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Silaboration

Au Nanoparticle-Catalyzed Silaboration of Aryl-Substituted Cyclopropyl Aldehydes Forming Rearranged β-Boronate Silyl Enol Ethers

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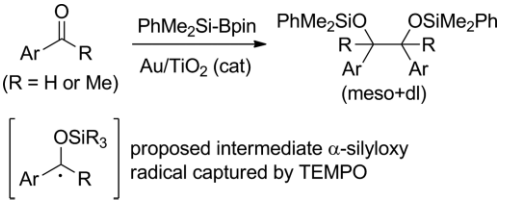
Abstract: 2-Aryl-substituted cyclopropyl aldehydes undergo an unprecedented Au nanoparticle-catalyzed silaboration leading to rearranged linear β-boronate-bearing silyl enol ethers. Formation of these products is attributed to the ring opening radical clock rearrangement of the intermediate α-cyclopropyl radical into a benzyl radical.

Introduction

Silylboranes, a class of compounds that possess a σ Si–B bond are fairly stable, especially if they bear electron rich substituents on the boron atom. Their chemistry has attracted the interest of organic chemists, as under certain reaction conditions they are capable of transferring their interelement bonded silicon and boron partners to organic substrates forming C-Si and/or C–B bonds.[1] The catalytic activation of the Si–B bond of silylboranes occurs either through oxidative addition on Pd(0) or Pt(0) complexes,[1] or via formation of the silyl bearing complex LCu-SiR_3, in case the catalyst is Cu(I) or Cu(II).[2]

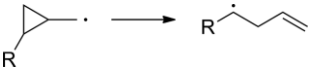
Our group was the first to report a few years ago the smooth activation of silylborane pinB-$SiMe_2Ph$ (pin: pinacolato) on Au nanoparticles supported on titania (Au/TiO_2), and its subsequent cis-1,2-addition to alkynes[3] or allenes,[4] and on the σ C–O bond of strained cyclic ether.[5] More recently we have presented its Au/TiO_2-catalyzed reaction with aromatic aldehydes and acetophenones which results to a C–C bond forming pathway, instead.[6] The activation of pinB-$SiMe_2Ph$ on Au/TiO_2 most probably involves the chemisorption of the interelement Si-B linkage on the electron deficient low-coordinated Au atoms, primarily at the corners of the Au nanoparticle,[7] and then follows the delivery of the two chemisorbed partners on the proximal physisorbed substrate.[8] While pinB-$SiMe_2Ph$ adds to alkynes, allenes, epoxides and oxetanes,[3,5] in the case of carbonyl compounds, a silylative pinacol-type reductive dimerization pathway is exclusively observed[6] (Scheme 1). It was clearly established that dimerization occurs through a radical-chain process, as the postulated intermediate α-silyloxy radical that eventually dimerizes was almost quantitatively captured in the presence of the free radical TEMPO.

Given the radical nature of the transformation shown in Scheme 1, we sought to study the Au/TiO_2-catalyzed reaction



Scheme 1. Reaction of silylborane pinB-$SiMe_2Ph$ with aromatic carbonyl compounds catalyzed by Au/TiO_2, and the proposed intermediate α-silyloxy radical.[6]

of pinB-$SiMe_2Ph$ with cyclopropyl aldehydes. α-Cyclopropyl carbinyl radicals, the anticipated reaction intermediates, are well-known to undergo on certain cases ring-opening rearrangement into homoallylic radicals, given their suitable substitution and lifetime (Scheme 2).[9] This radical-clock type rearrangement has been used in the past on many occasions either as an evidence of a radical mechanism, or as a mechanistic probe, to distinguish between polar or radical mechanisms in cyclopropyl substrates bearing an additional carbocation stabilizing methoxy group.[10]



Scheme 2. The radical clock rearrangement of an α-cyclopropyl carbinyl radical.

Results and Discussion

In this work we attempted to exploit synthetically such a possible radical clock rearrangement, by examining the Au nanoparticle-catalyzed silaboration of cyclopropyl-substituted aldehydes. For this purpose we synthesized a series of 2-aryl-substituted cyclopropyl aldehydes as a mixture of trans/cis isomers through the Cu(II)-catalyzed reaction between ethyl diazoacetate and alkenes followed by reduction of the produced esters and finally oxidizing the resulting alcohols (Scheme 3). The phenyl-substituted aldehyde **1**, whose possible silaboration was

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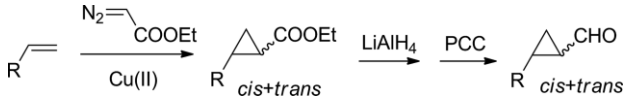
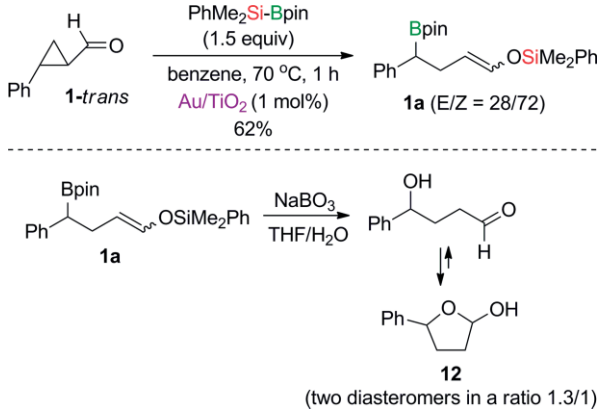
initially studied as a model-substrate (see Scheme 4), was synthesized as a single *trans*-diastereoisomer starting from the corresponding commercially available *trans*-carboxylic acid.



Scheme 3. General route for the synthesis of the 2-substituted cyclopropyl aldehydes.

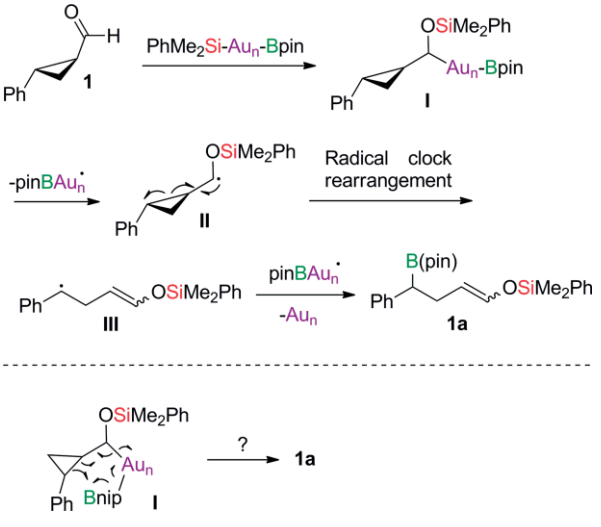


Scheme 4. Silaboration of aldehyde **1**-*trans* catalyzed by Au/TiO_2 and the structural proof of product **1a**.

Although, aliphatic aldehydes are unreactive against pinB-$SiMe_2Ph$,[6] the phenyl-substituted cyclopropyl aldehyde *trans*-**1** reacted smoothly with 1.5 equiv. of pinB-$SiMe_2Ph$ in the presence of Au/TiO_2 (1 mol-%), within 1 h at 70 °C, in anhydrous benzene as solvent. To our delight, no dimeric pinacol-type products are formed, as in the case of aryl aldehydes, but we isolated instead the ring-opened silaboration product **1a** (Scheme 4) as a mixture of geometrical isomers in relative ratio *cis*/*trans* = 72:28, and in 62 % yield. The structural assignment of the products was based on 2D-NMR data. It is possible that the prevailing *cis*-isomer is the thermodynamically more stable due to an intramolecular boron – silyloxy interaction. Simple MM3 calculations indicate that the cis isomer is more stable relative to the trans by 0.7 kcal/mol, while the more advanced MP2 (RI-MP2/def2-TZVP) calculations show that the trans isomer is more stable by merely ca. 0.5 kcal/mole. With the MP2 method there is not a very good agreement, nevertheless, calculations reveal that cis isomer is relatively more stable than anticipated. Notably, exactly the same stereochemical product outcome (**1a-*Z***/**1a-*E*** ca. 70:30) was observed in the silaboration of a mixture of diastereomers of aldehyde **1** (trans/cis = 60:40), which were prepared based on the general route shown in Scheme 3, indicative that both cis and trans cyclopropane isomers lead to the same products (apparently via a common intermediate, as it will be shown below). The silaboration products **1a** are somehow labile, as they easily undergo hydrolytic deprotection into the corresponding aldehyde, a process that is presumably accelerated by the Lewis acidic character of the boryl moiety. The resulting aldehyde in turn, transforms into a mixture of unidentified products, possibly through reaction of the aldehyde functionality with the pinacolato moiety. The silaboration product can be storred in $CDCl_3$ without decomposition by adding a base (e.g. pyridine).

As a further structural proof, the mixture of products **1a-*Z*** and **1a-*E*** was treated with $NaBO_3$, a reaction that transforms C–B bonds into C-OH. The only isolated product was hemiacetal **12**,[11] as a thermodynamic mixture of two epimers in a relative ratio *trans*/*cis* = 1.3:1 (Scheme 4). Apparently under the reaction conditions the silyl enol ethers were deprotected and the hydroxyl group installed at the former C-Bpin moiety reacted intramolecularly with the aldehyde forming lactol **12**. To the best of our knowledge, this is the first example in the literature of silaboration of cyclopropyl aldehydes. Somehow relevant could be considered the Rh(I)[12] or Pd(0)[13]-catalyzed hydrosilylation of cyclopropyl ketones leading to enol ethers, as well as, their Ni(0)-catalyzed borylation.[14] In addition, so far there is only one example in the literature involving a nano Au(0)-catalyzed cleavage of a σ cyclopropane bond, in the reaction between methylenecyclopropanes and diboron pinB-Bpin.[15] In this transformation occurs a direct 1,2-addition on a σ bond, while in our case we present a formal 1,4-O,C-addition.

It is reasonable that the initially formed α-silyloxy cyclopropyl radical (intermediate **II**, Scheme 5) from the cleavage of **I** undergoes ring-opening rearrangement into a benzyl radical (intermediate **III**), that is captured by the chemisorbed Bpin moiety forming the final silaboration product. It's also possible that coupling may occur in intermediate **I**, via the radical-type bond-forming and breaking concerted-like route shown in the bottom part of Scheme 5, as the σ cyclopropane bonds are rather loose.[16]



Scheme 5. Possible mechanisms for the formation of rearranged silaboration product **1a**.

Gratified by the results of silaboration of **1**, and given that the stereoselectivity of product formation is independent of the cis/trans arrangement of the phenyl group in **1**, we synthesized a series of *para*, *meta* or *ortho* 2-aryl-substituted cyclopropyl aldehydes as a mixture of cis/trans isomers based on the route shown in Scheme 3, and studied their reaction with pinB-

$SiMe_2Ph$ in the presence of Au/TiO_2. The conditions in all experiments were the same (1 mol-% catalyst, 1.5 equiv. silylborane, benzene as solvent, 70 °C, 1 h). The results are collectively summarized in Figure 1 and show that the transformation is quite general yielding β-boronate-substituted silyl enol ethers in moderate to good isolated yields, and as a mixture of geometrical isomers (cis/trans ca. 2–3:1). The transformation is quantitative, but the isolated product yield is somehow diminished because the silaboration products are in general labile, as it has been indicated aldready for the case of **1a**.

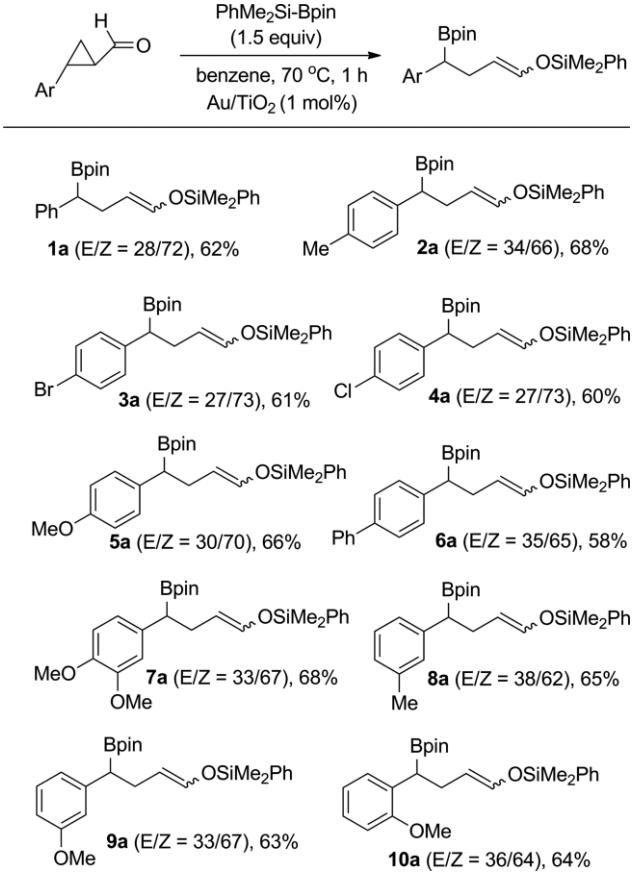
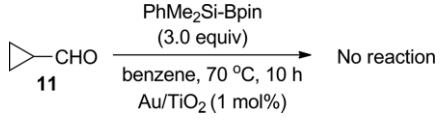


Figure 1. Products from the silaboration of 2-aryl-substituted cyclopropyl aldehydes catalyzed by Au/TiO_2.

Notably, the unsubstituted parent cyclopropanecarboxaldehyde (**11**) does not undergo any silaboration and remains intact, even under more forcing reaction conditions and excess of silyl borane (Scheme 6). Obviously, an aryl group at the 2-position is essential to drive the reaction, because it is capable of stabilizing the rearranged radical.



Scheme 6. Lack of reactivity in the attempted Au/TiO_2-catalyzed silaboration of cyclopropanecarboxaldehyde (**11**).

Conclusions

We present herein an unprecedented mode of reactivity catalyzed by supported Au nanoparticles, namely the silaboration of 2-aryl-substituted cyclopropyl aldehydes, which yields β-boronate-bearing silyl enol ethers. This pathway is explained in terms of a radical clock rearrangement of the initially formed α-carbinyloxy cyclopropyl radicals. This novel mode of reactivity show once more the powerful and unique nature of heterogeneous nano Au materials in catalysis.[17]

Experimental Section

Typical procedure of the Au/TiO_2-catalyzed silaboration of aryl-substituted cyclopropyl aldehydes: To a dried sealed tube containing *trans*-2-phenylcyclopropanecarbaldehyde, **1-trans** (15 mg, 0.1 mmol), Au/TiO_2 (20 mg, 1 mol-%) in 0.3 mL dry benzene were added via syringe 40 μL (0.15 mmol) of pinB-$SiMe_2Ph$. The mixture was heated to 70 °C, and after 1 h (100 % conversion as monitored by TLC) the slurry was filtered under reduced pressure through a short pad of silica gel with the aid of dichloromethane (ca. 2 mL) to withhold the supported catalyst. The filtrate was evaporated under vacuum and the residue was carefully chromatographed with hexane/ethyl acetate = 50:1 as eluent to afford 25 mg of **1a-*Z*** and **1a-*E*** (62 % yield) in a relative ratio 72:28.

Additional experimental details and product characterization are found in the Supporting Information.

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Keywords: Au nanoparticles · Catalysis · Silaboration · Cyclopropyl aldehydes · Radical clock rearrangement

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