Gold Catalysis

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Gold-Catalyzed Intermolecular Anti-Markovnikov Hydroamination of Alkylidenecyclopropanes**

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Abstract: *The cationic gold phosphine complex [{PCy_2(o-biphenyl)}Au(NCMe)]$^+SbF_6^-$ (Cy = cyclohexyl) catalyzes the intermolecular, anti-Markovnikov hydroamination reaction of monosubstituted and cis- and trans-disubstituted alkylidenecyclopropanes (ACPs) with imidazolidin-2-ones and other nucleophiles. This reaction forms 1-cyclopropyl alkylamine derivatives in high yield and with high regio- and diastereoselectivity. NMR spectroscopic analysis of gold π-ACP complexes and control experiments point to the sp hybridization of the ACP internal alkene carbon atom as controlling the regiochemistry of the ACP hydroamination reaction.*

Cyclopropyl rings are structural and/or reactive components of a large number of naturally occurring and biologically active molecules including potential therapeutics and are employed as mechanistic probes for use in chemical biology and enzymology.[1] Alkylidenecyclopropanes (ACPs) represent attractive substrates for the synthesis of functionalized cyclopropanes owing to the strain-driven reactivity[2–4] and synthetic accessibility[5,6] of ACPs. Indeed, ACPs have been employed widely as building blocks in organic synthesis,[6–8] and in this context, transition-metal-catalyzed methods have attracted particular attention.[8] Unfortunately, the vast majority of these catalytic transformations occur with concomitant cyclopropyl C–C bond cleavage and catalytic methods for the selective functionalization of the C=C bond of ACPs without ring opening are rare.[9] Therefore, the development of selective catalytic methods for the elaboration of ACPs without ring cleavage is of considerable significance.

The direct, transition-metal-catalyzed addition of the N–H bond of an amine or carboxamide derivative across a C–C multiple bond (hydroamination) represents a potentially expedient and atom-economical route to cyclic and acyclic amine derivatives.[10] Although hydroamination has been successfully applied to a broad range of unsaturated C–C bonds, the selective transition-metal-catalyzed hydroamination of the C=C bond of an ACP has not been realized.[11] Rather, the hydroamination of ACPs catalyzed by early[12] and late[13,14] transition-metal complexes leads exclusively to the formation of ring-opened products including allylic amines, imines, and/or pyrrolidines.[15–17] Herein, we report a gold(I)-catalyzed procedure for the selective intermolecular, anti-Markovnikov hydroamination of the C=C bond of ACPs without ring opening.

We targeted cationic gold(I) complexes supported by sterically hindered, electron-rich phosphine ligands as catalysts for the hydroamination of ACPs owing both to the high reactivity of these complexes with respect to alkene hydroamination[18,19] and to the absence of low energy β-migratory insertion/elimination pathways likely responsible for the ring opening of ACPs.[20–24] Drawing from our experience with the gold-catalyzed intermolecular hydroamination of 1-alkenes,[18] we similarly targeted imidazolidin-2-ones as nucleophiles for ACP hydroamination. An initial experiment was encouraging and reaction of a 1:1.1 mixture of 1-phenyl-2-methylenecyclopropane (**1a**) and 1-methyl-imidazolidin-2-one (**2**) catalyzed by a 1:1 mixture of (**P1**)AuCl (**P1** = $P(^tBu)_2$(*o*-biphenyl)) and $AgSbF_6$ in dioxane at 100 °C for 18 hours led to complete conversion of the starting materials to form a 1:2.2 mixture of the *trans*-α-aminocyclopropane **3a** and allylic amines **4** (Table 1, entry 1). Subsequent experiments identified improved conditions, and hydroamination of **1a** with **2** catalyzed by [(**P2**)Au(NCMe)]$^+SbF_6^-$ (**P2** = PCy_2(*o*-biphenyl); Cy = cyclohexyl) in dioxane at 60 °C for 18 hours led to complete conversion to form a 2.5:1 mixture of **3a**:**4** (Table 1, entry 5), from which **3a** was isolated in 63 % yield as a single regio- and diastereoisomer (Scheme 1).

Unknown to us at the time, ACP **1a** represented a particularly challenging substrate for selective anti-Markovnikov hydroamination and, in comparison, gold-catalyzed reaction of 1-benzyl- and 1-*n*-hexyl-2-methylenecyclopropane with **2** formed aminomethylcyclopropanes **3b** and **3c** with ≥25:1 regio- and diastereoselectivity which were isolated in 89 % and 85 % yields, respectively (Scheme 1). The gold-catalyzed anti-Markovnikov hydroamination of ACPs was likewise effective for both *cis*-1,2- and *trans*-1,2-disubstituted ACPs and tolerated a range of polar functional groups including acetate, tosylate, phthalimide, benzyl ethers, carboxylic esters, and free carboxylic acids (Scheme 1). Although less reactive than terminally unsubstituted ACPs, ethylidenecyclopropane **1i** underwent selective anti-Markovnikov hydroamination with **2** to form **3i** which was isolated in 71 % yield with ≥25:1 regio- and diastereoselectivity (Scheme 1). As well as **2**, a number of nucleophiles, including 1-*tert*-butyl-imidazolidin-2-one and 1-benzyl-imidazolidin-2-one, benzotriazole, and 5-chloro-2-hydroxypyridine underwent gold-catalyzed anti-Markovnikov hydroamination with **1g** to form the corresponding aminomethyl cyclopropanes **5** in good yield and with high regio- and diastereoselectivity (Scheme 2).

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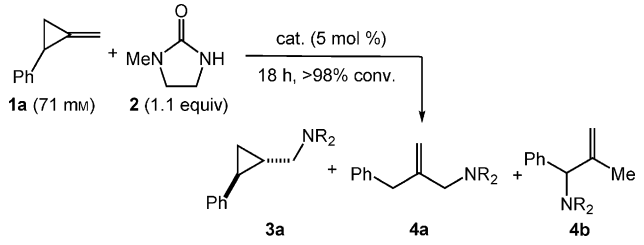
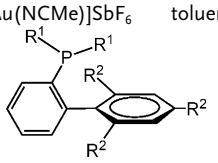
Table 1: Effect of catalyst, temperature, and solvent on the gold(I)-catalyzed hydroamination reaction of **1a** with **2**.



entry	catalyst	solvent	Temp. [°C]	**3a**/**4**[a]
1	(**P1**)AuCl/$AgSbF_6$	1,4-dioxane	100	1:2.2
2	(**P2**)AuCl/$AgSbF_6$	1,4-dioxane	100	1:2.2
3	[(**P2**)Au(NCMe)]SbF_6	1,4-dioxane	100	1:2.1
4	[(**P2**)Au(NCMe)]SbF_6	1,4-dioxane	80	1.5:1
5	[(**P2**)Au(NCMe)]SbF_6	1,4-dioxane	60	2.5:1
6	[(**P3**)Au(NCMe)]SbF_6	1,4-dioxane	60	1:6.8
7	IPrAuCl/$AgSbF_6$	1,4-dioxane	60	1:5
8	(Ph_3P)AuCl/$AgSbF_6$	1,4-dioxane	60	–[b]
9	[(**P2**)Au(NCMe)]SbF_6	DCE	60	>1:20
10	[(**P2**)Au(NCMe)]SbF_6	toluene	60	–[c]



R^1 = ^{t}Bu, R^2 = H (**P1**)
R^1 = Cy, R^2 = H (**P2**)
R^1 = Cy, R^2 = ^{i}Pr (**P3**)

[a] Determined by GC analysis of the crude reaction mixture. [b] TLC analysis revealed spot-to-spot conversion unless otherwise noted. [c] **2a** was consumed within 4 h without formation of **3** or **4**. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine.

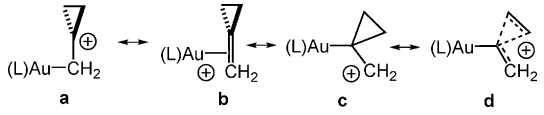
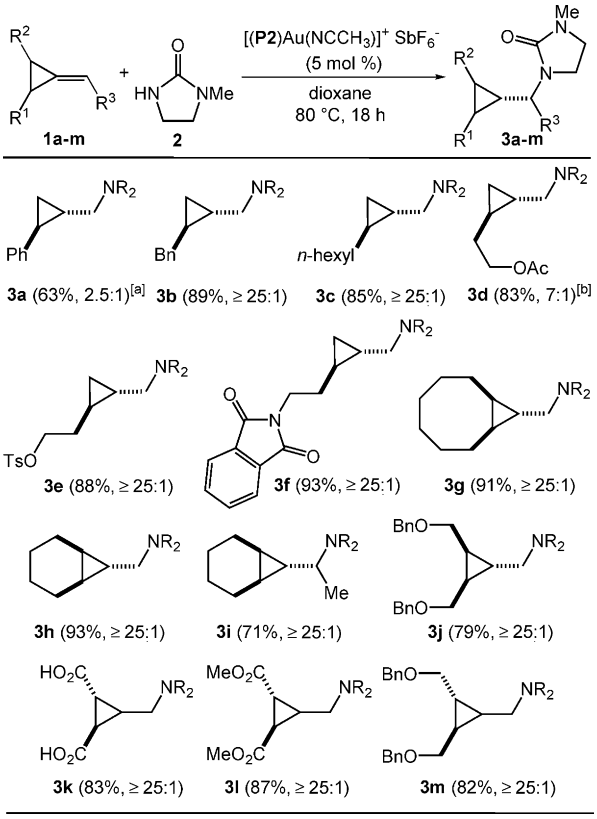


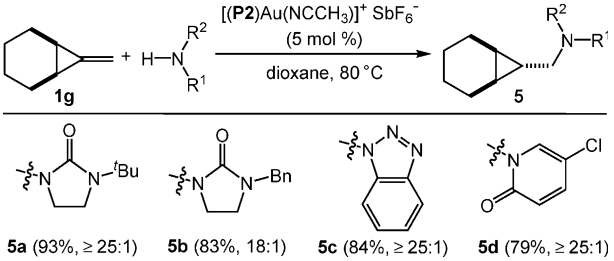
Figure 1. Potential resonance structures contributing to the gold–π-ACP bonding interaction.

Regarding the anti-Markovnikov regioselectivity of gold-catalyzed ACP hydroamination, we initially considered that the gold π-ACP bond might be polarized toward a cyclopropylcarbinyl cation-like structure (structures c and d, Figure 1), as has been invoked to account for Pt^{II}-[25] or Pd^{II}-catalyzed[26] ACP-to-cyclobutene isomerization and for the stoichiometric conversion of ACPs into Ru and Os cyclobutylidene complexes.[27] To evaluate this hypothesis, we generated the thermally unstable gold π-ACP complex [(**P1**)Au(η^2-**1a**)]$^+SbF_6^-$ (**6a**) as an equilibrium mixture (~25:1) of *trans*/*cis* isomers from reaction of **1a** with a 1:1 mixture of $AgSbF_6$ and (**P1**)AuCl at −80 °C to −40 °C [Eq. (1)]. Complex **6a** represents a rare example of a transition metal π-ACP complex and is the first gold π-ACP complex.[28] ^{13}C NMR spectroscopic analysis of *trans*-**6a** revealed large downfield ($\Delta\delta = +12.0$ ppm) and upfield ($\Delta\delta = -15.2$ ppm) shifts of the resonances attributable to the internal and terminal alkene carbon atoms, respectively, relative to those in starting material **1a**.[29] These chemical-shift perturbations mirror those observed for the corresponding isobutylene complex [(**P1**)Au(η^2-$H_2C{=}CMe_2$)]$^+SbF_6^-$ ($\Delta\delta(CH_2) = -15.4$ ppm, $\Delta\delta(CMe_2) = +20.9$ ppm)[30] and suggest the accumulation of positive charge at the internal alkene carbon atom of **6a** (a, Figure 1), which argues against significant contribution of structures c and d to the gold–π-ACP bonding interaction (Figure 1).

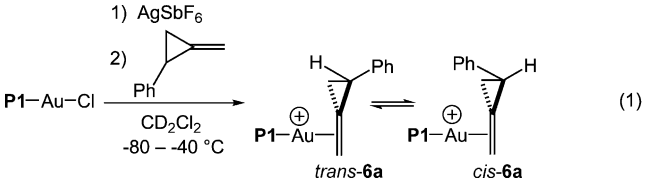
As gold-catalyzed hydroamination of isobutylene occurs with exclusive Markovnikov regioselectivity,[18] it appears that the anti-Markovnikov selectivity of gold-catalyzed ACP hydroamination is due either to the ring strain or the sp hybridization of the ACP. By analogy, allenes also have an internal sp-hybridized carbon atom and undergo gold-



Scheme 1. Scope of the gold-catalyzed intermolecular hydroamination of ACPs (**1a–m**) with **2**. Values in parenthesis refer to the yield of chemically and isomerically pure material and the isomer ratio of the crude material. [a] Reaction run at 60 °C. [b] Minor isomer not identified. OTs = *p*-toluenesulfonyl; Bn = benzyl.

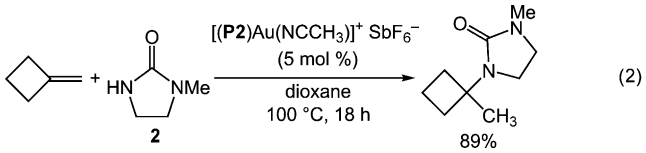


Scheme 2. Scope of the gold-catalyzed intermolecular hydroamination reaction of **1g** with nucleophiles. Values in parenthesis refer to yield of chemically and isomerically pure material and the isomer ratio of the crude material.



(1)

catalyzed hydroamination preferentially at the sp^2-hybridized carbon atoms.[31] To distinguish between these possibilities, we investigated the gold-catalyzed hydroamination of methylenecyclobutane (MCB), which is strained similar to an ACP but lacks the sp-hybridized carbon atom. Indeed, the exclusive Markovnikov regioselectivity of the gold-catalyzed hydroamination of MCB with **2** [Eq. (2)] points to sp hybridization, as opposed to ring strain, as the regiochemically controlling element of gold-catalyzed ACP hydroamination.[32,33]



(2)

In summary, we have developed an effective gold-catalyzed procedure for the selective intermolecular, anti-Markovnikov hydroamination of alkylidenecyclopropanes (ACPs) to form 1-cyclopropylamines in good yield and with high regio- and diastereoselectivity. These transformations represent both the first examples of the transition-metal-catalyzed hydroamination of an ACP without ring opening and the first examples of the transition-metal-catalyzed anti-Markovnikov hydroamination of an aliphatic, non-cumulated alkene.[34,35] Spectroscopic analysis of gold π-ACP complexes and control experiments point to the sp hybridization of the ACP alkene carbon atom, rather than ring strain, as the regiochemically controlling element in ACP hydroamination.

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