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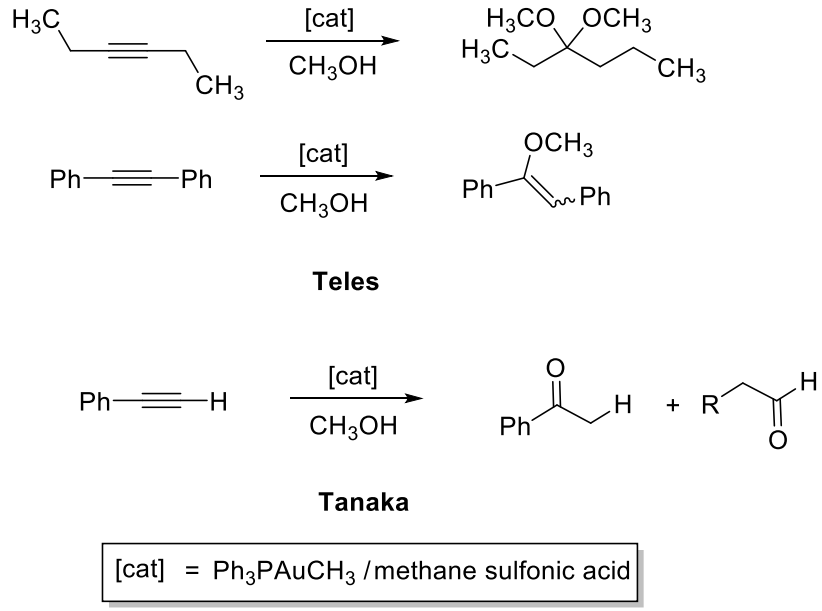
Abstract

The activation of π-bonds by Au(I) catalysts has emerged as a powerful method for building complex molecular architecture. These catalysts often have the motif R_3P-Au-R or $[R_3P\text{-Au-L}]^+$, which are derived from Au-Cl activation from R_3P-Au-Cl precursors. These catalysts are expensive to purchase, or involve a tedious multi-step synthesis starting from Au powder and aqua regia. Here we report the one pot synthesis of the synthetically valuable Echaverren's Au(I) catalyst $[\text{Johnphos-Au-MeCN}]^+$ directly from gold powder using $[NO][BF_4]$ in acetonitrile. While common for other metals, the synthesis of gold precursors from gold power and $[NO][BF_4]$ in acetonitrile is under utilized. Here we demonstrate it is an easy, cost effective method for the generation of an important gold catalyst.

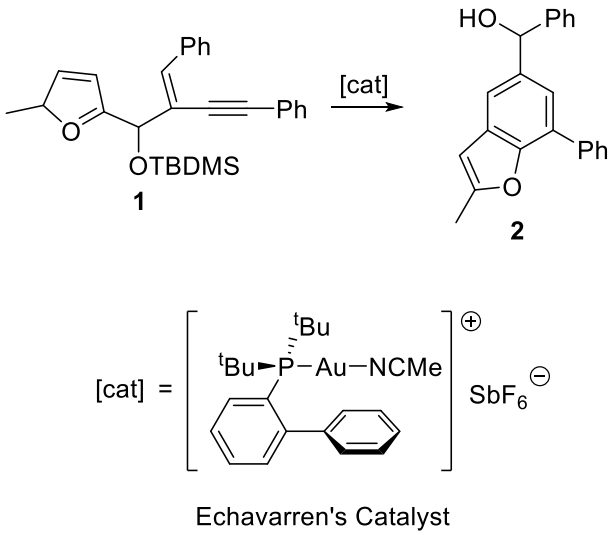
Introduction

In recent decades there has been a rapid growth in the development of both Au(I) and Au(III) catalysed reactions. With regard to Au(I) systems it was work reported by Teles and co-workers[1] describing the Au(I) catalysed nucleophilic additions to alkynes, and subsequent work by Tanaka[2] employing the same catalyst for alkyne hydration that sparked a marked interest in the area (Scheme 1).



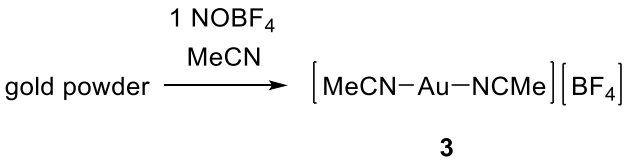
Scheme 1. Au(I) activation of alkyne precursors toward nucleophilic attack by methanol.

Building on this work the activation of π bonds by Au(I) has allowed for the development of a diverse range of organic functionalisations. For example, Au(I) catalysed intermolecular and intramolecular cyclisation reactions now allow for the rapid introduction of molecular complexity into organic frameworks from readily available precursors.[3-5] Scheme 2 depicts a Au(I) catalysed intramolecular cycloisomeration reaction utilizing Echavarren's catalyst [Johnphos-Au-MeCN]$^+$ to give access to substituted benzo[b]furans **1** from furan-yne precursors **2**.[6]



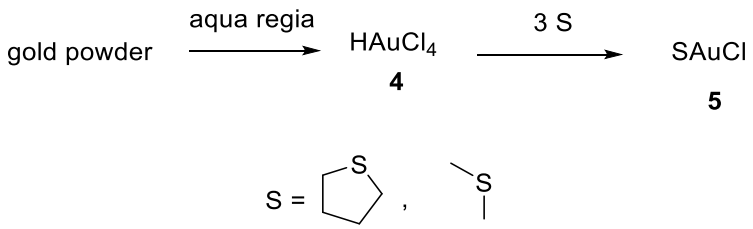
Scheme 2. Au(I) catalysed transformation of furan-ynes to yield substituted benzofurans.

Recently we became interested in the development of synthetic protocols for the generation of both Au(I) and Au(III) coordination complexes directly from gold powder. The oxidation of gold powder with the nitrosyl cation ($[NO]^{+}$) in CH_3CN has been shown to give direct access to bisnitrile salts of Au(I) including the cation **3**, however the use of such complexes for further synthetic application remains sparse (Scheme 3).[7-15] The first reports of compound **3** appeared in 1964, however, the instability of the isolated compound as a $[ClO_4]^-$ salt precluded structural characterisation.[16] Work by Wilner and co-workers in 1998 presented the first crystallographic support for a bisnitrile Au(I) complex, which was achieved *via* the treatment of $Au(CO)_2SbF_6$ with super acids to give the thermally stable $[SbF_6]^-$ salt of **3**.[17] Krossing and co-workers recently demonstrated the utility of the nitrosyl cation in accessing a host of isolable homoleptic Au(I) acetonitrile salts which differed in the weakly coordinating anion.[18]



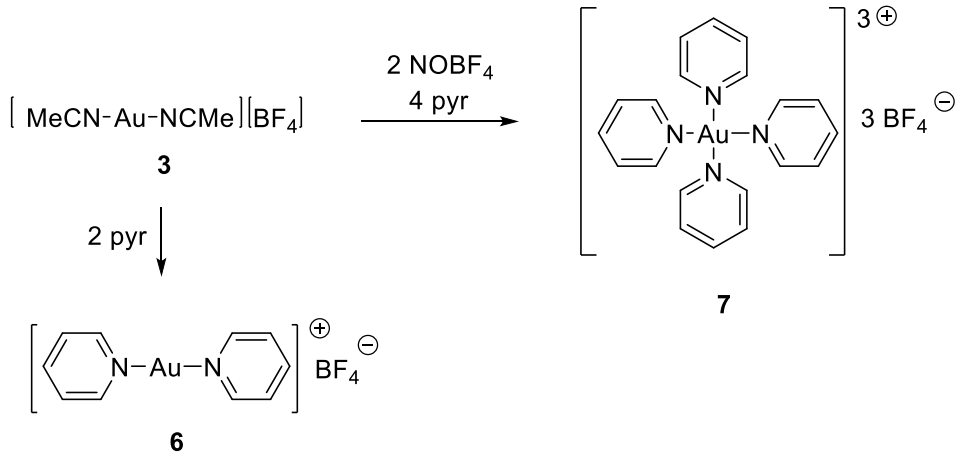
Scheme 3. Generation of the Au(I) monocation **3** as a $[BF_4]^-$ salt from gold powder.

We identified **3** as a readily accessible Au(I) precursor for the generation of synthetically valuable Au(I) complexes and a potential replacement for the commonly used Au(I) starting material [SAu(I)][Cl] (S = tetrahydrothiophene, dimethylsulfide) (**5**). In particular, the stoichiometric oxidation of gold powder using [NO][BF_4] avoids the cumbersome distillation of aqua regia necessary in accessing **5** from gold powder (Scheme 4).



Scheme 4. Common synthetic approach for the synthesis of **5**

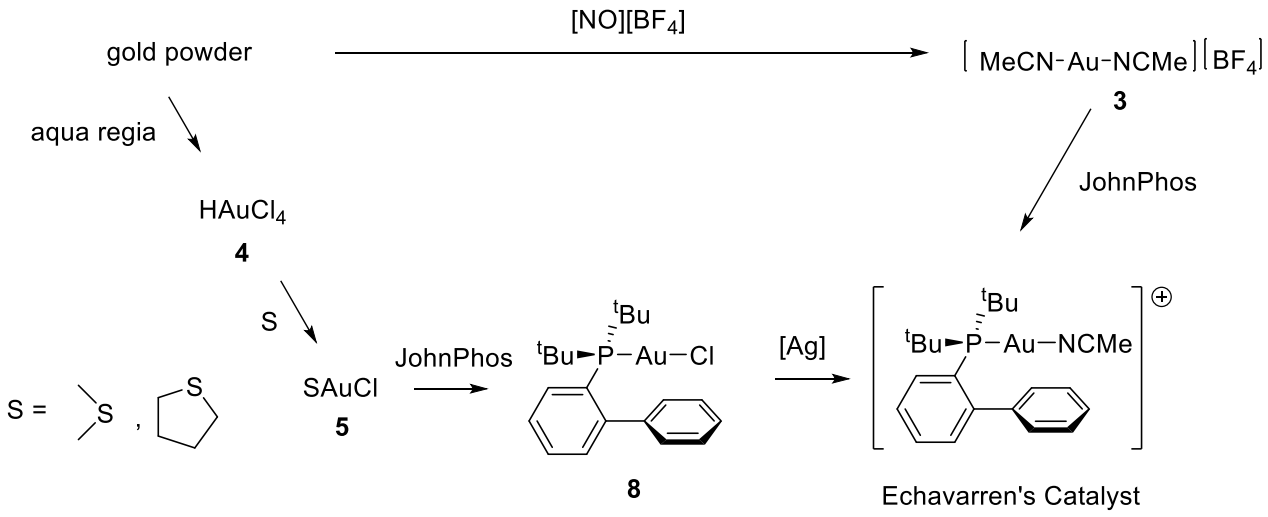
The synthesis of **5** requires the generation of $HAuCl_4$ (**4**) *via* the treatment of gold powder with aqua regia, which upon removal of the aqua regia is reduced back to Au(I) by the excess addition of an appropriate S-nucleophile. Initial investigations conducted by our lab into the utility of [NO][BF_4] as a convenient reagent for accessing gold salts directly from gold powder led to the isolation of the previously inaccessible bispyridine Au(I) tetrafluoroborate salt **6** and the homoleptic tetrakis pyridine Au(III) trication **7** (Scheme 5).[19] Wilgose also reports the use of the nitrosly cation for accessing Au(III) in the generation of pincer complexes from Au(I) precursors.[20]



Scheme 5. Utilisation of complex **3** to give the first example of a Au(I) monocation (**6**) and Au(III) trication (**7**) supported by a homoleptic pyridine ligand system.

A common motif utilised in Au(I) catalysis is that of $PR_3Au(I)$-Cl (R = Ar). These compounds can either be used directly or require activation *via* Ag mediated halide abstraction to generate a cationic species with a vacant coordination site for ligand or substrate binding. Echaverren's catalyst ([LAu(I)-NCMe][SbF_6], L = JohnPhos), for example, is generated by the treatment of **8** with $AgSbF_6$ in CH_3CN to generate the catalyst as an $[SbF_6]^-$ salt (Scheme 8). Access to the catalyst precursor **8** involves a simple ligand exchange reaction with **5** and the desired phosphine (JohnPhos), however, as mentioned earlier the synthesis of **5** is not trivial.

Herein we report a one-pot synthesis of Echavarren's catalyst from gold powder, which provides a significant reduction in cost compared to purchasing the catalyst directly, and avoids the need for the tedious procedure including distillation of aqua regia in the synthesis of $HAuCl_4$.



Scheme 6. Competing synthetic approaches for the generation of Echavarren's Au(I) catalyst.

Results and discussion

To a slurry of gold powder in CH_3CN 0.9 stoichiometric equivalents of $[NO][BF_4]$ was added and the resulting mixture was stirred in the absence of light for 3 hrs giving a colourless solution. The reaction mixture should be vented under a N_2 atmosphere to allow for the evolution of gaseous NO. The stoichiometry of $[NO][BF_4]$ was kept slightly below 1 equivalent to reduce the possibility of residual oxidant causing ligand oxidation upon addition of the phosphine, which was observed even at this stoichiometry if the addition of the phosphine was within the 3 hr window required for complete oxidation of the gold powder. Residual metallic gold was then removed *via* centrifugation before the addition of 0.9 stoichiometric equivalents of JohnPhos (Scheme 6). The reaction was shielded from light and stirred for a further 6 hrs. The solvent volume was reduced *in vacuo* and the addition of Et_2O yielded a fine white powder. Phosphorus and proton NMR analysis of the solids dissolved in $CDCl_3$ gave spectra consistent with previous reports for the synthesis of Echavarren's Au(I) catalyst as the $[SbF_6]^-$ salt, isolated as the $[BF_4]^-$ salt in our synthesis.[21]

Conclusion

We have presented a novel route to Echavarren's Au(I) catalysts *via* a one-pot synthetic approach which avoids the commonly employed aqua regia distillation required in accessing many Au(I) scaffolds. A cost comparison based on currently available pricings (Precious Metals Online for Au powder, Sigma-Aldrich from all other reagents based on a search on Oct 31st 2017) revealed an approximate 10 fold price decrease per mole between our method and a commercially bought sample of Echavarren's Au(I) catalyst ($75/mmol to $620/mmol, repectively). An extension of the cost analysis showed that the $[NO][BF_4]$ protocol presented within does not offer a direct reduction in cost compared the more traditional synthetic method using Au powder and aqua regia as in Scheme 6, however, the costings are comparable at $46/mmol to $75/mmol making the avoidance of a tedious aqua regia distillation and time savings from the other steps appear favourable.

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