, an additional experiment strongly suggests that this coordination of the substrate is not the only factor at play. The use of an equimolar mixture of IPrAuCl and NaBAr$_4$ as the catalyst in the reaction of styrene and EDA, with a *five-fold excess* of added acetonitrile, did not affect the course of the reaction, and led to the same mixture of products found in the absence of acetonitrile. We strongly suspect at this point that the counterion plays an important role in this catalytic transformation, a feature that is currently under investigation.

In conclusion, we have isolated, characterized by NMR spectroscopy, and for one example by X-ray diffraction, well-defined cationic (NHC)Au(I)(S)X complexes which are postulated as active catalysts in numerous gold-mediated organic transformations. The well-defined, isolated species IPrAu(NCMe)PF$_6$ (**1**) has been tested as catalyst for the carbene transfer reaction from EDA. The results suggest a large effect of the counterion on this transformation when compared with the already reported *in situ*-generated IPrAuCl + NaBAr$_4$ system.[17] Studies aimed at exploring this relative stability issue, as well as investigations focusing on the reactivity of NHC–Au complexes in organic chemistry, are presently ongoing in our laboratories.

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