

# Stereo- and Regioselective Alkyne Hydrometallation with Gold(III) Hydrides

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Dedicated to Prof. Dr. Gerhard Erker on the occasion of his 70th birthday.

**Abstract:** The reaction of  $\text{LiAlH}_4$  with  $(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuCl}$  pincer complexes provides a new, simplified route to Au(III) hydrides. The Au-H bonds of these complexes add to both terminal and internal acetylenes by an unexpected reaction pathway, which involves radical intermediates and proceeds via a bimolecular outer-sphere mechanism to cleanly form trans-insertion products. The reaction is greatly accelerated by the addition of a radical precursor such as AIBN. DFT calculations support the proposed radical mechanism, with very low activation barriers, and rule out mononuclear mechanistic alternatives. These alkyne hydroaurations are highly regio- and stereospecific for the formation of Z-vinyl isomers, with Z/E ratios of >99:<1 in most cases, and tolerate a range of functional groups including -OH, -NH, -CHO and -COOH. The gold vinyls are resistant to radical-induced isomerization but undergo E/Z isomerization under photochemical conditions.

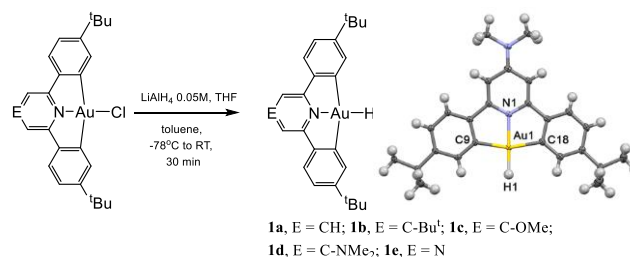
Main Gold vinyl complexes have frequently been implicated as intermediates in gold-catalyzed transformations of alkynes and allenes,<sup>[1]</sup> most commonly by intra- or intermolecular attack by O- or N-nucleophiles<sup>[2]</sup> or C-H bonds.<sup>[3]</sup> Although vinyl complexes can be obtained by transalkylation,<sup>[4]</sup> more interestingly, in a number of cases they could also be isolated as reaction intermediates and structurally characterized,<sup>[5,6]</sup> including some very rare examples of gold(III) vinyl compounds.<sup>[7]</sup>

The formation of gold vinyl complexes by hydroauration, i.e. addition of gold hydrides to C-C multiple bonds, has been reported in only two cases. Sadighi showed that the gold(I) hydride  $(\text{IPr})\text{AuH}$  reacts with internal alkynes  $\text{RC}\equiv\text{CR}$  under trans insertion if  $\text{R} = \text{COOMe}$ , but there was no reaction if  $\text{R} = \text{Et}$  or  $\text{Ph}$  ( $\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$ ).<sup>[8]</sup> More recently, we isolated the gold(III) hydride  $(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuH}$  (**1a**, Figure 1), which was found to insert allenes to give vinyl complexes, while acetylenes failed to react.<sup>[9,10]</sup> Given the coordinative saturation of square-planar gold(III) compounds and the reluctance of these complexes to bind a fifth

ligand, the mechanistic aspects of these formal insertion reactions remained obscure. On the other hand, such fundamental reactions have a direct bearing on the role of gold catalysts in organic transformations.

Gold(III) forms square-planar structures typical of  $d^8$  transition metals, a complex type where ligand exchange kinetics are largely controlled by the trans effect.<sup>[11]</sup> We therefore considered the possibility of enhancing the reactivity of the Au(III)-H bond by introducing  $\sigma$ - and  $\pi$ -donor substituents in *trans* position on the pyridine ring, e.g.  $\text{R} = t\text{Bu}$  (**1b**),  $\text{OMe}$  (**1c**) and  $\text{NMe}_2$  (**1d**).<sup>[12]</sup> However, initial attempts to determine the insertion kinetics for 1,1-dimethylallene gave confusing results: different, apparently spectroscopically identical batches of the same gold hydride showed rather varying reaction rates, and there seemed to be a dependence on the method of synthesis. Since such variable kinetic behavior could indicate that the reactions might be catalyzed by trace impurities, we decided to investigate the insertion reactions of gold(III) hydrides in more detail.

Our original preparation<sup>[9a]</sup> of a gold(III) hydride (**1a**) involved a 3-step procedure:  $(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuCl} \rightarrow (\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuOH} \rightarrow (\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuH}$ , which involved the somewhat tedious purification of the gold hydroxide.<sup>[13]</sup> A more convenient route to high-purity Au<sup>III</sup> hydrides had to be found. Fortunately, the most straightforward approach also proved to be the most effective: the reactions of  $(\text{L}^{\text{R}})\text{AuCl}$  with a THF solution of  $\text{LiAlH}_4$  gave high-purity samples of **1a-d** in high yields (Figure 1).<sup>[14]</sup> The pyrazine-based complex  $(\text{C}^{\wedge}\text{N}^{\text{pz}}\text{C})\text{AuCl}$ <sup>[15]</sup> reacted similarly to give the hydride **1e**.



**Figure 1.** Synthesis of gold(III) hydrides and crystal structure of **1d**. The Au-H hydrogen atom was identified in the electron density map. Selected bond distances (Å) and angles (°) for **1d**: Au1-H1 1.64(5), Au1-N1 2.019(3), Au1-C9 2.060(3), Au1-C18 2.058(4), N1-Au1-C9 81.06(13), N1-Au1-C18 80.79(13), C9-Au1-H1 98.2(19), C18-Au1-H1 100.0(19), N1-Au1-H1 179.2(19), C9-Au1-C18 161.85(14).

The hydrides show the expected <sup>1</sup>H NMR signals for the Au-H moieties, with only small chemical shift variations depending on the pyridine substituent:  $\delta = -6.51$  (**1a**),<sup>[9a]</sup>  $-6.41$  (**1b**),  $-6.48$  (**1c**),  $-6.26$  (**1d**), and  $-6.50$  (**1e**) (in  $\text{CD}_2\text{Cl}_2$ ). The nature of the compounds was confirmed by the crystal structure of **1d**, which shows the NMe<sub>2</sub> substituent co-planar with the pyridine ring. This suggests a

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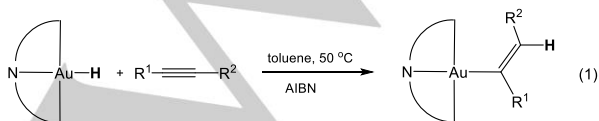
Supporting information for this article is given via a link at the end of the document. CCDC 1495244 - 1495246 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

contribution of a resonance structure with a partial positive charge on N; this planarity and the packing arrangements in crystal (see Supporting Information) may explain the comparatively poor solubility of this compound. On the other hand, an analysis of the molecular charge distributions by density functional theory (DFT) calculation showed only a very marginal effect of the pyridine *p*-substituents on the Au-H bond polarity (see SI), in line with the absence of significant chemical reactivity differences for **1a-1d**. The pyrazine complex **1e** proved less reactive than **1a**.

For reasons of solubility and stability we chose the methoxy derivative **1c** to explore the reactivity towards allenes and alkynes. As expected,<sup>[9a]</sup> there was a smooth reaction with 1,1-dimethylallene at room temperature to give quantitative conversion to the corresponding gold-trimethylvinyl complex. More interestingly, the hydrides thus prepared proved also reactive towards the hydroauration of internal and terminal alkynes ([D<sub>8</sub>]toluene, room temperature), although the reactions were slow and high conversions required reaction times of several days to weeks. Remarkably, the hydroaurations proceeded with essentially quantitative regio- and stereoselectivity, to give exclusively the *trans*-insertion products. On the other hand, alkyl and dialkyl acetylenes, i.e. 1-hexyne and 3-hexyne, reacted only very slowly, and attempts to accelerate the reaction by heating led to decomposition.









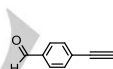

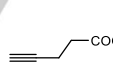



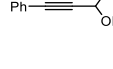

There remained of course the intriguing question of the mechanism of this alkyne insertion. Square-planar Au<sup>III</sup> compounds stabilized by rigid pincer ligands as in the case of **1** have no coordination sites available for substrate binding, and earlier computational attempts to search for a possible 5-coordinate Au<sup>III</sup> adduct, such as the coordination of a phosphine to the metal perpendicular to the molecular plane, had failed to find any evidence for an energy minimum.<sup>[16]</sup> Computations with an alkyne as possible ligand gave analogous results: there was no evidence for a coordinative alkyne-gold interaction. A [2+2] pathway by suitable alignment of the C≡C and Au-H bonds was therefore ruled out. This left the possibility of an outer-sphere mechanism, conceivably bimolecular, perhaps not unlike the proposed proton-assisted outer-sphere mechanism for the hydrogenation of ethylene by Au<sup>I</sup> hydrides in protic solvents, which was found to be energetically favored over intramolecular alternatives.<sup>[17]</sup> Such an outer-sphere pathway might be provided by the assistance of a cation, a Lewis acid, or possibly a radical. Given that our alkyne reactions were conducted in non-polar solvents under mild conditions, and also given the known light sensitivity of many gold compounds, the participation of traces of radical species seemed most plausible.

Indeed, a partially complete alkyne insertion reaction was found to stop as soon as TEMPO as radical scavenger was added (TEMPO = 2,2,6,6-tetramethylpiperidine *N*-oxide). Conversely, the addition of a radical source such as azobisisobutyronitrile (AIBN) greatly accelerated the alkyne insertions and reduced the reaction time from days to minutes, without affecting the regio- and stereoselectivity of the process. In order to accelerate the decomposition of AIBN, the reactions were carried out at 50 °C [Eq. (1)].



A survey of alkynes with different substitution patterns and functional groups resulted in the formation of the vinyl complexes **2-3** (Table 1).

**Table 1.** Alkyne hydroauration with **1c** in the presence of AIBN.<sup>[a]</sup>

Substrate	Major product	Yield (%) <sup>[b]</sup>	Z/E ratio <sup>[b]</sup>	time (min)
Ph-C≡C-H		90	>99:<1	85
Ph-C≡C-Me		>95	>99:<1	5
Ph-C≡C-Ph		>95	>99:<1	35
Me <sub>3</sub> Si-C≡C-H		>95	>99:<1	5
<sup>t</sup> BuMe <sub>2</sub> Si-C≡C-H		90	>99:<1	110
Bu <sup>n</sup> -C≡C-H		>95	>99:<1	35
Et-C≡C-Et		85	>99:<1	60
HO-CH <sub>2</sub> -C≡C-H		>95	>99:<1	60
		>95	82:18	40
		75	>99:<1	25
		>95	>99:<1	40
		>95	80:20	1020

[a] Conditions: [D<sub>8</sub>]toluene, 50 °C; conversion of **1c** was >95% in all cases; [b] Determined by NMR spectroscopy.

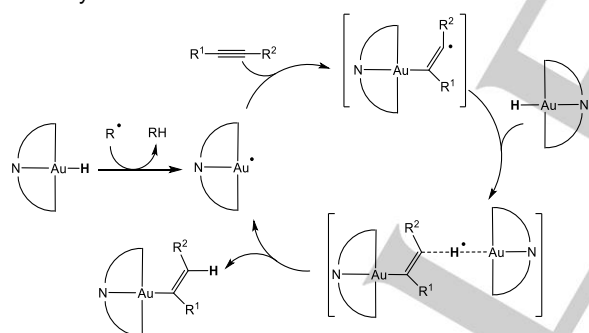
In most cases only the *Z*-vinyl products could be detected, the exceptions being **10** and **13** where minor amounts of the *E*-isomer were also formed. The structures were unequivocally assigned by NMR/NOE studies (see Supporting Information). In particular, vinyl <sup>13</sup>C resonances for α and β carbon atoms appear in the range δ=159.6–134.2 ppm and δ=130.8–123.9 ppm, respectively, in agreement with the data for the previously reported vinyl complex (C<sup>∧</sup>N<sup>Pv</sup>∧C)AuC(Me)=CMe<sub>2</sub>.<sup>[9a]</sup> In the case of terminal vinyl moieties, the <sup>3</sup>J(H,H) values fall within the range typical of *Z* couplings (9.0–10.8 Hz, the only exceptions being of **5** and **6**, for which a <sup>3</sup>J(H,H) of 13.5 Hz is observed owing to the β effect of silicon). For 1,2-disubstituted vinyl derivatives [Au]-

$C(R^1)=CHR^2$ ,  $^1H$  NOE experiments revealed the presence of dipolar interactions between the vinyl-H and both  $R^1$  and  $R^2$ , and the absence of such interactions between  $R^1$  and  $R^2$ .

The hydroaurations proceed with high regio- and stereospecificity; for example, of the four possible isomers of the  $MeC\equiv CPh$  insertion, only a single product was formed, structure **3**, in which the gold centre is bound in  $\alpha$ -position to the methyl, rather than the phenyl substituent. With silyl acetylenes, the gold is distal to the  $SiR_3$  group. This regioselectivity is in contrast to that obtained in a number of alkyne hydrometallation products, for example hydro-stannations,<sup>[18,19]</sup> hydrosilylations,<sup>[20]</sup> hydroaluminations<sup>[21]</sup> and hypopalladations,<sup>[22]</sup> where the metal is predominantly attached  $\alpha$  to the phenyl, or proximal to the higher substituent.

Gold(III) hydrides are stable to polar solvents, water and even acetic acid, and indeed a range of functional groups is tolerated, including  $-OH$ ,  $-NH$ ,  $-CHO$  and  $-COOH$ . Interestingly, *N*-propargyl carboxamides, which are well-known for their facile cycloisomerization to oxazoles in the presence of gold catalysts,<sup>[2,23]</sup> form exclusively the gold vinyl **13**, without cyclization. Less reactive internal alkynes such as 3-hexyne also gave clean hydroauration products.

The stereochemical stability of the gold(III) vinyl products in our system contrasts with Curran's recent report on the radical-initiated hydrostannation of propargylic ethers, where the presence of AIBN led to extensive *cis-trans* isomerization.<sup>[24]</sup> However, exposure of our gold vinyls to light induced slow isomerization; for example, irradiating a solution of **2** for 1 h with UV light ( $\lambda = 365$  nm) changed the *Z/E* ratio from  $>99:<1$  to about 1:1. Evidently the radical-induced *trans*-hydroauration produces a kinetic product, which is isomerized to the thermodynamic mixture.

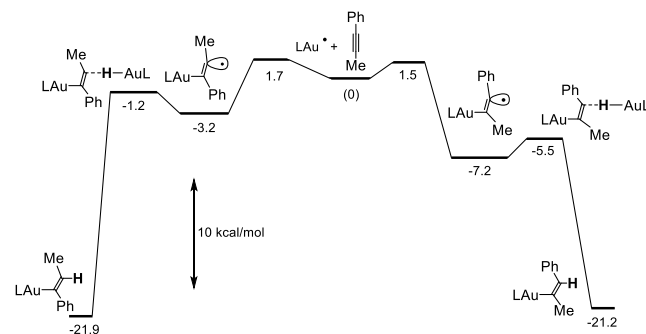


**Scheme 1.** Proposed alkyne *trans*-hydroauration pathway

A likely reaction sequence is depicted in Scheme 1. Thermal cleavage of AIBN provides radicals capable of initiating the sequence by H-abstraction from the gold(III) hydride. Since the reactions are conducted in the presence of excess alkyne, the  $Au^{II}$  radical thus formed is rapidly trapped by alkyne addition. Further reaction of the resulting gold-vinyl radical with a second molecule of gold hydride generates the Au-vinyl product. This scenario also effortlessly explains the observed *trans* hydroauration stereochemistry. The  $Au^{II}$  radical is evidently sufficiently long-lived to allow precise regiochemical control of the alkyne addition; for example, in the case of the

hydroauration of  $MeC\equiv CPh$ , a phenyl-stabilized vinyl radical will be preferred over its methyl-substituted isomer, resulting in the formation of **3**, which is precisely what is observed. Further support for the proposed intermediacy of  $(C^{\wedge}N^{\wedge}C)Au^{\bullet}$  is the formation of traces of the known<sup>[9,25]</sup>  $Au^{II}$  dimer  $[(C^{\wedge}N^{\wedge}C)Au]_2$ , which was detectable as a by-product in a number of cases.<sup>[26]</sup> We have previously shown that  $(C^{\wedge}N^{\wedge}C)Au^{\bullet}$  is capable of attacking  $(C^{\wedge}N^{\wedge}C)AuH$  to give a  $\mu$ -H intermediate as part of the electrochemical reduction of **1a**.<sup>[27]</sup>

The validity of this mechanistic proposal was probed by DFT calculations for the addition of  $(C^{\wedge}N^{\wedge}C)AuH$  to acetylenes  $H\equiv CH$ ,  $HC\equiv CPh$  and  $MeC\equiv CPh$ . All mononuclear pathways tried had prohibitive free energy barriers ( $>35$  kcal mol<sup>-1</sup>), excluding their contribution under the present reaction conditions. Acetylene coordination to  $(C^{\wedge}N^{\wedge}C)Au^{\bullet}$  was found to have a small barrier (1-4 kcal mol<sup>-1</sup>) and is modestly exergonic (2 to 12 kcal mol<sup>-1</sup>), and the most stable adducts have Au next to the H or Me substituent of the acetylene substrate. From there on, an incoming  $(C^{\wedge}N^{\wedge}C)AuH$  molecule moves without much distortion towards the second acetylenic C-atom on a potential-energy surface that is essentially flat. Transition states having one imaginary frequency with the correct motion were located in all cases, but the surface is so flat that not too much importance should be attached to the  $C\cdots H$  distances in these optimized transition states. After including thermal and dispersion corrections, the free energy barrier for hydride transfer from the incoming  $(C^{\wedge}N^{\wedge}C)AuH$  to the second acetylene carbon is 2-6 kcal mol<sup>-1</sup>, leading to the experimentally observed *trans* adduct. Structures for stationary points on the radical path towards the preferred adduct of  $MeC\equiv CPh$  are shown in the Supporting Information (Figure S50, see also Table S4 for total and relative energies for all species studied). The energy profiles for this path and its non-observed regio-isomeric alternative are summarized in Figure 2. The computational results therefore support the proposed radical chain mechanism and rule out alternative mononuclear mechanistic variations. An alternative pathway assisted by the  $(C^{\wedge}N^{\wedge}C)Au^+$  cation instead of a radical was also explored for comparison but appears less favorable (see Supporting Information). The observed capriciousness of this chemistry can also be understood based on the radical path:  $LAu^{\bullet}$  can dimerize, and this dimerization is irreversible ( $\Delta G \approx 55$  kcal mol<sup>-1</sup>) so that the reaction would extinguish itself unless new radicals are continually being generated.



**Figure 2.** Free energy profile (kcal mol<sup>-1</sup>) for  $LAu^{\bullet}$  mediated *trans* addition of  $LAuH$  to  $MeC\equiv CPh$ .



The release of the gold vinyl was exemplified in the case of **3**. Treating an NMR sample of **3** in [D<sub>6</sub>]benzene with a crystal of iodine at room temperature generated the iodoalkene Z-C(I)(Me)=CHPh in quantitative yield, with retention of stereochemistry. As in the case of alkyne hydroauration, the mechanism of gold-carbon bond cleavage is likely not to be straightforward; this aspect is currently under investigation.

In summary, the results provide the first experimentally and computationally supported demonstration of the addition of unsaturated substrates to gold-hydrogen bonds by a radical-initiated outer-sphere mechanism. Single-electron transfer leads to gold(II) species which help to overcome the coordinative saturation in square-planar gold(III) by enabling a low-energy binuclear pathway to the trans hydrometallation product. The resulting gold(III) vinyl complexes are formed with remarkably high regio- and stereoselectivity. The products are stable to radical-induced *E/Z* isomerization but may be isomerized photochemically.

This intermolecular pathway overcomes the inability of Au<sup>III</sup> complexes to bind unsaturated substrates and to follow intramolecular coordinative mechanisms of the type that are commonplace for other transition metals. There is a growing body of evidence that single-electron transfer steps may be important in other fundamental reactions of gold, notably the photochemically induced oxidative additions to gold(I).<sup>[28-31]</sup> The present results further support the notion of the importance of odd-electron Au<sup>I</sup> species in gold reaction pathways; they also illustrate the limitations of extrapolating mechanisms in gold catalysis on the basis of, for example, platinum or palladium chemistry.

## Acknowledgements

This work was supported by the European Research Council. M. B. is an ERC Advanced Investigator Award holder (grant no. 338944-GOCAT).

**Keywords:** Gold • hydride • reaction mechanisms • alkyne insertion • density functional calculations

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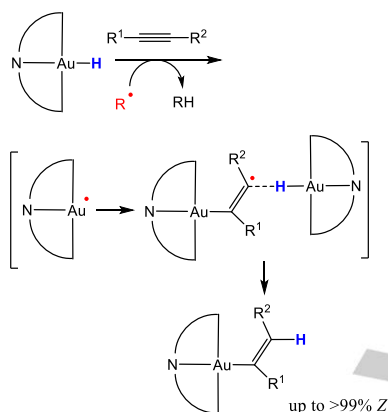
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**Gold(II) provides a helping hand:** Gold(III) pincer complexes overcome their lack of substrate binding sites by a radical-mediated bimolecular pathway. They react with acetylenes in the presence of a radical source in a kinetically controlled reaction to give *trans*-hydroauration products with high regio- and stereoselectivity.



Anna Pintus, Luca Rocchigiani, Julio Fernandez-Cestau, Peter H. M. Budzelaar,\*  
Manfred Bochmann\*

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**Stereo- and Regioselective Alkyne  
Hydrometallation with Gold(III) Hydrides**

Layout 2:

## COMMUNICATION

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