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COMMUNICATION

Allene-derived gold and platinum complexes: synthesis and first applications in catalysis.

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We report here the synthesis, full characterisation and first application in catalysis of novel Au(I), Au(III) and Pt(II) carbene-type complexes formed from bis(pyridyl)allenes. The catalytic activity of the new Au(I)-complexes in the cyclisation of 1,6-enynes, benchmark reaction for new Au and Pt complexes, was comparable to Au(I)-state-of-the-art catalysts used in these reactions. Reactions with the new Au(III)- and Pt(II)-complexes occurred under milder conditions than the reported with AuCl₃ and PtCl₂.

The allene functional group is known to act as a ligand in transition metal complexes through its double bonds,¹ but when decorated with two donor units on each of the terminal substituents (LB in Figure 1), it becomes a new attractive ligand scaffold with increased coordination sites. Since 2008 only a handful of such structures have emerged, incorporating mainly phosphorus-based groups capable of complexation to various metal centres (Figure 1, previous work). For example, bis-phosphine allene ligands have been reported in 1:1 (ligand to metal) complexes with Rh(I),² Pd(II) and Pt(II).³ Complexes of bis-phosphine allene ligands with Au(I) gave 1:2 or polymeric complexes.³

Pyridines in general constitute one of the most established and well performing classes of ligands for transition metal complexes, but their use in allene-containing ligands is limited. There is one reported example of bis(pyridyl)allene-metal complex in a 1:1 complex with Cu(I) (detected by ¹H NMR, Figure 1) and a 2:2 complex was crystallised with Ag(I).⁴ In all of these complexes, the allenic structure shows carbene character at the central carbon (as bent allenes)⁵ but retains its chemical integrity. However, very few catalytic reactions have been reported with some of these allene-metal complexes,^{2,3,6} and progress in this field is slow, probably due to the ability of metals to activate the allene^{1,7} towards nucleophilic attack,⁸ which disrupts the allene backbone. In this context, Fensterbank *et al.* reported in 2015 the reaction of allenes

containing a pyridine and a phosphine oxide substituents with Au(I) complexes to give Au(I)-carbene-type complexes from the nucleophilic attack of the pyridine into the allene (Figure 1, bottom).⁹ However, in terms of generality and metal used, the scope for the formation of this type of allene-derived metal carbene complexes and their potential catalytic activity is completely unexplored.

Here we report our results on the use of bis(pyridyl)allenes as precursors of novel Au(I), Au(III) and Pt(II) carbenes, as well as the preliminary results on the catalytic activity of the new complexes in benchmark reactions for Au and Pt catalysis (Figure 1, this work).

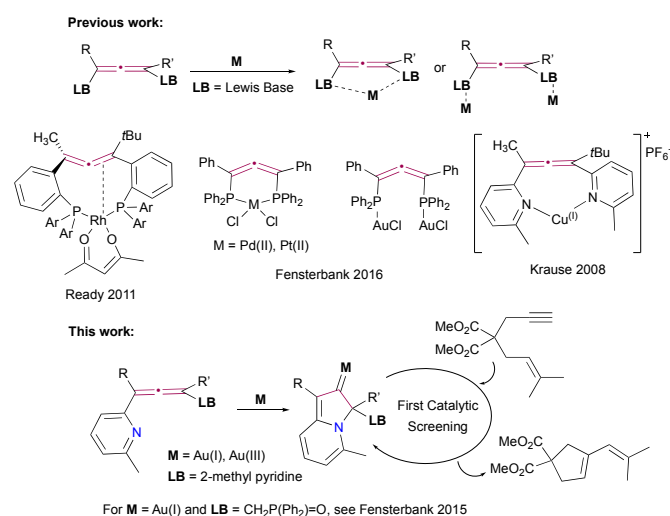


Figure 1. Previous work on allene-based metal complexes and summary of this work.

Bis(pyridyl)allenes **1a-b** were prepared according to modified literature procedures, the key step of the synthesis being a Pd-catalysed S_N2' substitution on propargylic ester precursors using organozinc derivatives.⁴ Having in mind the catalytic utility of Au(I) and Au(III) complexes, we attempted the coordination studies of the ligands with both.

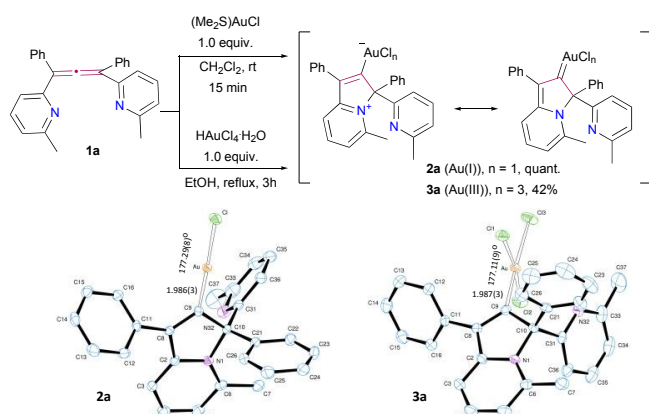
Allene **1a** was reacted with 1 equiv. of (Me₂S)AuCl at rt and after 15 min the quantitative formation of **2a** was observed (Scheme 1). Activation of the allene moiety by Au(I) promotes the attack of one of the pyridine nitrogen atoms on to the

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Electronic Supplementary Information (ESI) available: general experimental details, synthesis of allenes **1a** and **1b**, full characterisation of all compounds, NMR spectra, kinetic data on isomerisation of **2b'** to **2b''**, and details of the crystal structure analyses of complexes **2a**, **3a**, **2b'**, **3b''** and **5**. See DOI: 10.1039/x0xx00000x

terminal carbon atom of the allene, thus forming an indolizine-type core of the new Au species, where the Au is bonded to the former central carbon atom of the allene. **2a** resembles structures of isolated Au(I)-carbenes in which conjugation of heteroatoms, in this case from one of the pyridines, to the electron deficient former central carbon of the allene, contribute to stabilisation,¹⁰ and can be represented in its two resonance forms of zwitterionic vinyl-Au¹¹ and neutral carbene, with the remaining pyridine ring pendant on a newly created stereogenic centre.¹²

1a was also reacted with a Au(III) salt in a refluxing ethanol with the precipitation of yellow powder identified as **3a**, sharing most of its structural features with the Au(I) analogue (Scheme 1).¹³ Both compounds were fully characterised including X-ray diffraction analysis (*vide infra*, see ESI).

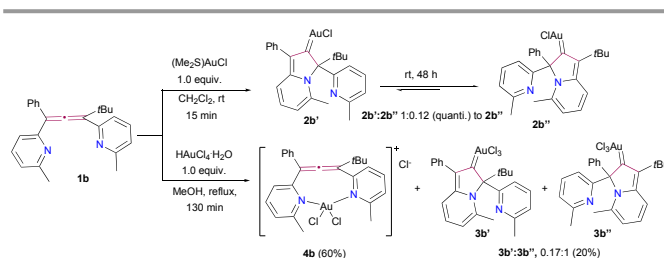


Scheme 1. Reactions of allene **1a** with Au(I) and Au(III) complexes and ORTEP representation of the X-ray structures of complexes **2a** and **3a** (Hs omitted).

The non-symmetric allene **1b** was also subjected to coordination with Au(I) and Au(III) under similar reaction conditions (Scheme 2). Interestingly, reaction with Au(III) gave a mixture of complex **4b** (60%), in which the Au is coordinated to the two pyridines with the allene backbone intact,¹⁴ with complexes **3b':3b''** that crashed out of methanol solution as a 0.17:1 mixture that did not change over time in solution (20%). Good quality crystals of **3b''** allowed full characterisation by X-ray crystallography (see ESI). On the other hand, the Au(I) complex was generated quantitatively in 15 min as a 1:0.12 mixture of **2b':2b''** that slowly equilibrated in solution to >99% of **2b''** ($k_{\text{isom.}} = 6 \times 10^{-4} \text{ s}^{-1}$). The equilibration process between the kinetic (**2b'**) and thermodynamic (**2b''**) product could be viewed as a reversible cyclisation/ring opening reaction with the AuCl fragment moving across the allene core *via* the carbene/vinyl-Au intermediate.¹⁵ Depending on the time of reactions involving **2b** as catalyst, the kinetic (**2b'**) or thermodynamic (**2b''**) complex can be identified as the active catalyst. Alternatively, the kinetic isomer **2b'** may be first allowed to equilibrate fully to the thermodynamic one, **2b''**, that can be used pure in catalytic reactions. Good quality crystals of **2b''** allowed full characterisation by X-ray crystallography (see ESI).

Solid state analysis of Au(I) and Au(III) complexes pointed to many structural similarities within the class and with the pyridine-phosphine complex reported by Fensterbank.⁹ The

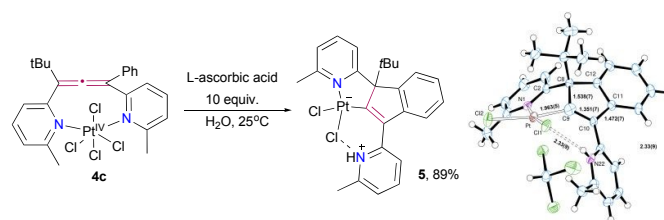
structures are based on an indolizine-type bicyclic core with the Au bonded to the formal allene central carbon neighbouring the stereogenic centre. The geometry around Au centres is close to linear for Au(I)- and square planar for Au(III)-compounds. The Au(I)-C bond distances of **2a** and **2b''** were found to be in the lower range of previously reported for Au(I) carbenes, 1.986(3) Å and 1.997(3) Å, respectively, supporting partial carbene character.¹⁶ The carbene *versus* vinyl-Au character was further probed by several attempts to functionalise the complexes but Au complexes proved to be quite robust. For example, reaction of complex **2b''** with NTF₂H led to decomposition after long times, and isolation of Au(III) complex **3b''** in 10-15% yield,¹⁷ but we could not identify any protodemetalation products. Other attempts to functionalise the complex by oxidation failed, recovering **2b''** unaltered,¹⁸ which further supports its dual carbene/vinyl metal character.



Scheme 2. Reactions of allene **1b** with Au(I) and Au(III) complexes.

Au(III) carbenes are less documented in the literature, but when comparing our structures with more prevalent Au(III)-NHC carbenes the Au-C distances of 2.004(2) for **3a** and 2.020(2) for **3b''** are in the mid-range of previously reported values,¹⁹ and slightly shorter than in reported vinyl-Au(III) complexes.^{13a}

During our studies on Pt complexes with allene-containing ligands we serendipitously discovered formation of Pt(II) complex **5** in the process of a reduction of bis(pyridyl)allene-Pt(IV) complex **4c**, analogous to the Au(III) complex **4b**, with ascorbic acid in aqueous media. Structure of **5** was unambiguously confirmed by X-ray crystallography (Scheme 3, see ESI). The expected Pt(II) equivalent of **4c** was not observed. Interestingly, it was a phenyl substituent that underwent carbocyclisation to the allene. Complex **5** exhibits an hexacyclic core with one of the central five-member rings being a platinacycle formed by the chelation of Pt by the pyridine N1 atom and former central carbon atom C9 of the allene ligand. The Pt atom is found in an approximately square planar geometry completed by two chloride ligands. The free pyridinium ring is a donor of a good intramolecular hydrogen bond N(22)-H(22)...Cl(1) at 2.33(9) Å.²⁰



Scheme 3. Reduction of Pt(IV)-complex **4c** to Pt(II)-complex **5** and ORTEP representation of the X-ray structure of **5**.

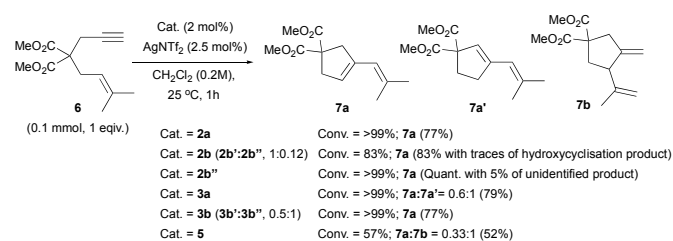
Au-vinyl and carbene complexes are commonly proposed intermediates in Au-catalysed addition to allenes.²¹ Besides, NHC (*N*-heterocyclic carbene)-Au complexes are very efficient catalysts due to the σ -donor properties of the carbenes, as compared with other ligands, e.g. phosphines.²² However, the use of Au-non-stabilised carbenes as direct catalysts are scarcely reported.²³ The catalytic activity of our new class of metal carbenes was assessed in the cycloisomerisation and alkoxylation of 1,6-enynes, benchmark reactions for evaluation of novel Au and Pt complexes.²⁴ Enyne **6** was subjected to a reaction with 2 mol% of the catalyst in CH₂Cl₂ at rt, standard conditions for reactions using [R₃PAu⁺] complexes, with a reaction time arbitrarily set at 60 min for comparison purposes (Scheme 4). For reactions with a nitrogen tether enyne derivative, see ESI. It was determined in initial experiments that reactions with neutral complexes proceeded very sluggishly or not at all, so all reactions were carried out in the presence of AgNTf₂ to generate cationic species.

Although NHC-Au complexes have not been widely used in the cycloisomerisation of 1,6-enynes, carbene-type complexes **2a** and **2b** (as a mixture of **2b'**:**2b''**, 1:0.12) efficiently catalysed the selective formation of skeletal rearrangement product **7a** with similar reactivity and selectivity to [R₃PAu⁺] complexes. Complex **2b''** gave similar results to the mixture **2b'**:**2b''**, where **2b'** is the major isomer (Scheme 4).

Use of Au(III) carbenes **3a-b** (Scheme 4) resulted in a full conversion of the enyne at room temperature, in milder conditions than AuCl₃ complexes, which normally require the reaction to be carried out in toluene at 80 °C. The reaction using complex **3a** yielded a mixture of isomeric products **7a** and **7a'**, the latter being predominant.

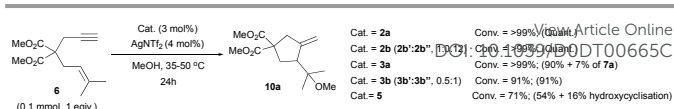
Pt(II)-complex **5** was less reactive than the Au complexes, however, it selectively promoted formation of the Alder-ene type compound **7b** under milder conditions than the commonly employed PtCl₂ that needs toluene at 80 °C to give good results (Scheme 4).

All reactions performed can achieve full conversion of the SM at room temperature, with prolonged reaction times or increased catalyst loading, which might be an advantage when carrying out reaction with Pt(II) and Au(III) complexes, that normally require harsher temperature conditions.



Scheme 4. Cycloisomerisation reaction of enyne **6**. (Isolated yields in brackets).

All catalysts were also found to be active in the alkoxylation reaction of **6** with 3 mol% catalyst loading in MeOH at rt to 50 °C, standard reaction conditions used with [R₃PAu(I)⁺], [NHC-Au⁺] and PtCl₂ catalysts (Scheme 5). The best results were obtained with Au(I) complexes **2a-b** resulting in quantitative formation of addition/cyclisation product **10a**.



Scheme 5. Alkoxylation reaction of enyne **6**. (Isolated yields in brackets).

In conclusion, bis(pyridyl)allenes are effective precursors for novel Au(I), Au(III) and Pt(II) complexes by nucleophilic attack of one of the substituents into the metal-activated allene. Although the new complexes could be initially described as vinyl-metal structures, X-Ray analysis showed that the new metal carbon bonds are in the same range as previously described metal-carbene complexes. The catalytic activity of these metal carbene-type complexes has been tested for the first time and probed against benchmark reactions for novel Au and Pt catalysts. Au(I) complexes **2** showed the more promising catalytic activity, in similar efficiencies to commonly used [R₃PAu⁺] complexes. Au(III) and Pt(II) complexes (**3** and **5** respectively) were also active in the tested reactions under mild conditions. Further screening in more challenging reactions and their asymmetric variant are currently undergoing in our laboratory.

Conflicts of interest

"There are no conflicts to declare".

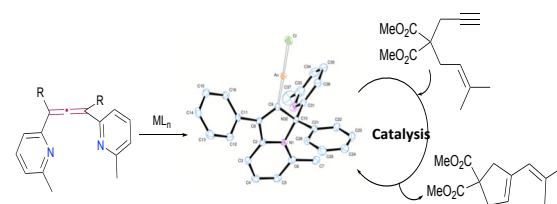
Acknowledgements

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Novel metal carbene complexes made from bis(pyridyl)allenes have promising catalytic activity.