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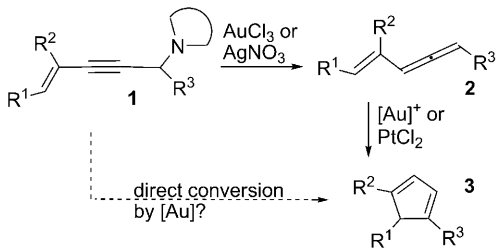
Isolation of a Zwitterionic Dienegold(III) Complex Intermediate in the Direct Conversion of Enyne–Amines to Cyclopentadienes

Michele Melchionna,[a] Martin Nieger,[b] and Juho Helaja*[a]

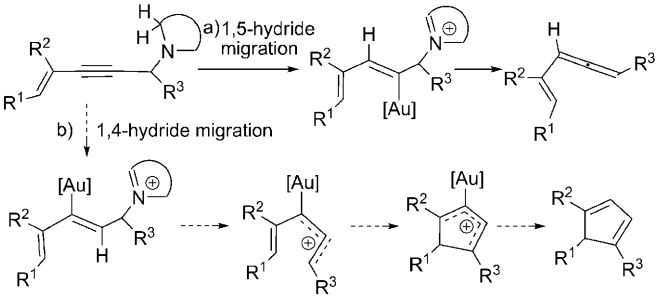
Gold-mediated homogeneous catalysis has shown, recently, its power, uniqueness, and versatility especially in electrophilic activation of alkynes for nucleophilic attack.[1] Cycloisomerization of enynes, and other alkynes carrying nucleophilic groups represents a large category in gold mediated catalysis. Due to the fact that this chemistry is in its infancy, only a few mechanistic studies have been reported.[1f,2]

The recent findings in gold and other late transition-metal catalysis have provided effective alternatives to classical Pauson–Khand cyclocarbonylation[3] and the Nazarov cyclization[4] for the synthesis of cyclopentadienes (Cp). Toste et al. have shown that the cationic Au^I species $Ph_3PAuCl/AgSbF_6$ catalyses the cycloisomerazation of 1,2,4-triene (enallene; **2**) to cyclopentadiene (Cp; **3**; Scheme 1) with high yields and turnover numbers.[5] In line with these findings, Iwasawa et al. have shown that the same conversion can be catalyzed by $PtCl_2$ with equal performance.[6] An evident restriction in these methods is that the synthesis of the prerequisite starting material (allenes) proceeds in many cases with modest or low yields when traditional methods are applied. Nevertheless, Che's group has recently introduced a facile method to access (asymmetric) allenes, **2**, from aminoalkynes, **1**, either by $KAuCl_4$ or $AgNO_3$ catalysis.[7,8]



Scheme 1. Transition-metal catalyzed stepwise conversions from enyne–amine, **1** via enallene, **2** to Cp **3**.

Inspired by these achievements we set out to investigate the possibility of a direct conversion of enyne–amine **1** to Cp **3**, thus reducing a two-step sequence (synthesis of allene followed by cycloisomerization) to a single catalytic event. For the gold-catalyzed allene formation from propargylamines, deuterium labeling experiments have proven that a 1,5-hydride migration from the amine moiety controls the progress and direction of the reaction (Scheme 2).[8] For systems in which intramolecular migrations occur by other nucleophiles than hydride, there are examples showing how the migration mode, and therefore the direction of reaction can be controlled, for example by the choice of cationic Au^I or neutral Au(I/III) catalysts, as well as by slight modifications of the substrate. These two factors can both have a



Scheme 2. Mechanistic pathways from enyne–amines by a) proven 1,5-hydride migration to enallenes, or b) hypothesized 1,4-hydride migration to Cps.

[a] Dr. M. Melchionna, Dr. J. Helaja
Department of Chemistry, University of Helsinki
A.I.Virtasen aukio 1, P.O. Box. 55, University of Helsinki
00014 Helsinki (Finland)
Fax: (+358) 919150466
E-mail: juho.helaja@helsinki.fi

[b] Dr. M. Nieger
Laboratory of Inorganic Chemistry, Department of Chemistry
University of Helsinki, A.I.Virtasen aukio 1
P.O. Box. 55, 00014 Helsinki (Finland)

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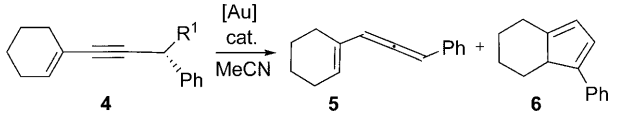
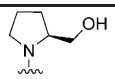
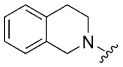
major impact on the regioselectivity of the nucleophilic attack and subsequently of the resulting cycloisomerization products.[11f,9,10] Analogous to this, our strategy was based on the assumption that a systematic variation of the catalyst and substrate could eventually lead to a change in the hydride migration mode, namely from a 1,5- to a 1,4-hydride shift, thus inducing a direct conversion to a Cp in place of an allene (Scheme 2).

Cyclohexene-functionalized propargylic amines, **4a**–**4f**, were chosen as substrates to create ring-fused Cp (Table 1). For substrate **4a**, Che and co-workers previously reported that pure allene was formed with 83% yield based on 77% conversion using the $KAuCl_4$ catalyst.[7] In our study the prolinol moiety was replaced by piperidine (**4b**), azepane (**4c**), indoline (**4d**), and 1,2,3,4-tetrahydroisoquinoline (**4f**) to assess whether a difference in steric and electronic properties of the amine would have an effect on the hydride transfer process. When catalysis was performed on **4b** only allene product was formed, while **4d** remained totally unreacted. The reaction with **4c** produced, somewhat promisingly, some Cp, **5**, with the allene, **6**, still being the dominating product. A far more encouraging result was obtained with substrate **4e**, with which a 4:6 mixture of **5** and **6** was isolated.

Table 1. Reaction of enynamines **4a**–**4f** with gold complexes.[a]



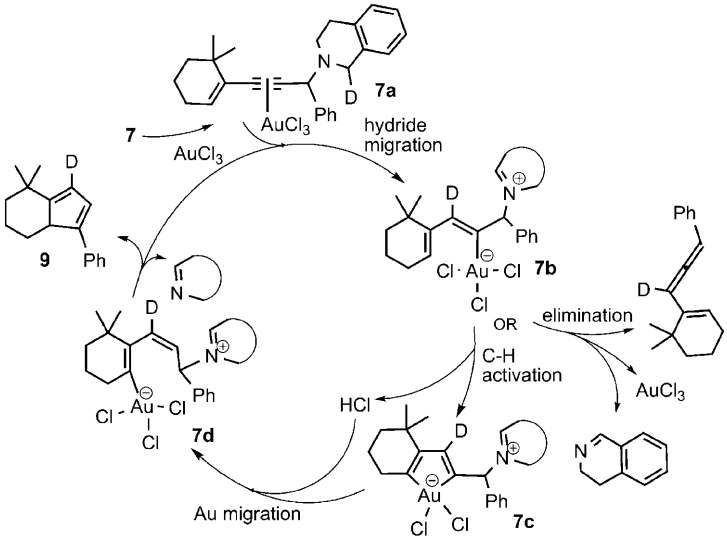
4 **5** **6**

Substrate	R^1	Catalyst (10%)	Conversion [%]	Yield of **5**+**6** [%][b]	Ratio **5**/**6**[c]
4a		$KAuCl_4$	77[d]	83[d]	100:0
4b		$KAuCl_4$	67	34	≈99:1
4c		$KAuCl_4$	69	76	77:23
4d		$KAuCl_4$	0	–	–
4e		$KAuCl_4$	56	91	40:60

[a] All reactions carried out at 40°C. [b] Yield of the isolated products (flash column) based on conversion. [c] Determined by ^{1}H NMR spectroscopy.[7] [d] Reported for the *S* enantiomer at the benzylic carbon.

Monitoring the catalysis of **4e** by ^{1}H NMR spectroscopy indicated that **5** and **6** were formed steadily in the course of the reaction. Moreover, the addition of extra catalyst into the reaction mixture did not lead to any further consumption of the formed allene. Together these facts suggest the existence of a distinct reaction pathway for the formation of Cp, rather than originating from an allene intermediate. This was somehow expected because if the Cp was to be produced in a second step from the initially formed allene, mixtures of **5** and **6** would be found regardless of what propargylamine is employed.

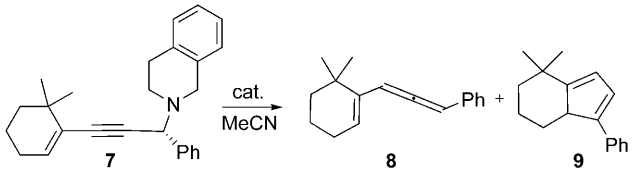
To probe the reaction mechanism the isoquinoline protons were deuterium labeled at the bridging amino benzylic position (Scheme 3). These experiments revealed that only a 1,5-deuteride transfer had taken place in contrast with our initial hypothesis. Apparently, the large isoquinoline moiety did not change the mode of hydride migration, but favored the Cp formation over the allene possibly due to electronic effects (i.e., the 3,4-dihydroisoquinolinium cation being a poorer leaving group than other iminium leaving groups).



Scheme 3. Proposed $AuCl_3$ catalytic cycle from enyne–amine **7** to enallene **8** or Cp **9**.

The latter hypothesis was further investigated by carrying out the catalysis on substrate **7**, in which the bulkiness of the cyclohexene moiety was also increased by replacing it with the more space demanding 2,2-dimethylcyclohexene moiety (Table 2). To our delight, conversion of **7** to Cp **9** by $KAuCl_4$ occurred with an increased Cp selectivity with only traces of allene **8**. Lowering the catalyst loading from 10 to 5% slightly increased the conversion (35→40%), but decreased the Cp formation selectivity. Meanwhile, a higher loading (15%) boosted the selectively towards Cp, but lowered the yield. Hashmi et al. have shown that N,O-ligated Au^{III} complexes (e.g., picolinate and pyridine) are beneficial precatalysts for chemical transformations of complex substrates.[11] However, in our case, it is noteworthy that the use of different gold catalysts resulted in relatively minor changes in terms of conversion (highest conversion taking place with (pyridine)$AuCl_3$; Table 2, entry 5), whereas the

Table 2. Reaction of **7** with various catalysts.[a]



	Catalyst (10%)	Conversion [%][b]	Yield of **8**+**9** [%][c]	Ratio **8**/**9**[b]
1	$KAuCl_4$	35	54 (15)	≈1:99
2	$KAuCl_4$ (5%)	40	89 (36)	19:81
3	$KAuCl_4$ (15%)	34	34 (12)	0:100
4	Picolinate$AuCl_2$	49	29 (14)	33:67
5	Pyridine$AuCl_3$	50	56 (28)	12:88
6	AuCl	41	40 (16)	50:50
7	AuCl[d]	35	39 (14)	90:10
8	K_2PtCl_4	–	0	–
9	$AgNO_3$	12	56 (7)	100:0

[a] All reactions carried out in MeCN at 40 °C for 18 h except where indicated. [b] Determined by ^{1}H NMR spectroscopy. [c] Yield of the isolated product based on conversion, absolute yields in the parenthesis. [d] Reaction carried out at RT.

Cp/allene ratio was more significantly affected. Most interestingly, use of AuCl resulted in the conversion of **7** to a mixture of **8** and **9** in a notably faster rate at 40 °C, whereas lowering the temperature to room temperature led to almost selective formation of the allene. All of the gold(III) catalysts were inactive at room temperature. No conversion was observed with K_2PtCl_4, whereas poor conversion to the allene only was obtained with $AgNO_3$.

The progress of the reaction of **7** with 15% of $KAuCl_4$ was monitored by ^{1}H NMR spectroscopy at 40 °C. The reaction was found to proceed in a stepwise manner; after an induction time of about 15 min, an intermediate was observed, which persisted for about another 15 min at 40 °C before slowly starting to convert into the Cp. The experiment was repeated with higher catalyst loadings (Figure 1) to trace possible intermediates. When the temperature was lowered to 10 °C, after 30 min the progress of the reaction stopped and the observed intermediate structure could be characterized at this temperature by 2D NMR spectroscopy experiments (COSY, NOESY, HSQC, HMBC). Interestingly the vinylic proton of the cyclohexenyl ring could not be traced in the spectra and full analysis of the 2D NMR spectroscopy couplings through bond and space was consistent with a gold metallacycle type structure. Furthermore, the assignment of the carbon signals at $\delta = 170$ and 160 ppm to carbon atoms adjacent to gold implies that the electronic nature of the gold species is either neutral or anionic, since strongly upfield-shifted δ_c values have been reported for cationic Au-coordinated olefinic carbons.[12] When the reaction was continued by warming either the reaction mixture or the crystallized complex **7c** at 40 °C, formation of Cp **9** was observed.

Final confirmation for the structure of this intermediate was obtained from single crystal analysis (Figure 2).[13] The gold atom is featured as Au^{III}, lying in a square planar geometry, with two covalent bonds to carbon atoms, and two chloride ligands still coordinated, therefore formally indicating an excess of negative charge on the metal. The C21–C20 and C1–C2 bond lengths are typical of C=C double bonds, whereas a distance of 1.465 Å for C20–C1 is characteristic for a conjugated single bond, thus supporting the view of a metallacyclopentadiene for the C_5 ring defined by the gold and the coordinated ligand. The N4–C5 distance is that of a C=N double bond, as expected once the hydride has been transferred. Since the bonding in the imine moiety denotes a positive charge on the nitrogen atom, a zwitterionic nature

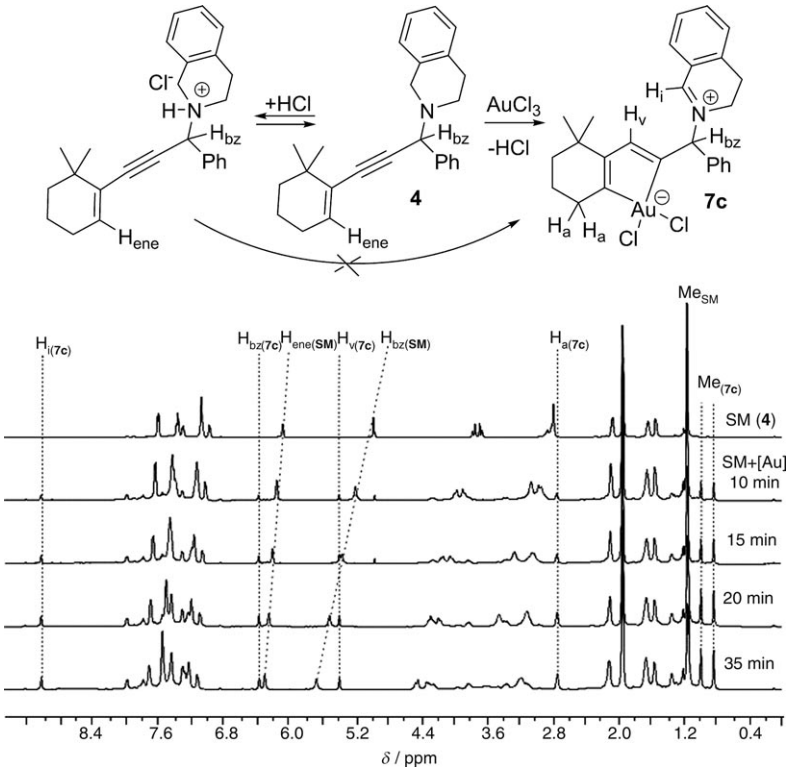


Figure 1. ^{1}H NMR spectroscopy monitoring of gold catalysis on enyne **4** (0–35 min time frame) with a stoichiometric amount of $KAuCl_4$ in CD_3CN at 40 °C. The characteristic signals identified are traced to **4** or its salt form and **7c**. From this mixture **7c** was crystallized out and fully characterized by using 2D NMR spectroscopy techniques and X-ray.

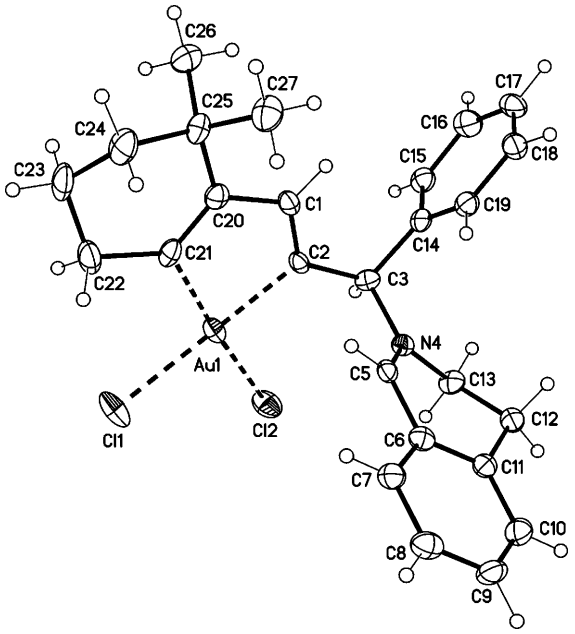


Figure 2. Molecular structure of **7c** (displacement parameters are drawn at 50% probability level). Key bond lengths (Å): Au1–C2 2.027(3), Au1–C21 2.043(4), Au1–Cl1 2.3664(10), Au1–Cl2 2.3988(12), C20–C21 1.344(6), C1–C20 1.465(6), C1–C2 1.343(5), N4–C5 1.283(5).[13]

for the neutral complex has to be invoked. The extraordinary stability of **7c** arises presumably from the fact that the cationic isoquinoline imine moiety (3,4-dihydroisoquinolinium) is a relatively poor leaving group, therefore providing the intermolecular counterion for the anionic gold moiety.

Overall the characterized Au^{III} metallacyclodiene structure is exceptional in itself,[14] but in particular because it is proposed as a catalytic intermediate. A number of neutral and cationic Au^{I} complexes have been reported as proposed catalytic intermediates.[15] Among these, only two have been structurally characterized as vinylic intermediates, both featuring cationic linear Au^{I} species. The $AuCl_3$ characteristic in C–H activation of aromatic compounds has been proven by a trapped Ar–$AuCl_2$–(ligand) structure and various analogous heterocyclic cycloaurated complexes.[16] Among them Cinellu et al. have reported the first anionic gold(III) oxo intermediate.[16f] However, to the best of our knowledge, the present structure represents the first example of a truly zwitterionic Au^{III} trapped intermediate in the gold-catalyzed activation of a π-system in which the Au moiety possesses anionic character.

The experimental data suggests that the zwitterionic structure **7c** is at least a resting structure along the catalytic pathway from enyne–amine **7** to Cp **9**. We propose that the complex is a key resting intermediate deriving from HCl elimination, which functions as a shuttle between two structures (**7b** and **7d**) in which the $AuCl_3$ group migrates from C2 to C21 (Scheme 3). In the proposed mechanistic pathway the allene **8** and Cp **9** formations are derived from the same catalytic cycle; the cycle starts with coordination of the C≡C triple bond to the gold followed by 1,5-hydride migration. The subsequent step is crucial for the direction of the reaction: a combination of the bulkiness of the cyclohexene and amine moieties drives the catalysis towards vinylic C–H activation and thereby $AuCl_3$ migration and Cp formation, whereas with less hindered substrates enallene **8** is formed. Presumably, steric crowding pushes the methyl groups away from both the gold and isoquinoline proximities bringing the vinylic proton into close contact with the anionic $AuCl_3$ (**7b**). It turns out that electronic properties of the amine also give an important contribution to the selectivity of the process, since it produces extra stabilization of the intermediate **7b** by delocalizing the positive charge onto the 3,4-dihydroisoquinolinium moiety.

To gain a theoretical insight into the proposed mechanism we studied computationally selected Au-complexed isoatomic intermediates (**7a**, **7b**, and **7d**) and hydride migration transition-state (TS) structures (1,4- and 1,5-shifts) with DFT theory (Figure 3).[17,18] In the energy-minimized starting geometry structure, **7a**, $AuCl_3$ is coordinated to the terminal enyne carbon against the expected bisected coordination to both triple bond carbons. This structure is also geometrically rather close to the TS of the 1,5-hydride migration, in which the free-energy barrier height is only 2.2 kcal mol^{-1}. In contrast to this, the TS for the 1,4-hydride migration is 19 kcal mol^{-1}, with this high energy level making it unlikely to occur. The overall inspection of the relative intermediate energies of **7b** and **7d** supports the proposed mechanism, that is, both the 1,5-hydride migration and the 1,4-$AuCl_3$ migration are energetically favorable steps. The details relating to the ring-closing steps to form **7c** and **9** will be investigated in future studies.

In summary, a direct $AuCl_3$ catalytic route from an enyne–amine to a Cp is reported and a related mechanistic pathway proposed, which is supported by the isolation of single crystals of one of the intermediates, as well as DFT calculations. We are currently applying these reactivity findings to other related Au^{III}-mediated catalysis. In a wider perspective the proposed novel gold metallacyclopentadiene intermediate, as characterized by the crystal structure, can be expected to inspire further reactivity-based method development of Au^{III}-mediated catalysis.

Experimental Section

See the Supporting Information for experimental details.

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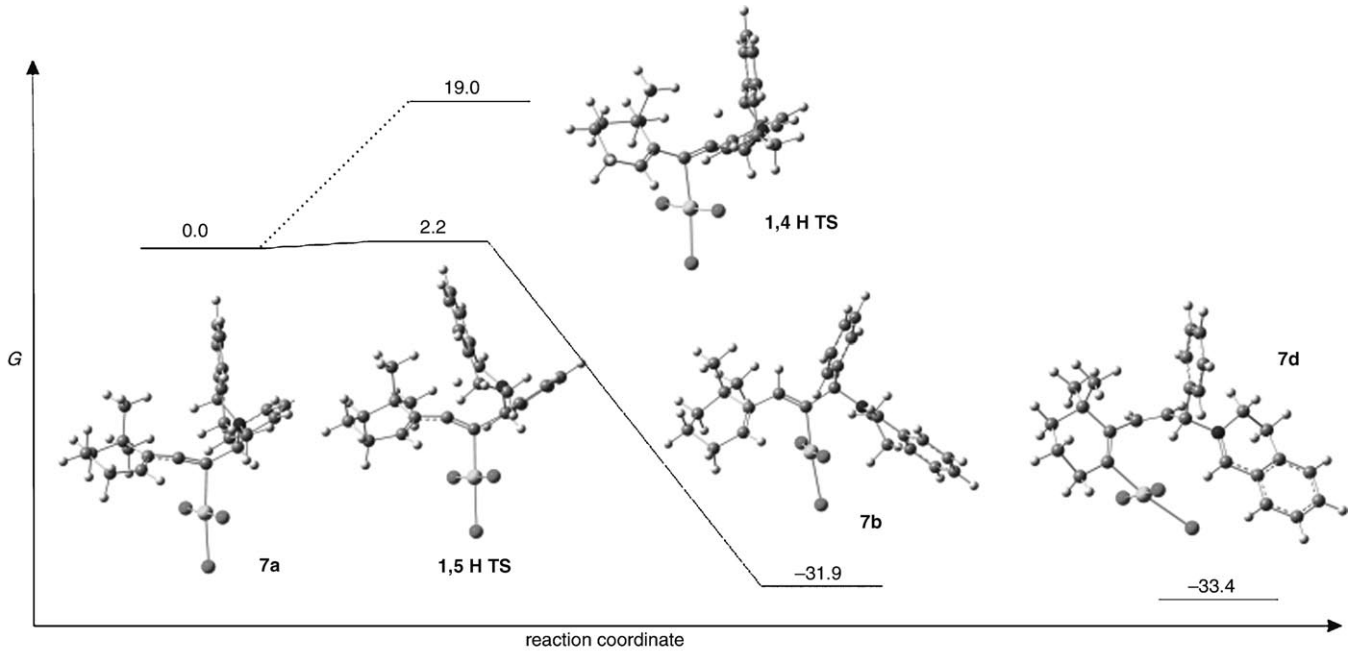

Figure 3. Structures and Gibbs free energies [kcal mol^{-1}] of $AuCl_3$ complexed intermediates and transition states related to Scheme 3 (B3LYP 6-31G-(d,p)/LANL2DZ).[17]

Keywords: alkynes · C–H activation · cyclopentadienes · gold · zwitterions

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