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Gold Catalysis: Evidence for the In-situ Reduction of Gold(III) During the Cyclization of Allenyl Carbinols

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Products of an oxidative coupling were obtained in the gold(III)-catalyzed cycloisomerization of tertiary allenyl carbinols. The absence of reduced organic products and an increase of these coupling products with the amount of gold(III) catalyst suggests that gold(III) is reduced in situ, possibly to gold(I) catalysts which were also shown to be active for these transformations.

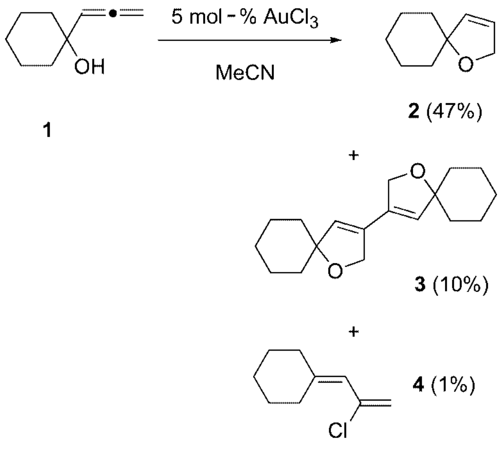
Introduction

One central question of gold catalysis is the oxidation state of the catalytically active species.[1] This is true for homogeneous[2] as well as heterogeneous catalysis.[3] For example the addition of oxygen nucleophiles like water or alcohol was first achieved by Utimoto et al.[4] with Au^{III} catalysts, later Teles et al.[5] prove Au^{I} catalysts to be very efficient, a similar behavior was observed by Utimoto et al.[6] and Lok et al.[7] for the hydroamination reaction. So far, neither an in situ detection of a catalytically active gold species was reported nor did comperative theoretical studies provide clear insight. Recent theoretical work of Straub[8] on the gold-catalyzed naphthalene synthesis of Yamamoto et al.[9] and theoretical studies accompanying the work of Periana et al.[10] on the C,H-activation of methane also showed that for both Au^{I} and Au^{III} the energies of activation calculated would allow an efficient conversion and suggested that even the ratio of both species might determine, which of the two species is responsible for the major amount of the product formed.

In work following our gold-catalyzed cycloisomerization/dimerization of allenyl ketones,[11] we now investigated the cycloisomerization of tertiary allenyl carbinols. Similar reactions of allenyl carbinols have been reported by Krause et al. earlier,[12] but here for the first time we observe side-products, which provide evidence for a mechanism of an in-situ reduction of gold(III).

Results and Discussion

We started with the terminal allene **1**, which, upon treatment with 5 mol-% $AuCl_3$ in acetonitrile, delivered **2**, **3** and **4** as the products (Scheme 1). The structure of **3** was deduced by the spectroscopic relationship to **2**, and the molecular weight obtained from the mass spectrum and finally proven by an X-ray crystal structure analysis (Figure 1).[13] Compound **4** is the product of a S_N'-like substitution of the hydroxy group by chloride.



Scheme 1. Formation of **3** by a gold(III) catalyst.

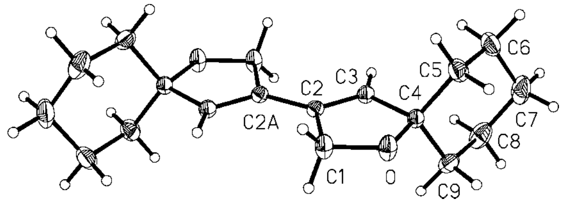


Figure 1. Crystal structure of **3**.

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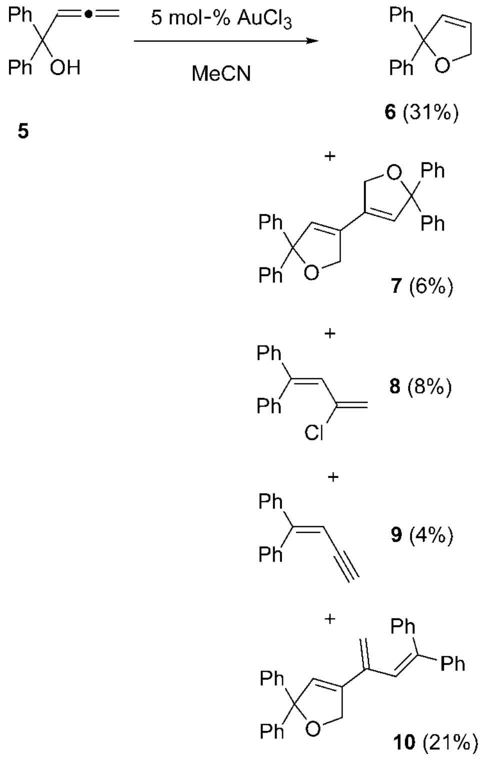
The diaryl-substituted compound **5** led to the products **6**–**10** (Scheme 2). Again the structure of **7** was unambiguously proven by a crystal structure analysis (Figure 2), the same is true for **6** and **9**.[13] Compound **8** is the analogue of the substitution product **4**, **9** the product of a 1,4-elimination instead of a substitution. Compound **10** would be the product of a dehydrative coupling, not a chloride ion but a dihydrofuryl moiety substitutes the hydroxy group. Selective routes to products of type **4**, **8** and **10** have been reported before.[14]



Scheme 2. Formation of **7** by a gold(III) catalyst.

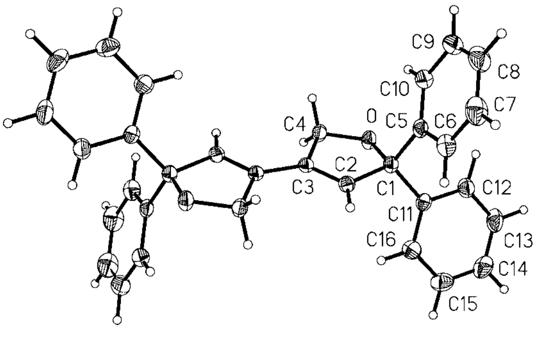
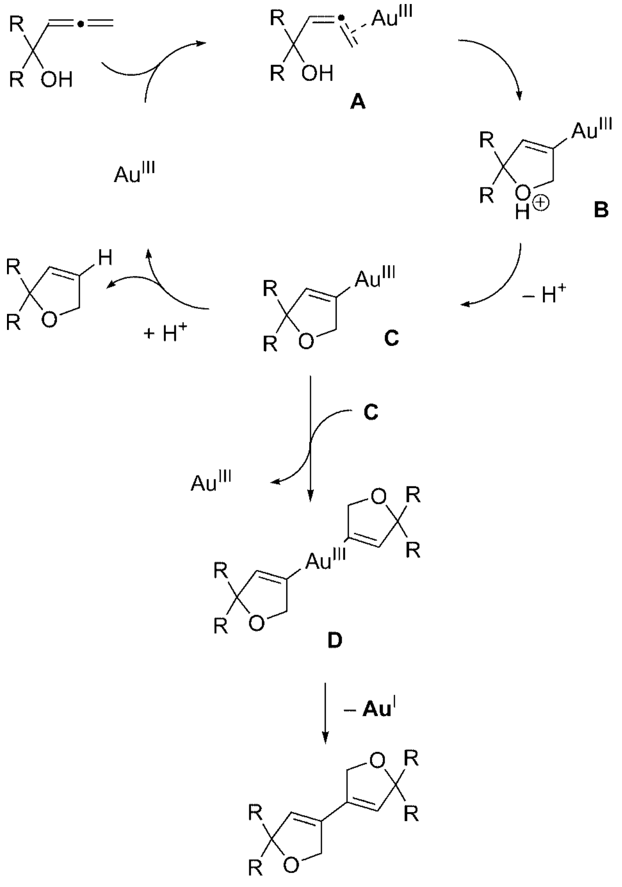


Figure 2. Crystal structure of **7**.

The crucial reactions are the oxidative coupling reactions to **3** and **7**, which go along with the reduction of one component. Since neither reduced allene is isolated or detected nor any other reduced organic species (as shown with compound **4**, our analysis includes species formed in 1% amounts) and no other oxidant like molecular oxygen is present, it is only reasonable to assume that the strongest oxidant present, Au^{III}, is reduced to Au^{I}. The yields of **3** and **7** were in agreement with the fact that the maximum yield of these dimers is twice the percentage of the gold(III) catalyst. Triplicating the amount of $AuCl_3$ (to 15 mol-%) also increased the amount of **3** or **7**, but only by a factor of 2.3 or 2.5, respectively; these reactions were even less selective, especially the amount of the chloro compounds **4** or **8** went up significantly (9% or 20%, respectively). A **possible** mechanism for the formation of **3** and **7** is shown in Scheme 3.



Scheme 3. Possible mechanism for the formation of **3** and **7** by gold(III).

The normal catalytic cycle is assumed to proceed via Au^{III} and consist of a coordination of the remote double bond in **A**, cyclization to **B** and deprotonation to **C** to afford the dihydrofurans after proto-demetallation of **C**. Calculations of Krause et al.[15] for allenyl carbinols back up such a mechanism, and a similar mode of reaction has been suggested for the cyclizations of the related allenyl ketones[16] and the ring-enlargement of alkynyl oxiranes.[17] However, a ligand exchange between two molecules of **C** can also lead to **D**, which then delivers the dimer and Au^{I} by reductive elimination. The latter step would be related to the oxidative dimerization of arylboronic acids reported by Corma et al.[18] The route through **D** sets free two protons (two equivalents of HCl in the case of $AuCl_3$), thus this process is ultimately combined with the substitution and elimination products **4**, **8** and **9**. Compound **10** could be formed by the reaction of **C** with the starting material activated by protonation of the hydroxy group.[19] Applying the Ag^I-catalysts we did not observe these side-products at all.

We finally tested Gagosz[20] new $(Ph_3P)AuNTf_2$ catalyst as a gold(I) catalyst for this reaction. Only 3 mol-% of this catalyst in dichloromethane at room temperature converted **1** to the volatile **2** in an essentially quantitative yield (in situ ^{1}H NMR) and **5** to **6** in 87% isolated yield.

Conclusions

Similar oxidative dimerizations of a substrate could reduce Au^{III} to Au^I whenever an organogold(III) intermediate is accessible. If this process is general, the question still remains: in the individual case, does this reduction convert one catalytically active species into another, is it a way of forming a catalytically active species from a precatalyst or is it even a method of catalyst deactivation?

Experimental Section

Reaction of 1 with $AuCl_3$: Compound **1** (250 mg, 1.81 mmol) was dissolved in absolute acetonitrile (5 mL) under dinitrogen and $AuCl_3$ (26.5 mg, 87.4 μmol) was added. The reaction was monitored by TLC, after consumption of the starting material the solvent was removed and the crude material was purified by column chromatography on silica gel (hexane/ethyl acetate, 40:1) to yield 118 mg (47%) of the known[21] compound **2**, 25.4 mg (10%) of the hitherto unknown **3** and 2.9 mg (1%) of the known[22] compound **4**.

3: M.p. 98 °C. $R_f = 0.46$ (hexane/ethyl acetate, 10:1). IR (neat): $\tilde{\nu} = 3069, 2923, 2856, 1742, 1450, 1312, 1091, 931\ cm^{-1}$. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.66$ (t, $J = 1.8$ Hz, 2 H), 4.74 (d, $J = 1.8$ Hz, 4 H), 1.70–1.30 (m, 20 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 131.0$ (s, 2 C), 130.1 (d, 2 C), 90.3 (s, 2 C), 73.0 (t, 2 C), 36.7 (t, 4 C), 25.1 (t, 2 C), 23.2 (t, 4 C) ppm. MS (70 eV): m/z (%) = 274 (100) [M$^+$], 203 (43), 231 (87). $C_{18}H_{26}O_2$ (274.4): calcd. C 78.79, H 9.55; found C 78.57, H 9.67.

4: $R_f = 0.78$ (hexane/ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 5.64$ (q, $J = 1.2$ Hz, 1 H), 5.36 (d, $J = 1.0$ Hz, 1 H), 5.12 (t, $J = 1.2$ Hz, 1 H), 2.42–2.35 (m, 2 H), 2.20–2.10 (m, 2 H), 1.70–1.40 (m, 6 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 146.8$ (s), 120.0 (d), 114.2 (t), 77.0 (s), 36.9 (t), 29.5 (t), 28.1 (t), 27.6 (t), 26.3 (t) ppm. MS (70 eV): m/z (%) = 156 (2) [M$^+$], 18 (100), 91 (44), 92 (34).

Supporting Information (for details see the footnote on the first page of this article): Procedures and identification data for the starting materials **1** and **5** and procedure for the gold-catalyzed reaction that leads to **6**–**10** including characterization data for these compounds.

Acknowledgments

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[13] CCDC-292999 (for **3**), -293000 (for **6**), -293001 (for **7**) and -293002 (for **9**) 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.

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[19] It is conceivable that the elimination of water is induced by Au^I, leading to a Au^{III} intermediate which then leads to **10** by a ligand exchange with **C** and a subsequent reductive elimination.

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