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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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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, [$^{-}NP^{r}Bu_{3}$] was attractive due to its large size introduced by ^tBu 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_nM -H) and release organoboron-phosphoranimide compound **C** as by-product.⁴ In the family of transition metal hydrides, organo-cop-

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ABSTRACT

Novel NHC copper(I) phosphoranimide complexes have been isolated and characterized by NMR and Xray 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 'BuPNB(pin), which is unveiled by excellent catalytic performance of [NHC]CuNP'Bu₃ for the alkyne hydroboration reaction with exclusive β -regioand *trans*-stereo-selectivity in mild reaction condition. The copper hydride intermediate could also be observed from stoichiometric reaction of [NHC]CuNP'Bu₃ with HB(pin) compound by NMR analysis. © 2017 Elsevier Ltd. All rights reserved.

> per(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 organoborane⁶ 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}











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

Table 1

Reaction condition optimization.^a

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^tBu₃ (**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 ¹H 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 B-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-



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
N.N. SIMes	$\sum_{\substack{n \in \mathbb{N}, \\ n \in \mathbb{N}}} \frac{1}{n} \sum_{\substack{n \in \mathbb{N}}} \frac{1}{n} \sum_{\substack{n \in \mathbb{N}, \\ n \in \mathbb{N}}} \frac{1}{n} \sum_{n$	N K ItBu		
SICy				

^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%), C₆D₆ (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 ^tBuOK (5 mol%).

part (entries 12–13, Table 1). The classic fashion of forming copper hydride using ¹BuOK as catalytic additive was compared with LiNP^fBu₃ (**1b**) as co-catalyst. 83% NMR yield of desired product could be obtained, however, the hydrogenation product was also observed with 8% in the crude reaction mixture (entry 14, Table 1). The hydrogenation product can also be obtained when SIMes and ¹Bu₃P were used as ligand, with 15% and 10% NMR yield respectively (entry 2 and entry 11). Therefore, the precursor SIPrCuCl (**c9**) was chosen as suitable partner for phosphoranimide (**1b**) with 89% of isolated yield for the next study of substrate scope (entry 9, Table 1).

Substrates scope

Several terminal alkynes were tested with the co-catalyst of LiNP^rBu₃ (**1b**) and SIPrCuCl (**c9**) (Table 2). A variety of terminal aryl alkynes can undergo β -selective hydroboration to form the desired vinylboronates, showing good tolerance for substituents on the phenyl ring with yields of 74–99% (**2b–2g**, **2k**). The alkyl-substituted vinylboronates can also be obtained under these reaction conditions (**2h–2i**, **2l**). An intramolecular olefin moiety remains intact under this reaction conditions (**2j**, Table 2); ester and toslate protected amide substrates can also undergo hydroboration to obtain the corresponding products (**2m** and **2o**¹³, Table 2).

Double hydroboration can be achieved as well by using diyne as starting material to afford diboronate compound **2p** with 81% isolated yield at slightly higher temperature. The *trans* geometry of C=C was confirmed by X-ray crystallography (see SI for full detail).

Preparation of copper(I) complex

With the optimized catalyst combination in hand, we attempted to isolate the catalytically active species. The stoichio-

Table 2



^a**1** (0.20 mmol), HBpin (0.22 mmol, 1.1 eq.), SIPrCuCl (0.010 mmol, 5.0 mol%), **1b** (0.010 mmol, 5.0 mol%), benzene (2 mL, 0.1 M) at rt, for 13 h. ^bThe reaction was conducted at 35 °C; Ts = 4-methyl-benzenesulfonyl.

metric reactions of [NHC]CuCl ([NHC] = IPr or SIPr) with LiNP⁴Bu₃ (**1b**) proceeded in dry THF instead of benzene due to the poor solubility of lithium salt (**1b**). Fortunately, the NHC coordinated copper(I) phosphoranimide complexes were obtained as colourless solids (**3**, **4**) with good isolated yields (Fig. 1). The solubility of these copper(I) complexes is extremely outstanding in hydrocarbon solvent such as pentane and hexane at room temperature. Complexes **3** and **4** were characterized by NMR, elemental analysis and X-ray crystallography. The latter technique revealed the monometallic, two-coordinate nature of **3** and **4** (structures shown in Fig. 1 with selected bond lengths and angles).

The phosphoranimide ligand in complex **3** and **4** approached closer (Cu–N 1.78 Å) to the metal centre than in LiNP^{*t*}Bu₃ (**1b**)¹³ (Li–N = 2.03 Å). The coordination geometry at Cu is close to linear: the donor atoms of the NHC and phosphoranimide bind the Cu centre with a C(1)–Cu(1)–N(3) angle of 177–179°, which is similar to IPrCuO^{*t*}Bu reported by the group of Prof. Sadighi.¹⁴ The cone angle is a little bit smaller than the corresponding titanium complex,¹⁵ which could be rationalized by the steric repulsion between the NHC moiety and ^{*t*}Bu group on phosphorus atom.

In order to examine the catalytic activity of the isolated copper complexes, the hydroboration reaction of diphenylacetylene as bulky substrate was also tried using complex **4** as catalyst to afford the *cis*-vinylborate **2q** with 78% isolated yield (Eq. (1)).¹⁶



Preliminary mechanistic study was undertaken through a deuterium labeling experiment and NMR study of a stoichiometric reaction. The terminal proton of the alkyne was kept intact during the hydroboration process, which was verified by the deuterated experiment using complex **4** as catalyst to afford the 82% isolated yield of deuterated product **2r** with 99% of deuterium retention (Scheme 3). Stoichiometric reaction of complex SIPrCuNP^tBu (**4**) with 1 eq. of HB(pin) was studied by NMR (see SI for full detail). SIPrCuH (**5**) could be observed from the ¹H NMR spectrum with the chemical shift of the copper hydride δ = 1.93 ppm.^{5g} This transformation was not clean after 10 h and the hydride peak will disappear as time extended. The by-product **6** can be observed as well by ³¹P NMR analysis with chemical shift δ = 39.5 ppm and its identity was confirmed by adding another 1 eq. of compound **6** synthesized according to literature³ into the reaction mixture (Scheme 3).

Based on the experiments above, we proposed the catalytic cycle for the reaction of alkyne hydroboration as below: the copper hydride intermediate **5** can be obtained by the reaction of catalyst **4** with coordinated HB(pin), then the *cis*-insertion will occur to give the vinylcopper species **1**' followed by the quenching step of reacting with HB(pin) to give the final β -selective vinylboronates **2** and regenerate SIPrCuH **5** (Scheme 4).^{7a,13}

In summary, we designed and synthesized the highly hydrocarbon soluble phosphoranimide [NHC]copper(I) complexes as the effective catalyst for the alkyne hydroboration reaction. The stoichiometric studies indicate that the copper hydride species could be formed when met with organoborane compound. This demonstrates a new way of forming the important metal hydride species. The specification of the phosphoranimide ligand could be utilized as a starting point into other base metals in periodic table to develop a new generation of catalysts for organic transformations. Some of the projects are being conducted in our laboratory.



ORTEP drawing of complex **3** with 50% thermal ellipsoids. Hydrogen atoms and co-crystallized molecular are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)-C(1) 1.847(4), Cu(1)-N(3) 1.784(4), P(1)-N(3) 1.510(4); C(1)-Cu(1)-N(3) 178.9(2); Cu(1)-N(3)-P(1) 151.2(3), C(39)-Cu(1)-C(31) 79.28 (Cone angle).

ORTEP drawing of complex 4 with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–C(1) 1.863(3), Cu(1)–N(3) 1.781(3), P(1)–N(3) 1.532(3); C(1)–Cu(1)–N(3) 177.76(15); Cu(1)–N(3)–P(1) 151.7(2), C(39)-Cu(1)-C(33) 78.93 (Cone angle).

Fig. 1. Preparation and ORTEP drawing of copper(I) complexes.



Scheme 3. Deuterium labeling and NMR in-situ experiments for mechanism study.



Scheme 4. Proposed catalytic cycle of alkyne hydroboration reaction.

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2017.03. 011.

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