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Silver-Catalyzed Highly Regioselective Formal Hydroboration of Alkynes

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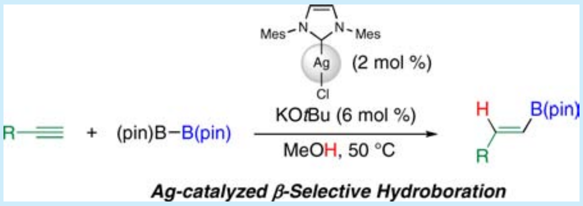
Ⓢ *Supporting Information*

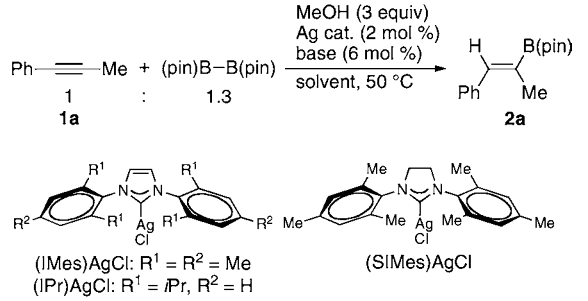
ABSTRACT: A silver(I)−*N*-heterocyclic carbene complex has proven to be a potent catalyst for formal hydroboration of alkynes, providing a variety of borylalkenes in regio- and stereoselective manners. Under the silver catalysis, allenes also undergo regioselective hydroboration to give borylalkenes.



Because of the high synthetic significance of organoboron compounds, whose carbon−boron bonds are utilizable for carbon−carbon bond formation and introduction of functional groups, development of new methods for accessing them has been a central subject in modern synthetic organic chemistry.[1] Recently considerable attention has been riveted on unique copper catalysis for carbon−boron bond-forming reactions[2] with unsaturated carbon−carbon linkages,[3,4] organic halides,[5] etc., where a borylcopper(I) species[6] arising from σ-bond metathesis between a copper(I) complex and a diboron acts as a key intermediate. In marked contrast to the great progress in the copper-catalyzed borylation reactions, the catalytic use of silver, which also composes group 11 elements, for synthesizing organoboron compounds remains almost totally unexplored, except for diborylation of alkenes with bis(catecholato)-diboron.[7] In view of the difference between copper and silver in fundamental properties such as atomic radius, electronegativity, softness as a Lewis acid, etc., we envisaged that borylation reactions of different mode and/or selectivity should be feasible under silver catalysis.[8] Herein we report on formal hydroboration of unsaturated carbon−carbon triple and double bonds with the aid of a silver(I) catalyst, demonstrating the potential silver catalysis toward carbon−boron bond-forming reactions.

We initially investigated the reaction of 1-phenyl-1-propyne (**1a**) with bis(pinacolato)diboron ((pin)B−B(pin)) in the presence of MeOH using $(Ph_3P)_3AgOAc$[9] (2 mol %) and KO*t*Bu (6 mol %) and found that (*Z*)-2-boryl-1-phenyl-1-propene (**2a**), a formal hydroboration product, was formed regio- and stereoselectively in 68% yield (entry 1, Table 1). The use of a silver−mesityl-substituted *N*-heterocyclic carbene (NHC) complex[10] ((IMes)AgCl or (SIMes)AgCl) improved the efficiency of the hydroboration to give an 85% yield of **2a** (entries 2 and 3), whereas the reaction did not proceed at all with a sterically more demanding complex ((IPr)AgCl) (entry 4). A drop in basicity of an added base (KOAc and K_2CO_3) led to decrease in yield (entries 5 and 6), and furthermore the combined use of a silver catalyst and a base was found to be indispensable for the reaction to proceed (entries 7 and 8). Among solvents surveyed, MeOH was the best, and the reaction smoothly occurred even at room temperature (entries 9−11).

Table 1. Optimization of Reaction Conditions for Ag-Catalyzed Hydroboration



entry	Ag	base	solvent	time (h)	yield (%)[a]
1	$(Ph_3P)_3AgOAc$	KO*t*Bu	toluene	33	68
2	(IMes)AgCl	KO*t*Bu	toluene	16	85
3	(SIMes)AgCl	KO*t*Bu	toluene	12	85
4	(IPr)AgCl	KO*t*Bu	toluene	48	<1
5	(IMes)AgCl	KOAc	toluene	43	<1
6	(IMes)AgCl	K_2CO_3	toluene	43	63
7	(IMes)AgCl	–	toluene	68	<1
8	–	KO*t*Bu	toluene	93	<1
9	(IMes)AgCl	KO*t*Bu	THF	42	37
10	(IMes)AgCl	KO*t*Bu	DMF	24	<1
11[b]	(IMes)AgCl	KO*t*Bu	MeOH	8	76[c]

[a]Determined by NMR. [b]Room temperature. [c]Isolated yield.

The intriguing feature of the silver catalysis in the present hydroboration is the higher regioselectivity as compared to that

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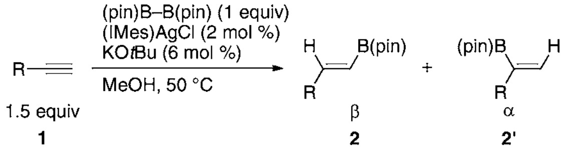
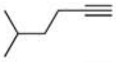
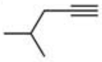
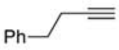
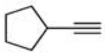
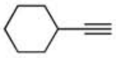
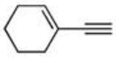
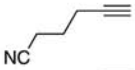
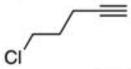
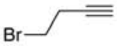
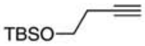
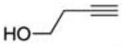
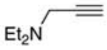
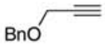
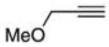
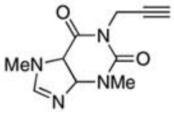
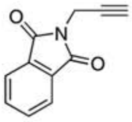
obtained with a copper catalyst:[11] such aliphatic terminal alkynes having *n*-hexyl (**1b**), isoamyl (**1c**), isobutyl (**1d**), or phenethyl (**1e**) were readily converted into the respective linear borylalkenes (**2b**–**2e**) with high *β*-selectivity (entries 1–4, Table 2).[12] The reaction could also be applied to cyclopentyl- (**1f**), cyclohexyl- (**1g**), and *tert*-butylacetylene (**1h**) to provide high yields of the products (**2f**–**2h**), irrespective of the steric congestion around the triple bonds (entries 5–7). Only a carbon–carbon triple bond of an enyne (**1i**) underwent the hydroboration to afford boryldiene **2i** (entry 8),[13] and furthermore high chemoselectivity of the present system has been demonstrated by the reaction of functionalized alkynes bearing a cyano (**1j**), halogen (**1k** and **1l**), silyl ether (**1m**), or hydroxy (**1n**) moiety, leaving these reactive groups intact (entries 9–13). The high *β*-selectivity was also observed with a propargylamine (**1o**) (entry 14), whereas the reaction of propargyl ethers (**1p** and **1q**), *N*-propargyltheobromine (**1r**), or *N*-propargylphthalimide (**1s**) gave *α*-adducts to some extent (entries 15–18). Although the hydroboration of **1b** also took place with (IPr)AgCl or (IMes)CuCl under the present reaction conditions, the regioselectivities became somewhat lower (entries 19 and 20). In contrast to the silver and the copper catalysis toward the hydroboration, a gold complex, $(Ph_3P)AuCl$, did not promote the reaction at all (entry 21).

Table 2. Ag-Catalyzed Hydroboration of Terminal Alkynes

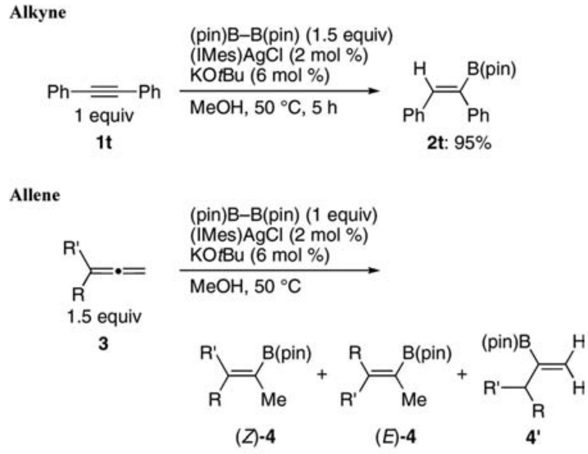


entry	alkyne		time (h)	yield (%)[a]	β:α[b]
1	*n*Hex—≡	(**1b**)	2.5	89	92:8
2		(**1c**)	3	70	89:11
3		(**1d**)	3	64	93:7
4		(**1e**)	7	62	>99:1
5		(**1f**)	5	85	95:5
6		(**1g**)	4	75	96:4
7	*t*Bu—≡	(**1h**)	3	83	>99:1
8		(**1i**)	8	63	95:5
9		(**1j**)	7	84	90:10
10		(**1k**)	6	72	94:6
11		(**1l**)	7	42	97:3
12		(**1m**)	2	51	>99:1
13		(**1n**)	2	40	>99:1
14		(**1o**)	10	33	>99:1
15		(**1p**)	2.5	70	67:33
16		(**1q**)	5	50	76:24
17		(**1r**)	2	51	53:47
18		(**1s**)	4	72	26:74
19[c]	*n*Hex—≡	(**1b**)	60	86[d]	76:24
20[e]	*n*Hex—≡	(**1b**)	2	98[d]	89:11
21[f]	*n*Hex—≡	(**1b**)	48	–	–

[a] Isolated yield. [b] Determined by NMR. [c] (IPr)AgCl was used instead of (IMes)AgCl. [d] NMR yield. [e] (IMes)CuCl was used instead of (IMes)AgCl. [f] $(Ph_3P)AuCl$ was used instead of (IMes)AgCl.

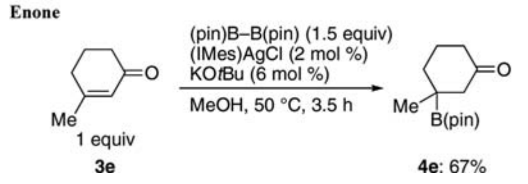
In addition to **1a**, diphenylacetylene (**1t**) also underwent the stereoselective hydroboration to afford (*Z*)-borylstilbene (**2t**) in 95% yield (Scheme 1). The wide applicability of the silver catalysis toward the borylation reaction has been shown by conversion of a carbon–carbon double bond: *n*-octyl- (**3a**), cyclohexyl- (**3b**), and phenylallene (**3c**) were facilely transformable into borylalkenes with high regio- and stereoselectivities, where boron and hydrogen were preferentially attached to the less congested double bond to provide (*Z*)-**4** as the major products.[3f,h,i] Besides, treatment of 1,1-diphenylallene (**3d**) led to the regioselective formation of **4d**, and boryl

Scheme 1. Ag-Catalyzed Hydroboration of Other Unsaturated C–C Bonds



R	R'	yield (%)[a]/time (h)	(*Z*)-**4**:(*E*)-**4**:**4'**[b]
n-Oct	H (**3a**)	77/5	>99:1:1
Cy	H (**3b**)	85/4	83:13:4
Ph	H (**3c**)	68/4	89:<1:11
Ph	Ph (**3d**)	43/4	90:10 (**4**:**4'**)

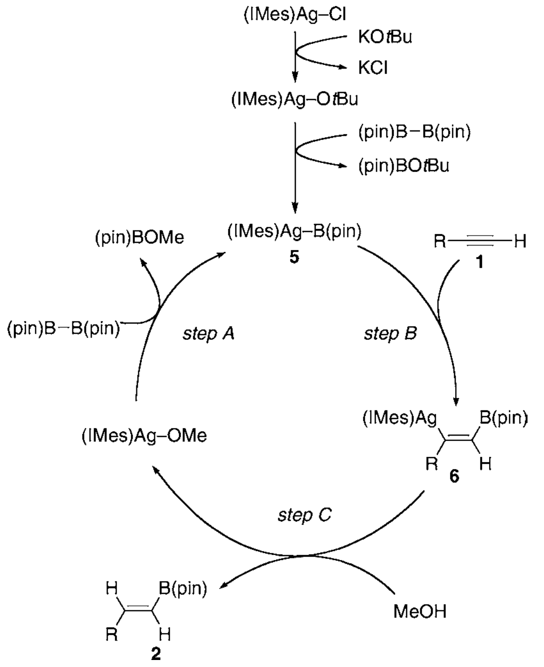
[a] Isolated yield. [b] Determined by NMR.



conjugate addition to 3-methylcyclohexenone (**3e**) also took place to give **4e** in 67% yield.[14]

The present hydroboration may be triggered by formation of a borylsilver(I) species[15] (**5**) arising from σ-bond metathesis between a silver(I) alkoxide and diboron as is the case in the copper(I)-catalyzed borylation reactions (*step A*, Scheme 2).

Scheme 2. A Proposed Catalytic Cycle for Ag-Catalyzed Hydroboration



Subsequent addition of **5** across a carbon–carbon unsaturated bond (*step B*, borylargentation), which produces a β-boryl organosilver species (**6**), followed by protonation with MeOH gives a hydroboration product with regeneration of the silver alkoxide (*step C*). The regiochemical outcomes of the hydroboration are decisively governed by the mode of the borylargentation, and the mode is similar to that of the well-studied borylcupration, where preferential addition of a boryl group to a terminal (with terminal alkynes)[11,16] or a central carbon (with allenes) occurs.[3f,h,i] At present factors responsible for the high β-selectivity with terminal alkynes still remain uncertain.

In conclusion, we have demonstrated that a silver complex exhibits potent catalysis toward the borylation reaction of unsaturated carbon linkages and that the method provides direct access to diverse organoboron compounds of high synthetic utility. The prominent feature of the silver catalyst has been exemplified in the β-selective hydroboration of terminal alkynes, and moreover the synthetic versatility of the present system may be expanded beyond hydroboration by capturing the key intermediate (**6**) with other electrophiles than proton.[17] Further studies on the silver-catalyzed borylation reactions as well as on the mechanistic details of the hydroboration are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) Solvent screening in the reaction of 1-octyne (**1b**) using 3 equiv of MeOH (NMR yield): toluene, 86% (β:α = 84:16, 26 h); THF, 38% (β:α = 84:16, 19 h); DMF, 19% (β:α = 83:17, 19 h).

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