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Communication

Copper(I) Diphosphine Bifluoride Complexes as Efficient Preactivated Catalysts for Nucleophilic Addition on Unsaturated Functional Groups

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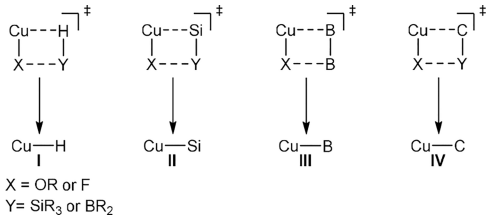
ABSTRACT: Herein we report the synthesis of a family of copper(I) diphosphine bifluoride complexes, their characterization, and their use as efficient preactivated catalysts for nucleophilic copper addition of pronucleophiles on unsaturations. Their use as mechanistic probes is also highlighted by the identification of two copper deuterides.

KEYWORDS: *copper complexes, bifluoride, asymmetric catalysis, diphosphine, vinylation*

INTRODUCTION

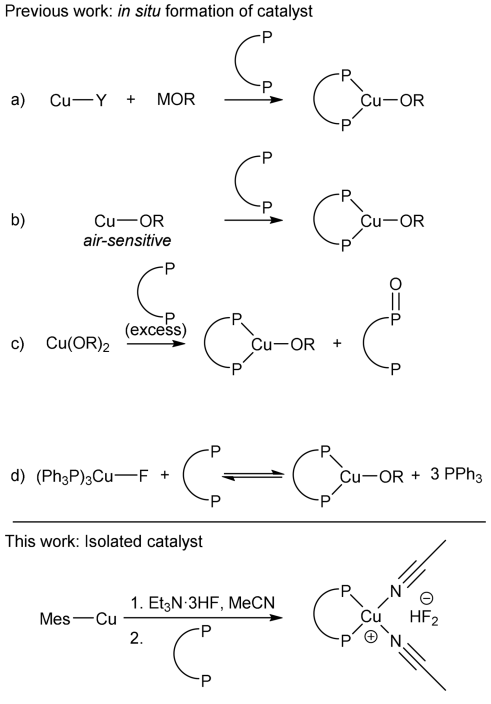
During the last decades, nucleophilic copper(I) chemistry has emerged as an efficient tool for the addition of pronucleophiles via the formation of Cu−H (**I**),[1] Cu−Si (**II**),[2] Cu−B (**III**),[3] or Cu−C (**IV**)[4] species and their reactions on various unsaturations. One of the main prerequisites to perform a σ-bond metathesis between a silylated or borylated pronucleophile and a copper(I) source (Cu−X) to generate the active catalytic species is to have either an oxygen derivative or a fluoride ion as the X ligand (Scheme 1). According to the hard−soft acid−base theory,[5] those "hard" ligands are mismatched with the "soft" copper(I) cation, which results in a more labile and reactive Cu−X bond.

Scheme 1. Formation of Nucleophilic Copper Species from Pronucleophiles and Activated Copper Sources



However, despite the increasing number of publications on this topic, to this day the classical protocols to obtain a diphosphine/Cu−X catalyst all present some drawbacks either from a practical point of view or to obtain well-defined species in solution. The first protocol consists of the combination of a copper source Cu−Y in which Y is softer (e.g., CuCl, CuBr, or CuCN), an oxygenated base (MOMe, MO*i*-Pr, or MO*t*-Bu), and a diphosphine to generate the diphosphine/Cu−OR catalyst (Scheme 2a).[6] This protocol is probably the most used in the literature and is compatible with most reaction conditions. However, the use of an alkoxide base can be problematic in the case of base-sensitive substrates. For the second protocol, an oxygenated copper(I) source such as CuOAc, $(CuOTf)_2{\cdot}C_6H_6$, or CuO*t*-Bu is directly used with a diphosphine to obtain the desired catalyst in situ (Scheme

Scheme 2. In Situ Preparation of Activated Copper Catalysts and Preparation of Copper Diphosphine Bifluoride Complexes



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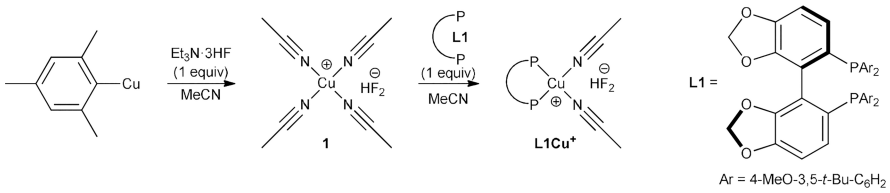
Scheme 3. Synthesis of the Copper(I) (*R*)-DTBM-Segphos Bifluoride Complex



2b).[7] Despite the simplicity of this system, the drawback is that this procedure is not easily applicable in laboratories not equipped with a glovebox because of the air sensitivity of the copper sources. A third possibility is to start from a stable copper(II) source such as $Cu(OAc)_2$, $Cu(OTf)_2$, or $CuF_2·H_2O$ and combine it with an excess of diphosphine to reduce the copper(II) to copper(I) and coordinate it (Scheme 2c).[8] The main problem with this protocol resides in the formation of phosphine oxides, which have been proved to be efficient ligands for copper and could therefore result in an undesired catalytic cycle.[9] A less used method consists of the use of bench-stable $CuF(PPh_3)_3·2MeOH$[10] in combination with a diphosphine (Scheme 2d).[11] However, this will generate an equilibrium between two active copper catalysts that can result in two different reactivities. We previously reported the synthesis of a copper diphosphine polyfluoride complex[2b] as well as some N-heterocyclic carbene (NHC)−copper bifluoride complexes.[12] Both complexes hinted at the possibility to synthesize well-defined copper complexes that could bypass the problems encountered in the classical methods.

RESULTS AND DISCUSSION

Herein we report the synthesis, characterization, and reactivity of a family of copper(I) diphosphine bifluoride complexes. As stated above, a copper diphosphine polyfluoride complex has already been synthesized. However, the quality and reactivity of the complex were greatly dependent on the quality of the starting materials. We therefore devised a new reproducible synthesis (Scheme 3). The reaction of mesitylcopper(I) with 1 equiv of $Et_3N·3HF$ afforded the intermediate tetrakis(acetonitrile)copper(I) bifluoride (**1**), which is characterized by a broad singlet at 14.1 ppm in the ^1H NMR spectrum in CD_3CN and a broad singlet at 166 ppm in the ^{19}F NMR spectrum in CD_3CN. This solution was then treated with 1 equiv of (*R*)-DTBM-Segphos (**L1**) to obtain the corresponding complex **L1Cu**$^+$ in quantitative yield after thorough drying. This complex is characterized by a broad singlet at 13.77 ppm in the ^1H NMR spectrum in CD_3CN, a broad singlet at 166.8 ppm in the ^{19}F NMR spectrum in CD_3CN, and a broad singlet at 2.8 ppm in the ^{31}P NMR spectrum in CD_3CN. Moreover, the ^{19}F NMR spectrum of this complex in CD_2Cl_2 exhibits two different peaks, one at −140.7 ppm, corresponding to the distal fluorine atom (Cu−F−H−*F*), and one at −191.3 ppm, referring to the proximal fluorine atom (Cu−*F*−H−F). These results are in agreement with those found for other transition-metal bifluorides[13] and bifluoride salts[14] in the literature. The fact that only one signal is visible in the ^{19}F NMR spectrum in CD_3CN while two are visible in CD_2Cl_2 shows that this complex can exist in either a cationic form in coordinating solvents or a neutral form in noncoordinating solvents.

To gain more insight into the nature of the counteranion, thermogravimetric analysis (TGA) was performed on a sample of **L1Cu**$^+$ and showed the loss of one HF molecule. When this sample after TGA was subjected to ^{19}F NMR analysis in CD_2Cl_2, only one broad singlet was visible at −197.9 ppm, corresponding to the proximal fluorine atom.[15] This combination of analyses showed that the counteranion was indeed a bifluoride. To further confirm this result, single crystals were grown in a toluene/hexane mixture, and X-ray analysis confirmed the presence of two fluorines (Figure 1).

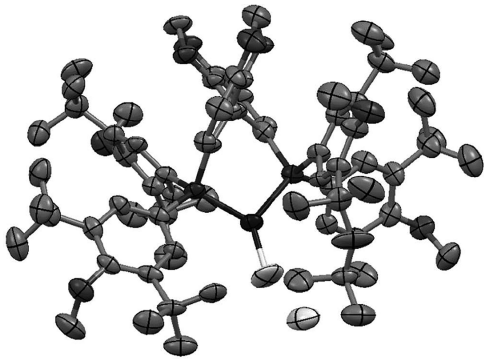


Figure 1. X-ray structure of **L1Cu**$^+$. Selected bond lengths (Å) and angles (deg): Cu−F(1) 1.915, F(1)−F(2) 2.308, F(1)−F(2)−Cu 120.52.

The analysis showed that the Cu−F bond (1.915 Å) is shorter than the one present in the crystal structure of $CuF(PPh_3)_3·2MeOH$ (2.062 Å),[16] which tends to indicate a covalent bond between the copper and the fluoride atom. Moreover the F···F separation (2.308 Å) is slightly bigger than the ones typically found in FHF salts (between 2.24 and 2.28 Å). This information proves that in this crystal structure the copper complex is present in a neutral form with a copper−fluoride covalent bond and an HF molecule in its surroundings. The complex **L1Cu**$^+$ was fully characterized and proved to be highly air-stable in the solid state for up to 3 years.

The next step was to extend this new method to other diphosphines in order to build a library of active copper complexes (Scheme 4). Various diphosphines were used, such as atropoisomeric diphosphines (**L1** to **L6′**) or ligands with a ferrocene core (**L7**, **L8**, and **L10**). The synthesis proved to be highly efficient, as all of the complexes were obtained in quantitative yield with only the copper bound to one ligand visible in the NMR spectra.

Since only copper complexes with one diphosphine ligand were obtained, the synthesis of the corresponding complexes with two ligands was envisioned using 2 equiv of diphosphine. This proved to be impossible using **L1** because of its steric hindrance, and the use of the less bulky (*R*)-Segphos (**L2**) resulted in a mixture of the biscoordinated copper complex **(L2)$_2$Cu**$^+$ with **L2Cu**$^+$ and **L2** in a 9:1:1 ratio. However, the use of smaller ligands gave only the desired complexes (Scheme 5).

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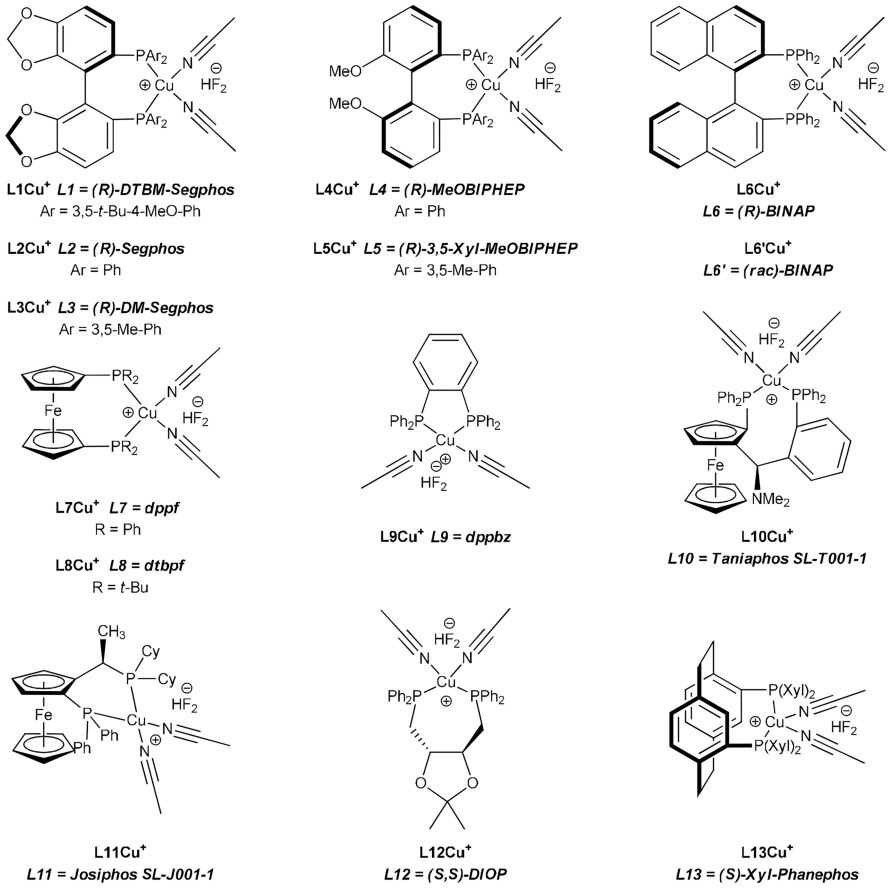
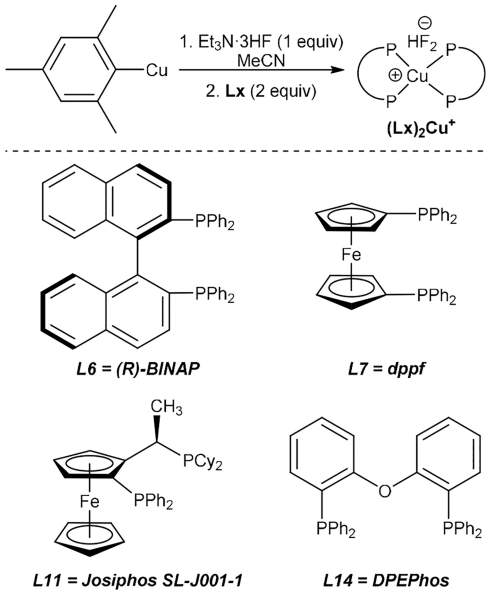
Scheme 4. Exemplification of the Synthesis with Various Diphosphine Ligands



Scheme 5. Formation of Copper Bis(diphosphine) Bifluoride Complexes



With these complexes readily prepared and characterized, it was decided to test their reactivities in catalytic transformations. The first reaction to be investigated was the enantioselective reduction of ketones to the corresponding alcohols. This reaction has notably been studied by Lipshutz and co-workers using various diphosphines, including **L1**.[17]

For this reason, we decided to reduce prochiral ketones using the same reaction conditions but replacing the CuCl/NaO*t*-Bu/**L1** catalytic cocktail by **L1Cu**$^+$ (Scheme 6) To our delight, the reaction occurred spontaneously without the requirement of an added activating agent, proving the preactivated character of the bifluoride complexes. Moreover, the reduction of acetophenone (**2a**) to the corresponding alcohol **3a** gave results comparable to the ones previously described by the team of Lipshutz (75% yield vs 73% and 96% ee in both cases).[17] For the other alcohols no comparison with the literature could be made using **L1**, but all of the aromatic ketones gave great yields with good to excellent enantiomeric excesses. The selectivities and ee can be explained by a previously described model.[18].

After these encouraging results, a more challenging reaction was investigated by performing the enantioselective vinylation of aldehydes described by Shibasaki and co-workers.[8d] To our dismay, applying the same conditions as the ones described, but with the CuF_2/**L1** system replaced by **L1Cu**$^+$, to the vinylation of benzaldehyde (**4a**) gave close to no allylic alcohol **6a** (Table 1, entry 1). Some tweaking of the reaction conditions was performed, and the best yield and enantiomeric excess were obtained using 4 mol % **L1Cu**$^+$ at 60 °C (Table 1, entry 3). Contrary to the results obtained for the reduction of ketones, in this case the yield and ee were lower than the ones previously reported (89% vs 99% yield and 91% ee vs 94% ee). This difference in results can be attributed to the probable presence of phosphine oxides in the original reaction.

Despite this difference in results, a small scope of the reaction was studied with the aforementioned conditions on

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Scheme 6. Enantioselective Hydrosilylation of Ketones Using L1Cu$^+$

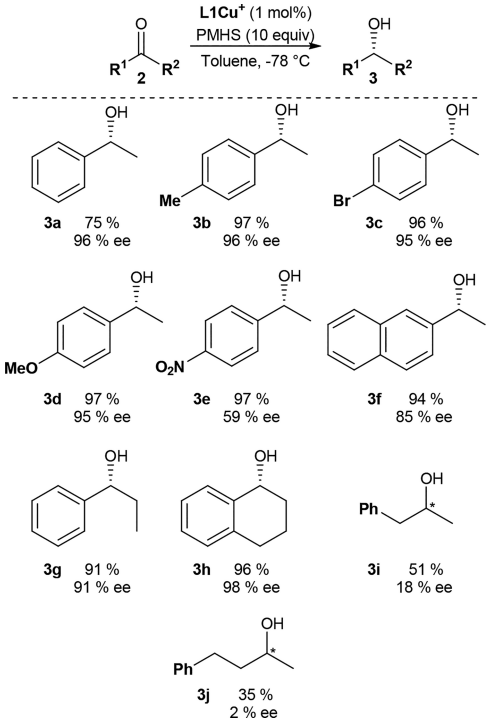
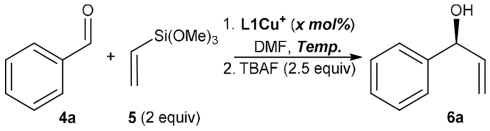


Table 1. Optimization of the Enantioselective Vinylation of 4a



entry	x mol %	temp. (°C)	yield (%)	ee (%)[a]
1	2	40	2	ND
2	2	60	24	92
3	**4**	**60**	**89**	**91**
4	4	50	39	90

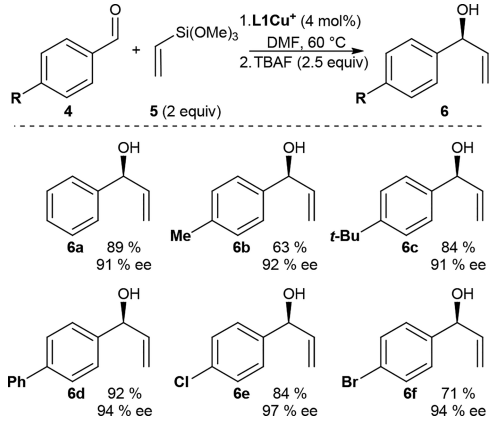
[a]Determined by chiral HPLC.

various aromatic aldehydes, and good to excellent yields and enantiomeric excesses were obtained (Scheme 7). It is to be noted that replacing DMF by THF and lowering the temperature to 50 °C gave **6a** in 91% yield with 95% ee.

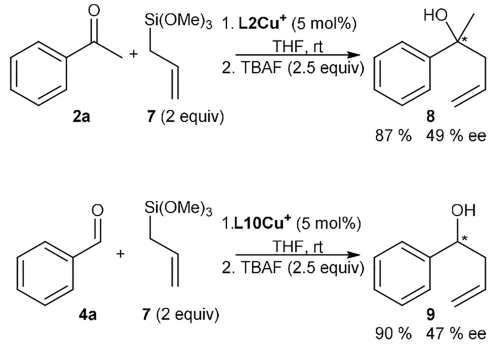
To further explore the various complexes synthesized, **L2Cu**$^+$ and **L10Cu**$^+$ were tested in the enantioselective allylation of **2a** and **4a**, respectively, using allylsilane as the pronucleophile (Scheme 8). Both complexes readily reacted without the use of an activating agent or additive to restore the catalytic cycle, in contrast to the previously reported allylation reaction.[19] However, the transformation afforded the products with only average enantiomeric excess. This could still be improved by a screening of complexes and reaction conditions.

Beside the use of these copper complexes as catalysts, they can also be used to study reaction mechanisms or reaction intermediates because of their well-defined character. **L9Cu**$^+$ was therefore reacted with 2 equiv of a deuterated silane to obtain the corresponding copper deuteride, which was visible in the ^{2}H NMR spectrum at 0.61 ppm (Scheme 9). The same chemical shift was observed when deuterated Stryker's reagent

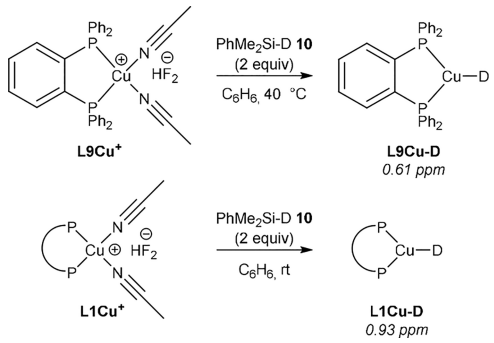
Scheme 7. Scope of the Enantioselective Vinylation Reaction



Scheme 8. Enantioselective Allylation of 2a and 4a



Scheme 9. Identification of Copper Deuterides



was mixed with 1 equiv of dppbz. These results are in accordance with the trimer [**L9CuH**]$_3$ isolated by Norton and co-workers.[20] Moreover, the same reaction was performed with **L1Cu**$^+$ to observe Cu−D with a chemical shift of 0.93 ppm in the ^{2}H NMR spectrum. This result differs substantially from the report of Lipshutz, who observed a shift attributed to **L1CuH** at 2.55 ppm in the ^{1}H NMR spectrum.[21] None of those results can be confirmed using either Stryker's reagent or its deuterated analogue because of the steric hindrance of **L1**, which does not allow its reaction with the hexamer. However, given the well-defined character of **L1Cu**$^+$ compared with the catalytic cocktail used by Lipshutz and given the verified results obtained with **L9Cu**$^+$, we are inclined to think that the result obtained with **L1Cu** $^+$ is correct.

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CONCLUSION

We have developed an efficient synthesis to obtain a wide library of copper(I) diphosphine bifluoride complexes. These complexes were fully characterized, and catalytic tests demonstrated them to be very efficient with no need for an additional activating agent. We also identified two copper deuteride intermediates, highlighting the utility of those complexes to perform mechanistic studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.oprd.9b00443.

NMR and TGA for the determination of bifluoride counteranion; ^{1}H, ^{19}F, and ^{31}P NMR spectra of copper complexes; NMR description of copper complexes **3**, **6**, **7**, and **9**; and GC and HPLC chromatograms for enantioenriched **3**, **6**, **7**, and **9** (PDF)

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Notes

The authors declare no competing financial interest.

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