Homogeneous Catalysis

International Edition: DOI: 10.1002/anie.201802533
German Edition: DOI: 10.1002/ange.201802533

Bifunctional Ligand Enables Efficient Gold-Catalyzed Hydroalkenylation of Propargylic Alcohol

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Abstract: *Using the previously designed biphenyl-2-ylphosphine ligand, featuring a remote tertiary amino group, the first gold-catalyzed intermolecular hydroalkenylation of alkynes has been developed. Synthetically valuable conjugated dienyl alcohols are formed in moderate to good yields. A range of alkenyltrifluoroborates are allowed as the alkenyl donor, and no erosion of alkene geometry and/or the propargylic configuration are detected. DFT calculations confirm the critical role of the remote basic group in the ligand as a general-base catalyst for promoting this novel gold catalysis with good efficiency.*

For the past several years we have developed several new phosphine ligands[1] for homogeneous gold catalysis.[2] These ligands, as shown in Figure 1, share the privileged biphenyl-2-ylphosphine framework,[3] but are unique and hence novel in their featured basic functional groups at the lower half of the pendant benzene ring. They are designed to achieve beneficial interactions between such a basic group and either the substrate or incoming nucleophiles by harnessing the robust linear organization of ligating atom–gold–alkyne centroid in gold(I) complexes (Figure 1 a). With the amine-based ligands, including **L1**–**L4**, several gold catalysis reactions are enabled by interactions between the basic nitrogen atom and alkyne/allene substrates.[1a,c,e] With WangPhos featuring a remote amide group as a ligand, nucleophilic additions to alkynes are accelerated owing to hydrogen bonding between the amide group and incoming nucleophiles, in the form of general-base catalysis.[1b,d,f] This phenomenon has recently been used to achieve highly enantioselective allenol cyclizations.[1g] However, the nucleophiles are so far limited to heteronucleophiles because of the necessity of hydrogen bonding.

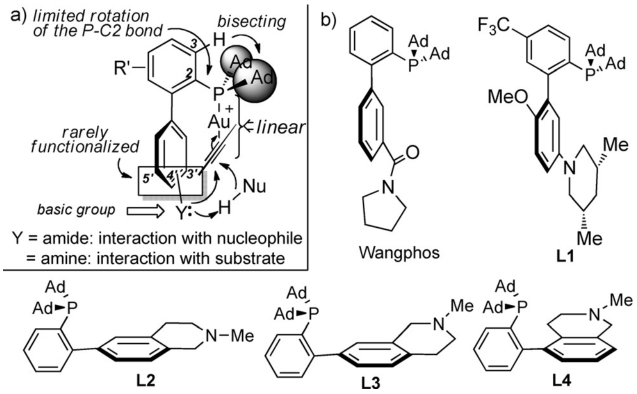
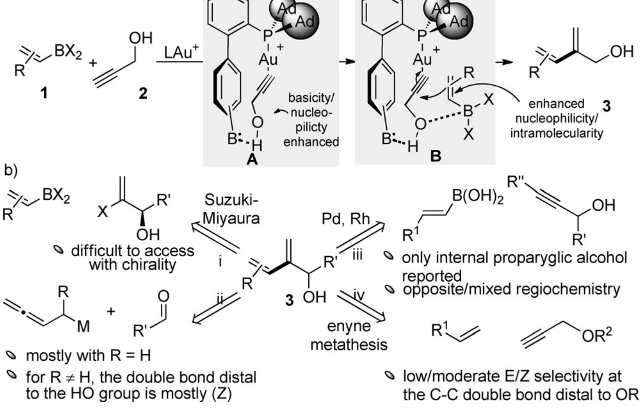


Figure 1. Development of gold-specific biphenyl-2-ylphosphines featuring remote basic groups: a) Design. b) Selected examples. Ad = adamantyl.

It is envisioned, however, that a ligand-enabled relay strategy could allow the use of alkenyl-based nucleophiles. As shown in Scheme 1 a, with a propargylic alcohol as the substrate, the hydrogen bonding between the hydroxy group and the remote basic site should form the structure **A**, and thus enhance the basicity/nucleophilicity of the oxygen atom, which would in turn exhibit an increased tendency to recruit an alkenylboron reactant by the formation of the Lewis pair in **B**. Such an interaction would, in a "relay" fashion, enhance the nucleophilicity of the alkenyl moiety and achieve intramolecularity of the alkene attack at the C–C triple bond. As such, the reaction would constitute a novel bimolecular synthesis of dienols and conceptually achieve a gold-catalyzed intermolecular hydroalkenylation of C–C triple bonds. Notably, intermolecular[4] hydroalkenylation[5,6] has not been reported in gold catalysis.



Scheme 1. Synthesis of dienols: a) Our design: a relay strategy based on ligand-enabled gold catalysis. b) Prior art and their limitations.

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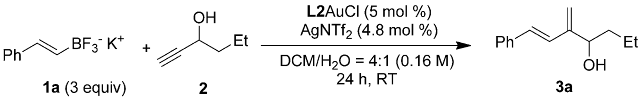
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201802533.

The dienol motif of **3** can be found as key structural components of either natural products[7] or in key intermediates in natural product synthesis[8] and, because of its densely packed functionalities, is rich with reactivity.[8b,9] As summarized in Scheme 1b, it can be mainly assembled in the following manners, but with limitations: i) the Suzuki–Miyaura coupling,[10] which is straightforward but requires difficult-to-access chiral α-haloallylic alcohols to prepare chiral **3**; ii) the addition of buta-2,3-dien-1-ylmetal species to aldehydes, which are mostly explored without substitution (i.e., $R=H$)[9e,11] or lead selectively to the formation of products possessing a *Z*-configured double bond distal to the hydroxy group when $R\neq H$,[12] and hence display limited product scope; iii) transition metal catalyzed hydroalkenylations[6b–d,f,13] of propargylic alcohols using boronic acids, and the reported examples employ only internal propargyl alcohol substrates[13c–e] and exhibit either the opposite[13c] or poor[13d] regiochemistry; iv) intermolecular enyne metathesis, which displays low/moderate *E*/*Z* selectivities;[9d,14] v) one related case of an oxidative Heck reaction (57% yield; not shown).[15]

Herein, we report that the implementation of our design (Scheme 1a), which permits for the first time, gold-catalyzed intermolecular additions of alkenyltrifluoroborates to C−C triple bonds. Moreover, it provides a broadly applicable and expedient access to 2-methylene-3-buten-1-ol derivatives with well-defined regio- and stereochemistry.

At the outset, we chose the terminal secondary propargylic alcohol 1-hexyn-3-ol (**2**) as the substrate and the *trans*-styryl-based trifluoroborate (*E*)-**1a** as the nucleophilic alkenyl species for reaction discovery and optimization (Table 1). Extensive exploration of ligands and reaction conditions revealed that the optimal reaction conditions are: (*E*)-**1a**/**2** = 3:1, **L2**AuCl (5 mol%), $AgNTf_2$ (4.8 mol%), $DCM/H_2O = 4:1$, 24 hours, ambient temperature. As shown in entry 1, under these reaction conditions, the desired dienol product **3a** was formed in 77% yield. The organic phase could be replaced by either DCE (entry 2) or $PhCF_3$ with only minor impact on yield, but not by toluene (entry 4) because of the poor solubility of (*E*)-**1a**. Besides $AgNTf_2$, other typically employed chloride abstractors including NaBARF (entry 5), AgOTf (entry 6), and $AgBF_4$ (entry 7) were effective but led to slightly lower yields. Decreasing the amount of (*E*)-**1a** to 2 equivalents resulted in a notable drop in yield (56% in entry 8 vs. 69% in entry 2). With 2 equivalents of (*E*)-**1a** and DCE/H_2O (4:1) as reaction media, the performance of various other ligands is shown in entries 9–12. Not surprisingly, commercially available and typically employed ligands such as Ph_3P, IPr, JohnPhosm, and MorDalPhos were largely ineffective (entry 9). In the presence of exogeneous Et_3N (1 equiv to Au), the yield was notably improved, but still poor (entry 10). These results highlight the enabling role of the basic tertiary amino group in **L2**. Notably, the other tertiary-amine-functionalized ligands, **L3** (entry 11) and **L4** (entry 12), that we previously developed[1c] along with **L2** are inferior to **L2**, and **L4** is only marginally better than the JohnPhos/Et_3N combination (see entry 10). These results reveal the importance of properly positioning the basic group in this catalysis and affirm the advantage of our designed bifunctional ligands in achieving it. Without adding H_2O, no desired product was observed (entry 13), and thus suggests that that the trifluoroborate salt needs to undergo (partial) hydrolysis during the reaction.[16] When the corresponding boronic acid was used in place of (*E*)-**1a**, the reaction did occur, but was contaminated by competing hydration and afforded a lower yield (entry 14). In entries 9–12 and 14, protodeboronation leading to styrene is a significant side reaction and responsible for the low yields. When (*Z*)-**1a** was used, neither **3a** nor its double isomer were detected, and its protodeboronation appeared to be more facile than that of (*E*)-**1a**, and is the major pathway for its decomposition (entry 15).

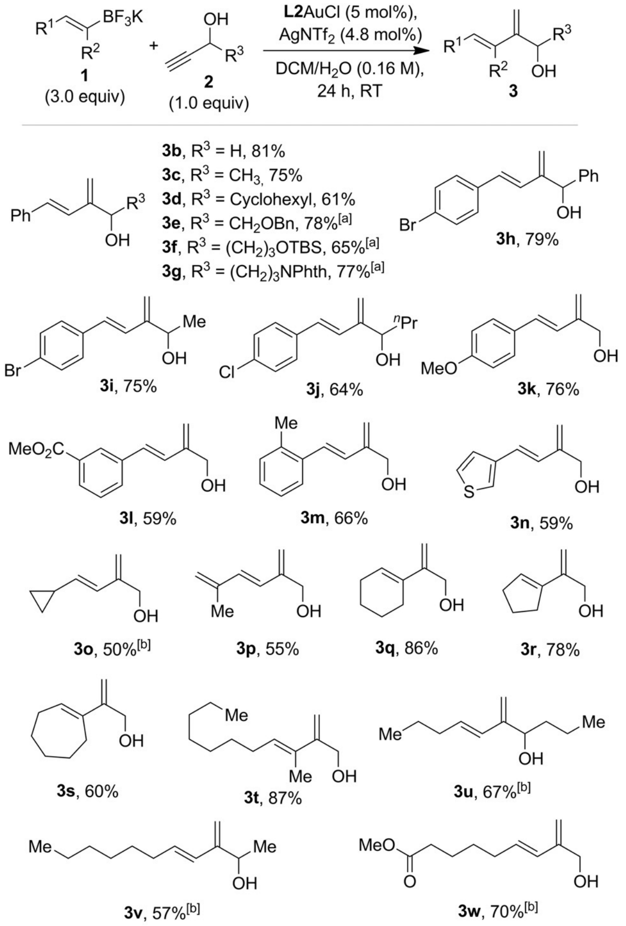
Table 1: Reaction conditions optimization.[a]



Entry	Deviation from the optimized conditions	Yield [%][b]
1	–	77
2	DCE/H_2O (4:1) as reaction media	69
3	$PhCF_3/H_2O$ (4:1) as reaction media	67
4	$PhCH_3/H_2O$ (4:1) as reaction media	0
5	NaBARF instead of $AgNTf_2$ as chloride abstractor	70
6	AgOTf instead of $AgNTf_2$ as chloride abstractor	70
7	$AgBF_4$ instead of $AgNTf_2$ as chloride abstractor	61
8	2 equiv of **1a**; DCE/H_2O (4:1) as reaction media	56
9	Ph_3P, IPr, JohnPhos or MorDalPhos as Au ligand; 2 equiv of **1a**; DCE/H_2O (4:1) as reaction media	≤ 6
10	JohnPhos as Au ligand, 2 equiv of **1a**; DCE/H_2O (4:1) as reaction media; 5% Et_3N	16
11	**L3** as Au ligand; 2 equiv of **1a**; DCE/H_2O (4:1) as reaction media	37
12	**L4** as Au ligand; 2 equiv of **1a**; DCE/H_2O (4:1) as reaction media	18
13	dry DCM used as solvent	0
14	(*E*)-styrylboronic acid instead of **1a**	35[c]
15	(*Z*)-**1a** instead	0[d]

[a] Used 0.1 mmol of 1-hexyn-3-ol (**2**). [b] Yields determined by NMR spectroscopy. [c] 27% **2** remained along with 22% of hydration product. [d] Mostly protodeboronation. DCE = 1,2-dichloroethane, DCM = dichloromethane, Tf = trifluoromethanesulfonyl.

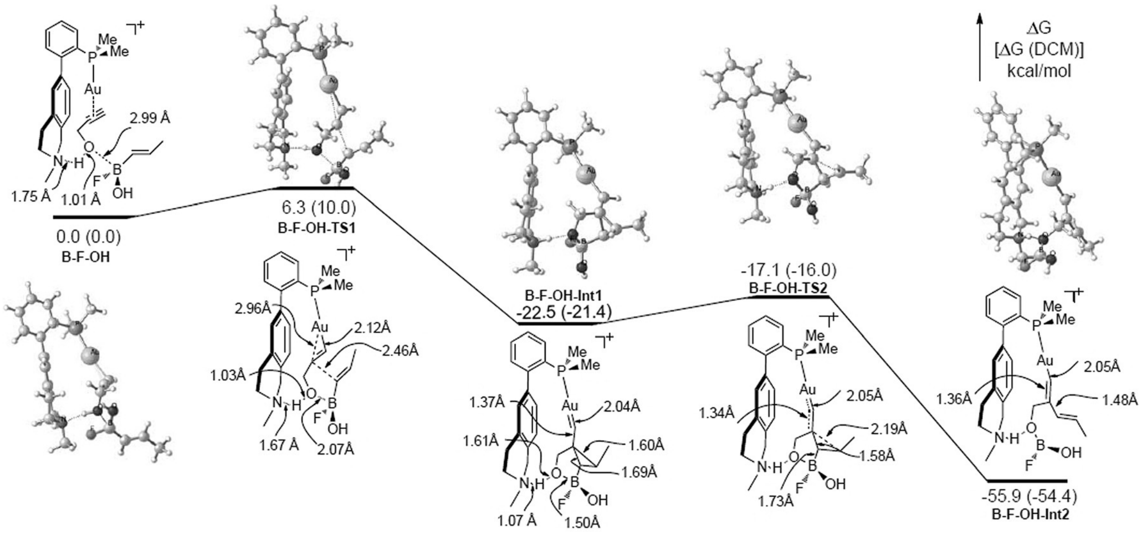
The reaction scope is shown in Scheme 2. Firstly, a range of the terminal secondary propargylic alcohols (**2**) was examined. Various R^3 groups of **2** are allowed, including H, sterically demanding cyclohexyl (in the case of **3d**), O-/N-functionalized alkyl groups (in the cases of **3e**,**f**) and a phenyl moiety (**3h**). Fairly good to excellent yields of **3b**–**g** were realized. In the series of **3b**–**d**, it is clear that the reaction efficiency correlates inversely with the sterics of the R^3 group. In contrast, terminal tertiary or internal propargylic alcohols do not lead to observable reaction. The scope of the (*E*)-styryltrifluoroborates was then examined. As shown in the cases of **3h**–**m**, substitutions, such as halides, an electron-donating MeO, electron-withdrawing ester, and a sterically congested 2-methyl group, on the benzene ring were all tolerated. Of note are the cases of **3h** and **3i**, the C−Br bonds of which should be a liability in relevant Ph/Rh catalysis. The scope with respect to **1** can be substantially broadened beyond styryl to include those substituted by a heteroarene, a cyclopropyl, and another alkenyl groups to afford highly function-



Scheme 2. The reaction scope. Yields of isolated products reported. [a] Used 8% cat. and 6.0 equiv of borates. [b] Used 6.0 equiv of borates.

alized products (**3n**–**p**) in serviceable yields. Furthermore, the conjugative substituents on **1** as featured in the cases discussed so far are not prerequisites for this gold catalysis. As shown with the cases of **3q**–**w**, monoalkyl substitutions (**3u**–**w**) and bisalkyl substitutions in cyclic forms (**3q**–**s**), and an acyclic one (**3t**), were all smoothly accommodated, and in some cases (e.g., **3q** and **3t**) the yields were excellent. Of note is that the alkyl substitutions *ipso* to boron in the cases of **3q**–**t** could hinder the reaction, but to the contrary they appear to be somewhat beneficiary. For the cases of **3o** and **3u**–**w**, 6.0 equivalents of the corresponding borates were needed for full conversion, and is attributed to their susceptibility to protodeboration. In all these cases, the double-bond geometries of **1** were completely maintained in the dienol products.

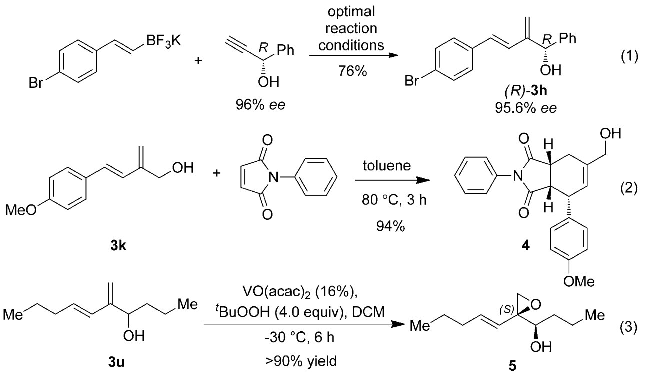
To understand the reaction mechanism and substantiate the essential role of the remote tertiary amino group of **L2** in facilitating the reaction, we performed DFT-B3LYP[17] calculations on the energetics of the reaction up to the step resulting in the formation of the dienylgold intermediate. To simplify the calculations, the 1-adamantyl groups of **L2** were replaced by methyl groups. As alluded to above, the trifluoroborates should undergo hydrolysis[16] at the beginning. We have examined both hydrolyzed boron species, RB(OH)F and $RB(OH)_2$. In the case of RB(OH)F, the two diastereomers of the initially formed ternary complexes (e.g., **B-F-OH** in Scheme 3), differing by the orientation of the F and OH substituents on boron are separately calculated. Among the three reaction paths, the one shown in Scheme 3 is energetically most favorable and has the lowest free-energy barrier in the critical first step [10.0 kcal mol^{-1} vs. 15.3 kcal mol^{-1} for $RB(OH)_2$ and 15.2 kcal mol^{-1} for the other RB(OH)F path, DCM, for details, see the Supporting Information]. This finding is consistent with $RB(OH)_2$ leading to a lower yield (see Table 1, entry 14). The initial ternary complex **B-F-OH** in Scheme 3 exhibits an expected hydrogen bond between the **L2** amino nitrogen atom and the propargylic hydroxy proton, and some electrostatic attraction between the propargylic oxygen atom and the boron center. The transition state **B-F-OH-TS1** is only 10.0 kcal mol^{-1} higher in free energy and reveals the migration of the



Scheme 3. B3LYP/6–31+G(d,p)/LANL2DZ(Au) energetics of the reaction with alkenyl(fluoro)(hydroxy)borane as a nucleophilic reagent in the gas phase and in DCM (number within parentheses, calculated with PCM as single point and with def2-TZVP for Au).

hydroxy proton from O to N at an early stage, and the significant shortening of the nascent B–O bond. The subsequently formed cyclopropyl gold carbene intermediate **B-F-OH-Int1** is 21.4 kcal mol^{-1} (DCM) more stable than **B-F-OH** and the original propargyl hydroxy proton has completely migrated to the ligand amino nitrogen atom while maintaining a hydrogen bond with its initially bonded oxygen atom. The next step, that is the fragmentation of the C–B bond, has an even lower barrier of $\Delta G^{\neq} = 5.4$ kcal mol^{-1}, and throughout the process the hydrogen bond between the protonated ammonium and the original propargylic oxygen atom is maintained. Subsequent protodeauration of the resulting intermediate **B-F-OH-Int2** by the ammonium proton (not calculated) should afford the final product. These theoretical studies largely support our original design and confirm that the properly positioned remote tertiary amino group plays the intimate role of a general-base catalyst in proton shuttling. The reaction energetics corresponding to Scheme 3, but with either **L3** or **L4** as ligand (the Ad groups are again replaced by methyl groups; see the Supporting Information), were also calculated. The barrier for first step in DCM is 17.4 kcal mol^{-1} and 16.3 kcal mol^{-1} for **L3** and **L4**, respectively, which is in line with the observed lower efficiencies in entries 11 and 12 of Table 1.

To establish the synthetic utility of this chemistry, we first examined whether the reaction would erode the *ee* value of a chiral propargylic center. As shown in Equation (1), essentially no racemization is detected in the formation of (*R*)-**3h**. Combined with readily available chiral propargylic alcohols, this chemistry offers valuable access to chiral dienols. A Diels–Alder cycloaddition was performed by using **3k** and *N*-phenylmaleimide as substrates, and only the *endo*-cycloadduct was obtained with an excellent yield [Eq. (2)]. Finally, a selective epoxidation of the allylic C–C double bond was achieved. The epoxy alcohol product **5** is not stable on a silica gel column and hence isolated crude yet mostly pure because of the high reaction efficiency [Eq. (3); acac = acetylacetonate]. Only one diastereoisomer of **5** was detected, and the relative stereochemistry was assigned based on literature precedent.[17]



In summary, we have developed the first gold-catalyzed intermolecular hydroalkenylation of propargylic alcohols. A designed biphenyl-2-ylphosphine ligand featuring a remote basic tertiary amine is experimentally proven as critical in enabling this novel gold catalysis with high efficiency. DFT calculations reveal the role of the amino group as a general base catalyst. Synthetically valuable conjugated dienyl alcohols are formed in moderate to good yields. A range of alkenyltrifluoroborates are allowed as the alkenyl donor, and the reaction is highly regioselective with regard to the propargylic alcohol, stereospecific with regard to the alkene geometry, and does not erode the propargylic configuration.

Acknowledgements

S Liao thanks the China Scholarship Council for scholarship. LZ thank NIGMS R01GM123342 for financial support and the NIH shared instrument grant S10OD012077 for the acquisition of a 400 MHz NMR spectrometer. GZ thanks Regione Lombardia—Cariplo Foundation Grant (Sottomisura B/2016), POR FESR 2014–2020/Innovazione e competitività, progetto VIPCAT for financial support.

Conflict of interest

The authors declare no conflict of interest.

Keywords: conjugation · gold · ligand design · reaction mechanisms · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2018**, *57*, 8250–8254
Angew. Chem. **2018**, *130*, 8382–8386

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Manuscript received: February 27, 2018
Revised manuscript received: April 23, 2018
Accepted manuscript online: April 27, 2018
Version of record online: June 4, 2018