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Isolation and characterization of hydrocarbon soluble NHC copper(I) phosphoranimide complex and catalytic application for alkyne hydroboration reaction

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ABSTRACT

Novel NHC copper(I) phosphoranimide complexes have been isolated and characterized by NMR and X-ray crystallography studies. The feature of this hydrocarbon soluble mononuclear copper complex as effective hydroboration catalyst could be attributed to the rapid forming of copper hydride intermediate with the generating of more stable bulky borate by-product ^{t}BuPNB(pin), which is unveiled by excellent catalytic performance of [NHC]CuNP^{t}Bu$_3$ for the alkyne hydroboration reaction with exclusive β-regio- and *trans*-stereo-selectivity in mild reaction condition. The copper hydride intermediate could also be observed from stoichiometric reaction of [NHC]CuNP^{t}Bu$_3$ with HB(pin) compound by NMR analysis.

Introduction

Main group and transition metal complexes involving phosphinimine and phosphoranimide ligands were discovered and studied by Dehnicke and Weller around 20 years ago.[1] Stoichiometric reactions between transition metal halide precursors and phosphoranimide ligands have also been systematically studied. However, the utility of these ligands in catalysis was unknown until Stephan's report on alkene polymerization research in 1999.[2] The affordability and amenability to modification of phosphoranimide ligands was detailed for the first time. Among those ligands, [$^-$NP^{t}Bu$_3$] was attractive due to its large size introduced by ^{t}Bu group around phosphorus atom and strong σ-donating ability on the nitrogen atom. More importantly, organo-boranes undergo σ-bond metathesis with bulky phosphinimines under mild reaction conditions and release hydrogen as by-product at the same time (Scheme 1).[3]

We hypothesized that replacing the hydrogen atom on the phosphinimine (red **H**) with a ligated transition metal (purple **ML$_n$**) would produce the desired metal hydride complex (**L$_n$M-H**) and release organoboron-phosphoranimide compound **C** as by-product.[4] In the family of transition metal hydrides, organo-copper(I) hydride complexes have been considered as interesting catalytic intermediates in selective reductions of unsaturated organic compounds.[5] Cu(I) hydride complexes can be synthesized from phosphine or NHC coordinated copper(I) *tert*-butoxide or fluoride complex by reaction with organosilane[5a,f–g] or organoborane[6] compounds. The alkyne hydroboration reaction was selected in order to verify this hypothesis of forming a copper hydride intermediate with assistance from the phosphoranimide ligand. Vinylboronates, the products of alkyne hydroboration, are a class of useful building blocks in organic synthesis, which are ready for further transformation to form C—C or C—X bonds via Suzuki-Miyaura cross coupling, boron-Heck reaction, etc.[6g] There are many methodologies to make vinylboronates by the alkyne hydroboration reaction under transition metal catalysis.[7] In recent years, copper catalyzed hydroboration has received much attention due to its efficiency, and its mild and environmentally friendly reaction conditions. There are two major pathways to undergo hydroboration reaction for copper(I) catalysts: One is the [Cu]-H intermediate formed from organoborane [B]-H compound can undergo *syn*-addition with alkyne to yield the direct hydroboration product via alkenylcopper species; the other one is the [Cu]-Borane formed with diboronate compound, followed by the *syn*-addition with alkyne to get the alkenyl copper intermediate then quenched with alcohol additive in order to regenerate the catalytic species [Cu]-OR′ (Scheme 2).[8] Control of selectivity between α and β isomers can be generated through different copper catalytic species ([Cu]-H and [Cu-B]).[8b]

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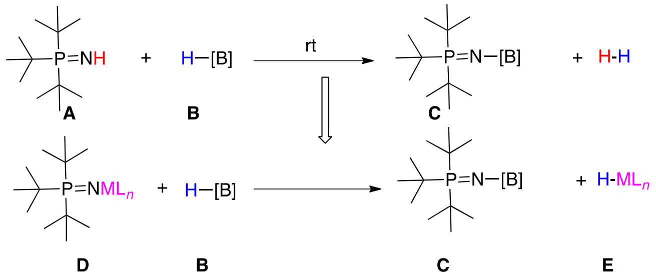
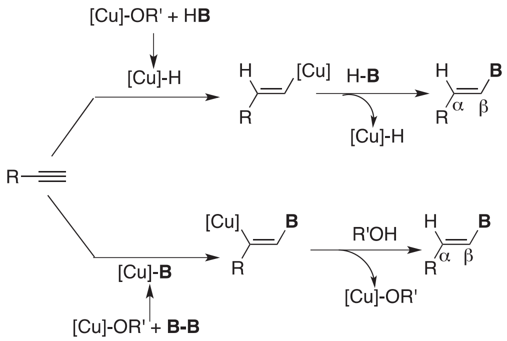


Scheme 1. The hypothesis of forming metal hydride.



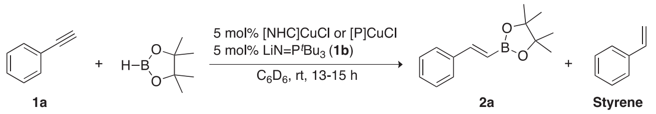
Scheme 2. General approaches of copper catalyzed alkyne hydroboration.

The copper catalyzed direct hydroboration reaction ([Cu]-H) will be more straightforward, atom economical and has been studied in recent years.[9] The regio-selectivity could also be determined by using phosphine or NHC ligand respectively coordinated with same catalytic species.[9e] The steric bulk of phosphoranimide ligands have the potential as well to be tuned to achieve higher selectivities in the alkyne hydroboration reaction. Herein, we wish to report the catalytic reactivity of bulky phosphoranimide Cu complexes in alkyne hydroboration reaction, and the first isolation of an NHC copper(I) complex bonded with a phosphoranimide ligand as the highly hydro-carbon soluble catalyst for the alkyne hydroboration reaction with excellent yield and exclusive *β*-regio- and *trans*-stereo-selectivity.[10]

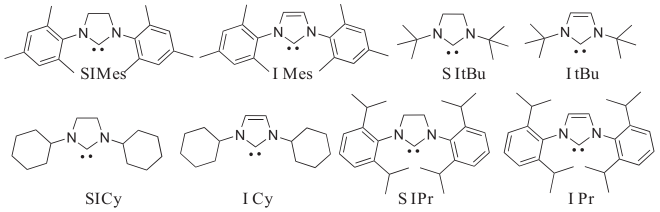
Optimization of the reaction conditions

Hydroboration of phenylacetylene (**1a**) with HB(pin) as the boron source was selected as a model reaction in order to find the suitable combination of copper(I) precursor for LiNP^{t}Bu$_3$ (**1b**) as co-catalyst at room temperature. The results are summarized in Table 1. A few classic NHC and phosphine copper(I) chloride precursors (**c1**–**c11**) were synthesized and used as catalysts.[11] The yield of product **2a** was measured by proton NMR analysis of the crude reaction mixture using mesitylene as internal standard. The hydrogenation by-product of styrene was also listed in the table. However, there is no any *Z*-vinylboronates product formed according to the analysis of ^{1}H NMR spectra of crude reaction mixture in all the cases.[12a] When simple copper chloride **c1** was used (entry 1, Table 1), only 18% of product **2a** was observed. Several kinds of NHC ligands with different steric size and electronic donating ability were screened as well (entries 2–9, Table 1). The suitable precursors are SIPr or IPr ligated Cu(I) complexes with the result of nearly quantitative yield and clean β-regioselectivity[12b] (entries 8–9, Table 1). Use of Cu(I) precursors with phosphine ligands led resulted in low conversion (entries 10–11, Table 1). The SIPr ligand gave better catalytic performance than its IPr counter-

Table 1
Reaction condition optimization.[a]



Entry	Cu(I) precursor	**2a** (%)[b]	**1a** (%)[b]	Styrene (%)
1	CuCl (**c1**)	18	53	<1
2	SIMesCuCl (**c2**)	<1	48	15
3	IMesCuCl (**c3**)	34	38	5
4	SItBuCuCl (**c4**)	n.d.	65	<1
5	ItBuCuCl (**c5**)	13	52	2
6	SICyCuCl (**c6**)	Trace	33	<1
7	ICyCuCl (**c7**)	22	47	4
8	IPrCuCl (**c8**)	>99	<1	<1
9	SIPrCuCl (**c9**)	>99 (**89**)[d]	<1	<1
10	(PPh$_3$)$_3$CuCl (**c10**)	n.d.	71	<1
11	tBu$_3$PCuCl (**c11**)	10	78	10
12[c]	IPrCuCl (**c8**)	82	18	<1
13[c]	SIPrCuCl (**c9**)	94	6	<1
14[e]	SIPrCuCl (**c9**)/tBuOK	83	3	8



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[a] **1a** (0.20 mmol), HBpin (0.22 mmol, 1.1 eq.), [Cu] (0.010 mmol, 5.0 mol%), **1b** (0.010 mmol, 5.0 mol%), C$_6$D$_6$ (2 mL, 0.1 M) at rt, for 13–15 h.
[b] The yield was calculated based on the integration of proton NMR compared with mesitylene (1 eq.) as internal standard.
[c] The reaction time was controlled within 30 min to qualify the catalytic efficiency by the ratio of **2a**/**1a** and there is no internal standard when running proton NMR.
[d] Isolated yield.
[e] **1b** was replaced by ^{t}BuOK (5 mol%).