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Inter- and intramolecular hydroamination of unactivated alkenes catalysed by a combination of copper and silver salts: the unveiling of a Brønsted acid catalysis.

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Abstract : The combined use of a copper halide, a silver salt and a phosphane ligand was applied for the catalysis of inter- and intramolecular hydroamination of alkenes. The reactions of unactivated olefins with nitrogen substrates were investigated. Mechanistic investigations demonstrated that the catalytic system generated a Brønsted acid which appeared to be the prominent catalytic species. **Keywords:** hydroamination; alkenes; copper; silver salts; Brønsted acid.

Introduction

Amines are ubiquitous in natural products, building blocks or targets for fine chemicals, farming related chemicals and biologically active compounds^[1]. The hydroamination of unactivated alkenes is the shortest synthetic way to secondary and tertiary amines. That atom-economic reaction can be performed on unactivated alkenes according three methods: radical transfer^[2], metal-catalysis^[1,3,4] and acid-catalysis^[4,5,6]. That last method can imply a pure Brønsted acid^[5,6] or the combination of a metal and an acid^[3]. For the enantioselective synthesis of optically pure amines, the most studied and privileged hydroamination method is metal-catalysis. Lanthanides and actinides (f-block) were widely screened and significant achievements were reported for intramolecular reactions. By comparison, applications in asymmetric catalysis of transition metals from groups 3-11 (d-block) remain scarce and that's where the hydroamination challenge seems to be. Moreover, the development of recoverable catalysts may favour groups 3-11 metals which may form stable and easy to handle organometallic catalysts.

Recently, group 11 metals have been highlighted by various contributions. The usefulness of gold was pointed out on alkene^[7] and allene^[8] substrates for both intra- and intermolecular hydroamination reactions as well as for diaminations. Silver was recently shown to be active for hydroamination of alkenes^[9]. Copper was successfully used for diamination^[10] and carboamination^[11] reactions, but it was less applied for hydroamination. Hii et al. reported on the use of copper triflates in

intermolecular reactions between vinyl arenes and amines^[12]. Gunnoe et al. applied NHC-Cu-amido complexes to the intermolecular addition of amines to activated olefins^[13]. Recently, Sawamura et al. reported the efficiency of a copper-alkoxyde catalyst in various intramolecular hydroamination reactions^[14].

Following the past interest of some of us on amination reactions^[15], we started studying the use of copper catalysts in hydroamination. Initially, alkene coordination to copper complexes was extensively studied^[16] for various applications like biomimetic models for the ethylene receptor site of plants^[17]. Interestingly, Okamoto et al.^[18] used copper-halide complexes for the catalysed intramolecular hydroamination of allenylamines.

Relying on the Dewar-Chatt-Duncanson model of olefin bonding^[19], the activation of alkenes by metals can be rationalised. We assumed that copper cationic or dicationic species coordinated to π -acceptor ligands would exhibit reduced π -backdonation on the coordinated olefins which would consequently be more reactive. Hence, such cationic copper catalysts would be of interest for hydroamination reactions.

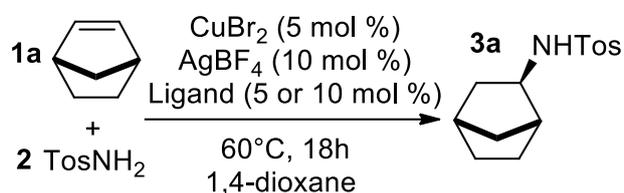
Herein, we would like to report on our investigations of the combined use of phosphanes, copper halides and silver salts applied to the catalysis of inter- and intramolecular hydroamination reactions.

Results and discussion

Reactivity Studies

The reaction of norbornene with tosylamine was used as a model to optimise the experimental conditions, the exo-addition product^[20] **3a** (Table 1) being formed selectively. Regarding the metal source, copper(II) bromide led to higher conversion than copper(II) chloride when AgBF₄ was used. The use of a glovebox for transfers improved drastically the yields, demonstrating the negative impact of water. Then, various phosphane ligands were screened (Table 1). 1,2-bis(diphenylphosphino)ethane, e.g. dppe (entry 4), showed to be the most efficient, even if conversion was higher without the use of any phosphane ligand (entry 7).

Table 1. Phosphane ligand screening.

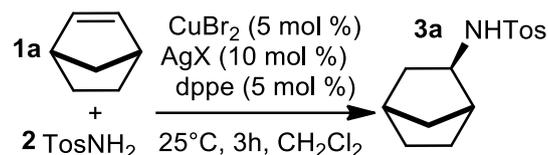


Entry	Ligand	Loading (mol %)	Conversion (%) ^a
1	P(OPh) ₃	10	5
2	P(Ph) ₃	10	30
3	PCy ₃	10	-
4	dppe	5	80
5	dppeO	5	20
6	dppb	5	5
7	-	-	> 95
8	P(C ₆ H ₄ F) ₃	5	18
9	P(C ₆ F ₅) ₃	5	16
10	Xantphos	5	34
11	Davephos	5	0

^a) Conversion determined by GC.

Screening of silver(I) salts confirmed the less coordinating the anion was, the higher the conversions were (Table 2). Activity decreased according the order: SbF₆⁻ > TfO⁻ >> PF₆⁻ > NTf₂⁻ >> ClO₄⁻ > BF₄⁻ >> BARF⁻. Surprisingly, BARF⁻ salts led to poor conversions (entries 9-10). Silver cation confirmed to be the most appropriate as compared to alkaline-earth salts (entries 2, 9). As expected, no conversion was observed using silverbenzoate (entry 7), benzoate anion coordinating most probably to copper^[21].

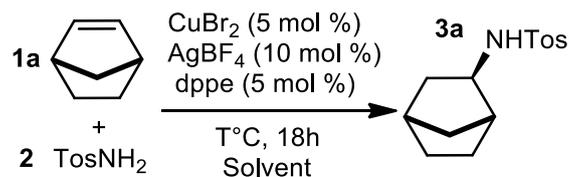
Table 2. Silver- and related salts screening.



Entry	AgX	Conversion ^a (%)
1	AgBF ₄	47
2	NaBF ₄	0
3	AgPF ₆	75
4	AgSbF ₆	> 95
5	AgOTf	95
6	AgClO ₄	45
7	AgPhCO ₂	0
8	AgN(Tf) ₂	68
9	KBARF	9
10	AgBARF	5

^a) Conversion determined by GC. Average of 2 runs.

Table 3. Solvent screening.



Entry	Solvent	T (°C)	Conv. ^a (%)
1	Toluene	60	90
2	"	25	70
3	1,2-dichloroethane	60	95
4	"	25	85
5	1,1',2,2'-tetrachloroethane	25	> 95
6	"	60	> 95
7	Dichloromethane	25	> 95
8	Chloroform	25	25
9	Diethyl ether	25	-
10	THF	60	5
11	DME	60	30
12	CH ₃ CN	60	70
13	1,4-Dioxane	60	80

^a) Conversion determined by GC.

Among the various solvents screened (Table 3), 1, 1', 2, 2'-tetrachloroethane (entries 5, 6) showed to be the most interesting considering its polarity and high boiling point. Other chlorinated solvents were also suitable (entries 3, 4, 7, 8) with the exception of chloroform. Toluene (entries 1, 2) and 1,4-dioxane (entry 13) led to good conversions as well.

Next, various olefins were allowed to react with tosylamine in the presence of either copper(I)- or copper(II)-bromide in combination with AgSbF_6 and dppe (Table 4). As a general trend, copper(II)-bromide proved to be more reactive than copper(I)-bromide as reactions were requiring less time and lower temperatures. This was observed in the case of cyclohexene (entry 3) and norbornene which lead to the exclusive formation of an exo product (entry 1). Otherwise, dihydrofuran showed no reactivity (entry 7). Branched “Markovnikov” products were obtained for vinylcyclohexane (entry 4), and allylbenzene (entry 5). Reaction of *n*-hexene (entry 2) proceeded well with some isomerised product resulting from the addition on position 3^[3h]. With the exception of 2-vinylpyridine leading to linear “anti-Markovnikov” product (entry 6), conjugated olefins (e.g. styrene, 1,3-cyclohexadiene, 4-vinylpyridine) didn’t react (entries 8-10).

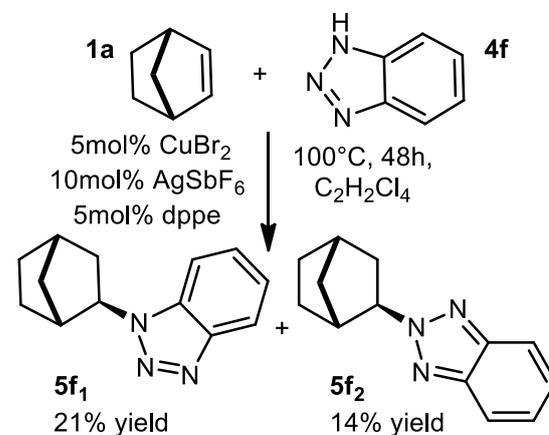
To check the range of applicable nucleophiles, various amine derivatives were allowed to react with norbornene (Table 5). Exo-addition products were exclusively formed as confirmed by NMR^[20]. Benzyl- and methyl-carbamates (entries 3-4), para-nitroaniline (entry 5) and oxazolidone (entry 7) provided the related hydroamination products in good yields. For amides, whereas no reactivity was noticed for acetamide (entry 1) and trifluoroacetamide (entry 8), benzamide (entry 9) gave the hydroamination product in modest yield and an improved conversion was found for chloroacetamide (entry 2). Benzylamine, *N,N*-dimethylurea and succinimide (entries 11, 12 and 13) didn’t react, nor phthalimide and hydrazones. Moreover, stronger nucleophiles like morpholine, di-*n*-propylamine or butylamine didn’t react with any screened olefins. Finally, weak basic amines didn’t react with cyclohexene (see supporting information). Hence, the range of reacting nucleophiles and olefins proved to be quite narrow using such catalyst.

Mechanistic investigations.

We were particularly interested by two other results. First, benzotriazole reacted with norbornene to afford, in moderate yields, two hydroamination products **5f₁** and **5f₂** (Table 5-entry 6 and Scheme 1). Such reaction implying triazole-derivatives is usually performed by an acid-catalysis^[22]. Second, the reaction between aniline and norbornene lead to a mixture of hydroamination and Friedel-Crafts alkylation products, **5j₁** and **5j₂** (Table 5-entry 10 and Scheme 2) without any product resulting from a Hofmann-Martius rearrangement^[6k]. Hydroarylation products like **5j₂** are typical for hydroamination reactions using an acid^[5,6,23e-g] or metal-acid^[3,23a-d,23f-g]

catalyst. At that point, we started suspecting the generation of acid along our hydroamination reactions and performed control experiments.

Scheme 1. Reactivity of benzotriazole with norbornene.



Scheme 2. Reactivity of aniline with norbornene.

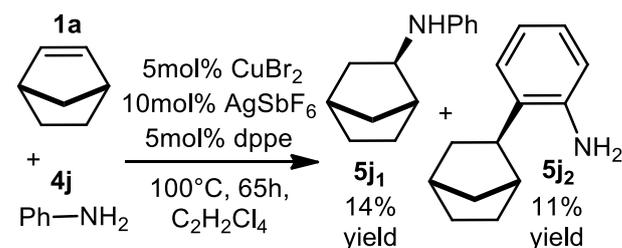
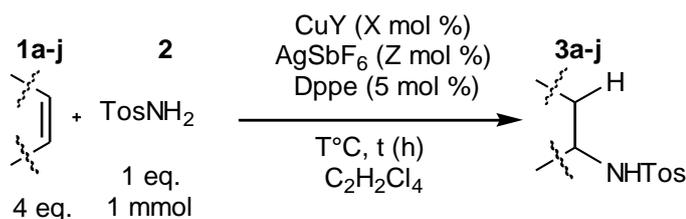


Table 6 shows the effects of additives on the hydroamination reaction of norbornene with tosylamine catalysed by a combination of copper(II)-bromide and AgBF_4 . Reaction could be stopped by the addition of an inorganic base like Cs_2CO_3 (entry 3), an organic base like triethylamine (entry 4) or the non-coordinative base 2,6-di-*tert*-butyl-pyridine (entry 2). The use of a weak Lewis and Brønsted base like phenothiazine decreased the yield to 29% (entry 5). Phenothiazine is also known as a radical polymerization inhibitor^[24a] but such property might not be applicable here. Addition of another proton scavenger like calcium hydride decreased the yield to 10% (entry 6). We should also recall that reaction didn’t proceed well in THF (5% conversion, Table 3-entry 6) which can be considered as a Lewis basic and coordinating solvent.

These results supported that some acid (HBF_4) was formed during the hydroamination reaction. The use of a proton source like hydroquinone (entry 7) which can reduce Cu(II) inhibited the reaction.

Table 4. Olefin reactivities with tosylamine.



Entry	Alkene 1 a-j	Copper salt (mol %)	Silver salt (mol%)	Time (h)	T (°C)	Isolated yield ^a (%) 3 a-j
1	1a	CuBr ₂ (5)	AgSbF ₆ (10)	3	25	95 (exo) ^b
		CuBr (5)	AgSbF ₆ (5)	20	100	95 (exo) ^b
2	1b	CuBr ₂ (5)	AgSbF ₆ (10)	20	100	90 (4/6) ^c
		CuBr (5)	AgSbF ₆ (5)		100	2
					150	< 5
3	1c	CuBr ₂ (5)	AgSbF ₆ (10)	20	100	96
		CuBr (5)	AgSbF ₆ (5)		100	57
					150	82
4	1d	CuBr ₂ (5)	AgSbF ₆ (10)	30	100	50 (branched) ^d
		CuBr (5)	AgSbF ₆ (5)	20	100	14 (branched) ^d
				150	20 (branched) ^d	
5	1e	CuBr ₂ (5)	AgSbF ₆ (10)	48	100	88 (branched) ^d
		CuBr (5)	AgSbF ₆ (5)	20	100	21 (branched) ^d
				150	25 (branched) ^d	
6	1f	CuBr ₂ (5)	AgSbF ₆ (10)	20	100	16 (linear) ^e
		CuBr (5)	AgSbF ₆ (5)		100	10 (linear) ^e
					150	0
7	1g	CuBr ₂ (5)	AgSbF ₆ (10)	24	100	0
		CuBr (5)	AgSbF ₆ (5)		100	0
					150	0
8	1h	CuBr ₂ (5)	AgSbF ₆ (10)	30	100	0
		CuBr (5)	AgSbF ₆ (5)	20	150	0
9	1i	CuBr ₂ (5)	AgSbF ₆ (10)	20	100	0
10	1j	CuBr ₂ (5)	AgSbF ₆ (10)	20	100	0
		CuBr (5)	AgSbF ₆ (5)	20	150	0

^a) Average of 2 runs.

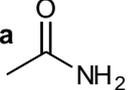
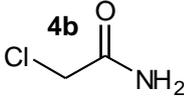
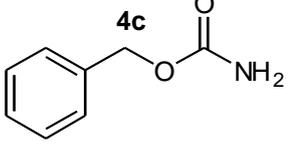
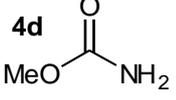
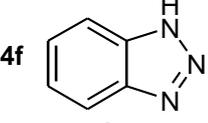
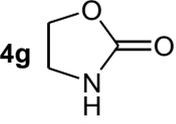
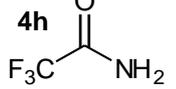
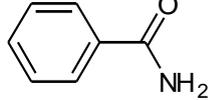
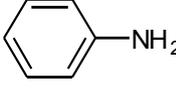
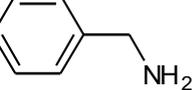
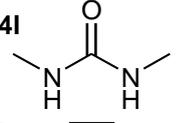
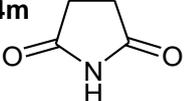
^b) Exo-product as shown by NMR.

^c) Branched/isomerised ratio of 4/6 shown by NMR (isomerization by TosNH₂ addition on position 3 of *n*-hexene).

^d) Branched product from Markovnikov addition.

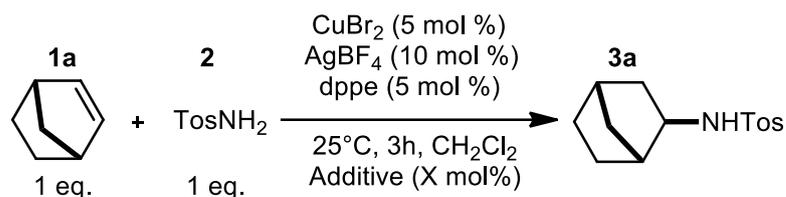
^e) Linear product from anti-Markovnikov addition.

Table 5. Amine substrate reactivities with norbornene.

Entry	Reagent 4a-m	Time (h)	Silver salt	Product 5a-m Yield ^a (%)
1		70	AgSbF ₆	0
2		48	AgSbF ₆	72
3		30	AgBF ₄	80
4		30	AgBF ₄	86
5		20	AgBF ₄	95
6		48	AgSbF ₆	21 ^b :14 ^c
7		20	AgSbF ₆	95
8		20	AgBF ₄	0
9		20 48	AgSbF ₆	27 ^d 35
10		65	AgSbF ₆	14 ^e :11 ^f
11		20	AgBF ₄	0
12		20	AgSbF ₆	0
13		20	AgSbF ₆	0 ^a

^a) Isolated yield, average of 2 runs. ^b) Hydroamination product **5f**. ^c) Rearranged product **5f**.

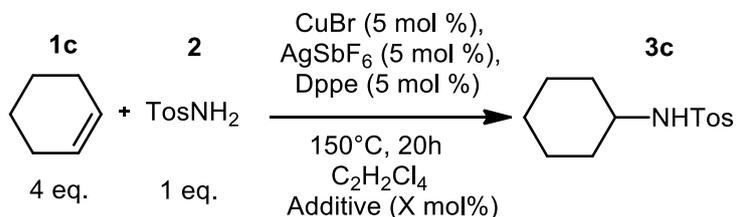
^d) At 150°C. ^e) Hydroamination product **5j**. ^f) Arylation product **5j**.

Table 6. Additive effects on Cu(II) and Silver(I) salts catalysed reaction of norbornene with tosylamine.

Entry	Additive (mol%)	Conversion ^a (%)
1	No additive	47
2	2,6-Bis(<i>t</i> -Butyl)-pyridine (5.5)	0
3	Cs ₂ CO ₃ (5)	0
4	NEt ₃ (5)	0
5	Phenothiazine (25)	29
6	CaH ₂ (10)	10
7	Hydroquinone (5)	15
8	Benzoquinone (5)	2
9	TEMPO (5)	0
10	PhSiMe ₃ (1 eq)	0
11	HBF ₄ .OMe ₂ (5)	92
12	HBF ₄ .OMe ₂ (5) ^b	75 ^b

^a) measured by GC, average of 2 runs.

^b) conversion with 5mol% HBF₄ alone, without use of [CuBr₂+AgBF₄+dppe].

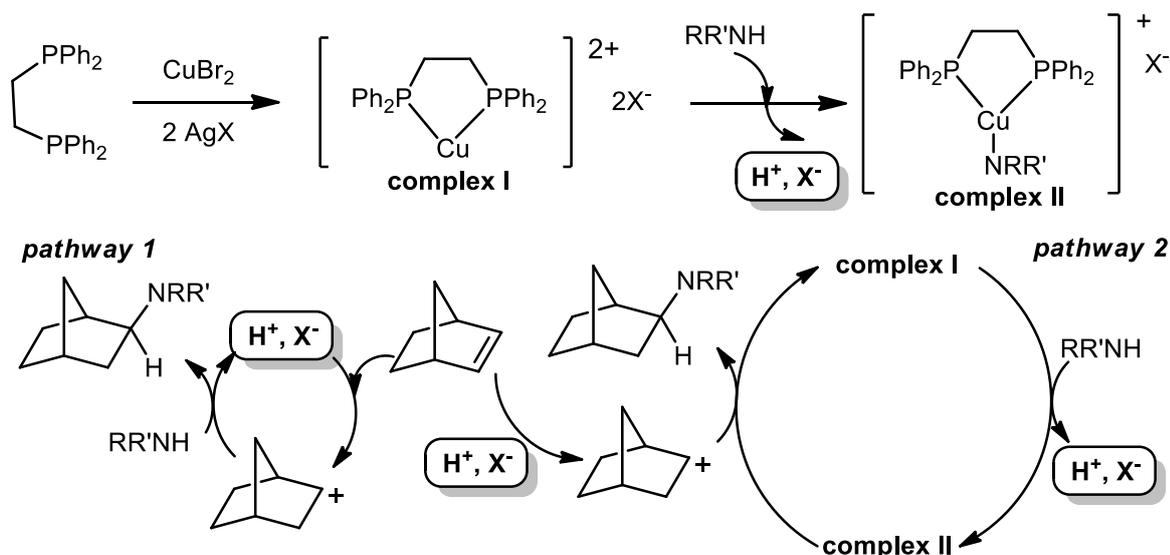
Table 7. Additive effects on Cu(I) and Silver(I) salts catalysed reaction of cyclohexene with tosylamine.

Entry	Additive (loading mol %)	Isolated yield ^a (%)
1	None	82
2	Cs ₂ CO ₃ (5)	0
3	2,6-Bis(<i>t</i> -Butyl)-pyridine (5.5)	0
4	Phenothiazine (25)	0
5	TEMPO (5)	0
6	CaH ₂ (10)	32
8	Hydroquinone (5)	23
10	Benzoquinone (5)	0
11	PhSi(Me) ₃ (1eq.)	0
12	HBF ₄ .OMe ₂ (5)	90
13	HBF ₄ .OMe ₂ (5) ^b	50 ^b

^a) Average of 2 runs.

^b) reaction with 5mol% HBF₄ alone, without use of [CuBr₂+AgBF₄+dppe].

Scheme 3. Proposed reaction pathways for intermolecular hydroamination reactions.



This suggests that the dicationic copper complex may be involved in the reaction process. Unlike benzoquinone (entry 8), triethylamine (entry 4) can be considered as a reducing agent^[24b]; none of these reagents allowed the reaction to occur. Otherwise, a radical scavenger like TEMPO (entry 9) inhibited the reaction. But TEMPO is also known to react irreversibly with acids by disproportionation^[24c]. The addition of a proton trap like PhSi(Me)₃ (entry 11) stopped the reaction and confirmed the presence of free protons in the reaction medium. It's worth to note the reaction proceeded well in the presence of 5 mol% HBF₄·O(Me)₂ with (92% yield, entry 12) or without (75% yield, entry 13) copper-silver salts.

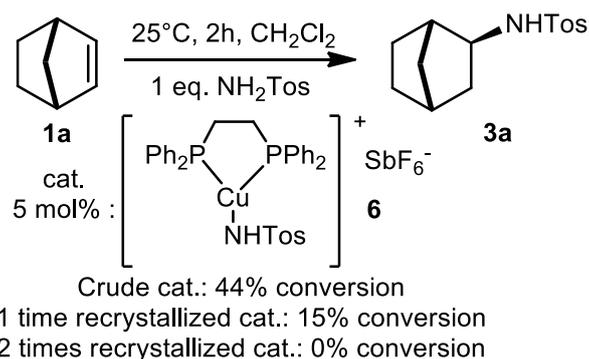
A similar screening was carried out with cyclohexene (Table 7). The hydroamination reaction of cyclohexene with tosylamine catalysed by a combination of copper(I) bromide and AgSbF₆ was also stopped by the addition of an inorganic or organic base (entry 2-4). Addition of calcium hydride (entry 6) scavenged some protons and reduced the reaction yield to 32%. The use of a proton source like hydroquinone (entry 8) decreased the reaction yield to 23%. TEMPO (entry 5), benzoquinone (entry 10) and PhSi(Me)₃ (entry 11) inhibited the reaction. The reaction proceeded well in presence of 5 mol% HBF₄·O(Me)₂ with (90% yield, entry 12) and without copper-silver salts (50% yield, entry 13). Hence, it was very likely some Brønstedt acid was formed during the hydroamination reaction, by coordination of the nitrogen substrate to the cationic copper(II) or copper(I) complex followed by the release of a proton and formation of a metal-

amido complex (Scheme 3). That confirmed a hypothesis which was previously advanced for other hydroamination reactions performed in the presence of a Brønstedt acid source^[3c,3g,6c,6d,12].

For intermolecular hydroamination reactions, two pathways can thus be reasonably considered after the olefin protonation (Scheme 3). Pathway 1 would allow the addition of the free amine to the protonated olefin and release of the acid catalyst, the amido-copper complex being an unactive specie. Pathway 2 would allow the amine from copper complex II to react with the protonated olefin releasing the hydroamination product and the dicationic copper complex I.

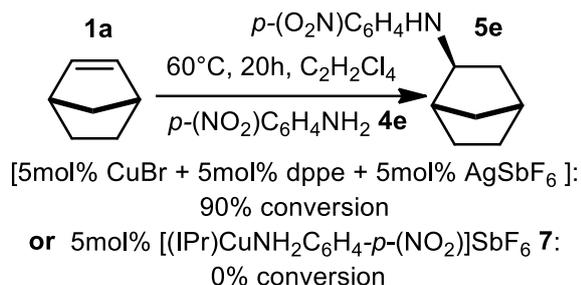
To check such hypotheses, we performed control experiments. By reacting complex I with tosylamine, complex **6** was isolated and used as catalyst for the reaction of norbornene with tosylamine in dichloromethane at room temperature (Scheme 4).

Scheme 4. Influence of acid amount on the reaction of norbornene with tosylamine.



When a crude batch of **6** was used, a 40% conversion was obtained. Repeated recrystallizations of **6** led to complete deactivation of the catalyst without any decomposition. In a second control experiment, norbornene reacted with para-nitroaniline using two types of catalysts (Scheme 5).

Scheme 5. Comparison of catalytic activities of in-situ generated and isolated Cu(I) catalysts.



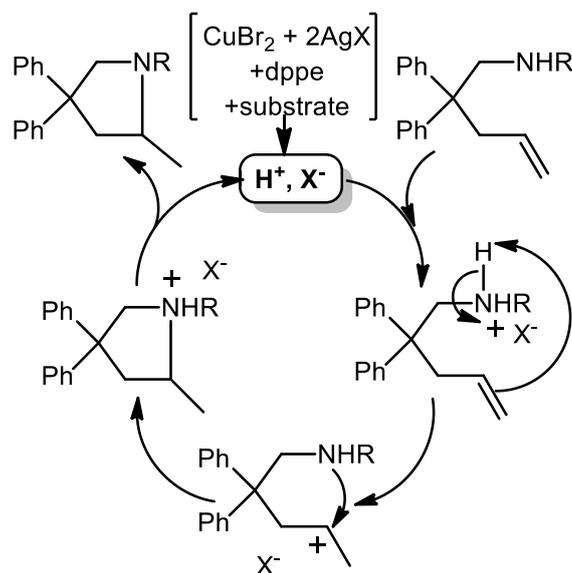
Whereas the hydroamination reaction proceeded well using a one-pot combination of CuBr-AgSbF₆-dppe, the use of isolated NHC-Cu(I) complex **7** was not successful. Hence, the involvement of such amino-^[13a] or amido-^[25] copper complex as a catalyst was unlikely. Moreover, the reaction of norbornene with 4-nitroaniline worked fine when catalysed by a combination of CuBr₂-AgBF₄-dppe or simply by HBF₄. For both catalysts, rates of conversion were quite similar when followed by NMR and GC (see supporting informations). Hence, according to all these observations, these intermolecular hydroamination reactions may proceed following pathway 1 (Scheme 3), Brønstedt acid catalyst being formed when the amine coordinates to the copper cationic complex.

In addition, though the screening of various enantiopure phosphane ligands, no enantioselectivity was obtained for the addition of tosylamine to norbornene (see supporting informations). Obviously, these catalyses were not likely to allow any asymmetric induction as far as they involved the protonation of the olefin before the nucleophile addition of the nitrogen substrate.

For intramolecular hydroamination reactions (Table 8), the catalysis proceeded only for electron rich amine substrates substituted by a benzyl (**8b**, entries 3-4,6), a methyl (**8c**, entries 7-10), an isobutyl (**8d**, entries 11-14) and a methyl-cyclohexane (**8e**, entries 15-16). Reactions required long heating (20-30h) at high temperatures (130-150°C). No reactivity was observed for a primary amine derivative (**8a**, entries 1-2) as well as for amides, e.g. electron-poor substrates like tosyl- (entries 17-18), acetyl- (entries 19-20), benzoyl-

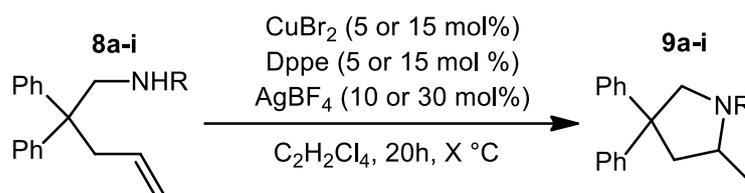
(entries 21-22) and benzylcarbamate derivatives (entries 23-24). Acid catalysis using HBF₄.O(Me)₂ improved conversions with benzyl (**8b**, entry 5) and isobutyl derivatives (**8d**, entry 13). Previously, intramolecular hydroamination reactions were reported to proceed efficiently with Brønstedt acid catalysts for amides^[6g,i,l,o,p] or basic amines^[6c,d], metal catalysts being also effective for various substrates^[1]. In comparison to Ackermann et al. work^[6c,d], our acid-catalysed reactions for compound **8b** (entries 3-6) gave quite similar results at lower catalyst loading (5 against 10-20 mol%) but at higher temperature (150 against 80-130°C). The reactivity of electron-rich substrates confirmed that an acid-catalysed pathway is likely to take place during intramolecular hydroamination reactions (Scheme 6).

Scheme 6. Proposed mechanism for intramolecular hydroamination reactions.



Coordination of the nitrogen substrate to cationic Cu(II) complex would liberate inorganic acid. Amine would be then protonated; and a proton-exchange with the olefin would operate allowing the cyclization to occur and the proton to be released.

Attempts to isolate intermediates were difficult regarding the sensitivity to air and moisture of these Cu complexes. However, diffusion of an equimolar solution of [dppeCu][SbF₆]₂ and norbornene in dichloromethane with pentane afforded highly sensitive colorless single crystals. X-ray diffraction analysis showed that norbornene-dppeCuSbF₆ complex **10**^[26] was formed (Figure 1). To the best of our knowledge, this is the first structure determination of a phosphane-Cu(I)-norbornene complex.

Table 8. Intramolecular reaction screening.

Entry	R, Reagent 8 a-i	Conditions ^a	Temperature (°C)	Conversion (%) ^b [isolated yield %] 9 a-i
1	H, 8a	A	100	0
2	H, 8a	A or B or C	150	0
3	Bn, 8b	A	100	0
4	Bn, 8b	A	150	79
5	Bn, 8b	D	150	91
6	Bn, 8b	A	150	100 ^c [85]
7	Me, 8c	A	100	0
8	Me, 8c	A	130	40
9	Me, 8c	A	150	80
10	Me ^c , 8c	A	150	100 ^c [89]
11	<i>i</i> -Bu, 8d	A	100	10
12	<i>i</i> -Bu, 8d	A	130	62
13	<i>i</i> -Bu, 8d	D	130	82
14	<i>i</i> -Bu, 8d	A	150	100 [93]
15	CH ₂ Cy, 8e	A	130	41
16	CH ₂ Cy, 8e	A	150	100 [94]
17	Ts, 8f	A	100	0
18	Ts, 8f	A	150	0
19	Ac, 8g	A	100	0
20	Ac, 8g	B or C	150	0
21	Bz, 8h	A	100	0
22	Bz, 8h	B	150	0
23	CBz, 8i	A	100	0
24	CBz, 8i	B	150	0

- a) Conditions A: 5 mol% CuBr₂, 5 mol% Dppe, 10 mol% AgBF₄. Conditions B: 15 mol% CuBr₂, 15 mol% Dppe, 30 mol% AgBF₄. Conditions C: 5 mol% CuBr₂, 5 mol% Dppe, 10 mol% AgSbF₆. Conditions D: 5 mol% HBF₄.O(Me)₂
- b) Average of 2 runs. Measured by ¹H NMR with 1,3,5-(MeO)₃C₆H₃ as internal standard.
- c) 30h reaction.

As demonstrated previously by EPR^[24b], the present X-ray diffraction analysis confirmed that norbornene could reduce copper(II) to copper(I), standard reduction potential of (Cu²⁺/Cu⁺) being low ($E^0 = +0.159\text{V}$). The C=C double bond C3-C8 was lengthened [1.375(5) Å] as compared to the free norbornene^[27a] [1.334(1)Å] suggesting π -back donation from the metal to the olefin. Compound **10** showed a weak Cu-olefin interaction as confirmed by the large bond distances Cu-P1 and Cu-P2 [2.2876(8) and 2.2834(8)], as well as by the large bite angle P1-Cu-P2 [90.71(3)°], values of c.a. 78° being usually found for stable copper-olefin complexes with nitrogen ligands^[27b-f]. This may explain the high instability of compound **10** which decomposed

readily during all other isolation and characterization attempts.

Otherwise, the diffusion of an equimolar solution of [dppeCu][SbF₆]₂ and tosylamine in dichloromethane with pentane afforded colorless single crystals. X-ray diffraction analysis showed no amido-copper species but a Cu(dppe)₂SbF₆ complex **11**^[26] (Figure 2). Similar complexes with different anions^[28] were already characterized by X-ray determination and compound **11** exhibited the same structural properties. First, this result confirmed the propensity of copper(II) to be reduced to copper(I) by diphenylphosphinoethane or tosylamine. Second, as previously shown with such phosphane ligands, copper behaves often as a hemilabile metal changing

easily its coordination^[29] unless bonded to strong σ -donor ligands^[25]. Hence, several copper organometallics may be formed and stay in equilibrium leading to potent catalytic species.

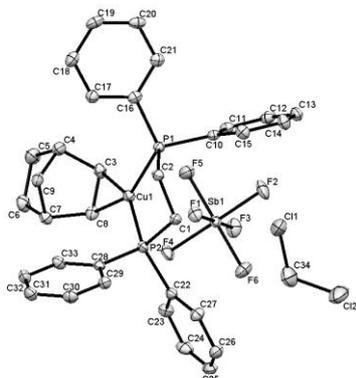


Figure 1. Compound **10** [dpeCuNorbornene]SbF₆·CH₂Cl₂. Thermal ellipsoids are shown at 50% level and hydrogen atoms are omitted for clarity²⁷. Selected bond length (Å) and angles (°): Cu-C3 2.097(3), Cu-C8 2.108(3), Cu-P1 2.2876(8), Cu-P2 2.2834(8), C3-C8 1.375(5), P1-Cu-P2 90.71(3), C3-Cu-C8 38.18(13), P1-P2-C3-C8 0.63(5), P1-C2-C1-P2 60.2(2).

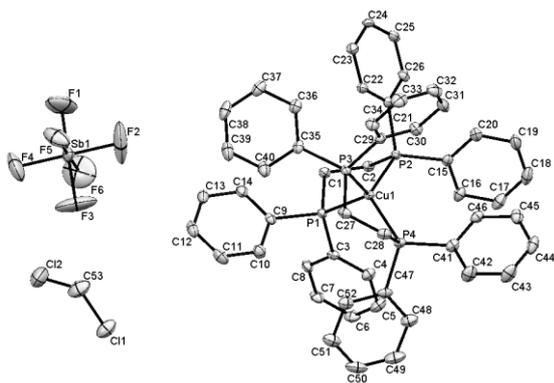


Figure 2. Compound **11** [(dpe)₂Cu]SbF₆·CH₂Cl₂. Thermal ellipsoids are shown at 50% level and hydrogen atoms are omitted for clarity²⁷. Selected bond length (Å) and angles (°): Cu-P1 2.2906(8), Cu-P2 2.2902(8), Cu-P3 2.2863(8), Cu-P4 2.2940(8), P1-Cu-P2 89.22(3), P1-Cu-P3 115.83(3), P2-Cu-P3 120.65(3), P3-Cu-P4 88.63(3), Cu-P1-C1-C2 49.06(19), P1-C1-C2-P2 59.0(2), C1-C2-P2-Cu 39.0(2), Cu-P3-C27-C28 48.6(2), P3-C27-C28-P4 49.6(3), C27-C28-P4-Cu 25.7(2).

Conclusion

The combined use of copper halides, phosphine ligands and silver salts was applied in the hydroamination of alkenes. Intermolecular reactions of unactivated olefins and nitrogen compounds of moderate nucleophilicity were carried out successfully. Mechanistic investigations demonstrated that the coordination of the amine to the copper cationic complex was generating a Brønsted acid which was the prominent catalytic

species. Intramolecular reactions of electron-rich amine derivatives were most likely following an acid-catalysed pathway too. Hence, when a copper halide in combination with a silver salt and a phosphane ligand catalyse the additions of weakly basic amine substrates to olefins, it may be asked whether a true metal-catalysed process is involved or if the metal simply generates a Brønsted acid.

Experimental Section

General remarks.

All solvents were dried using standard methods. Alkenes were distilled under vacuum over CaH₂ and stored over molecular sieves (4 Å). Norbornene was sublimated under vacuum and stored in a glovebox. Amine substrates were placed under vacuum during one hour before use, or distilled over CaH₂ if they were liquid. All silver salts, copper salts and ligands were weighted in a glovebox. All reactions were carried out under a dry nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV₂₅₄ plates. Flash chromatography was carried out with Macherey silica gel 60 M. ¹H (300MHz), ¹³C (75MHz) and ³¹P (121MHz) NMR spectra were acquired on a Bruker Avance spectrometer. Chemical shifts are reported downfield of Me₄Si and coupling constants are expressed in Hz. 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed. Gas chromatography analyses were done on GC Varian 3900 and 430 using Alltech EconoCap EC-5™ 30m column with program (5°C/min, 100-230°C, 36min.) and with tetradecane as internal standard. Infrared spectra were recorded on a ThermoScientific-Nicolet 6700 spectrometer; the samples being prepared with KBr powder. HPLC analysis was performed on a Thermo-Finnigan 1000 apparatus with a diode array detector. HRMS analyses were performed at CUMA-Pharm. Dept.-University Lille Nord de-France. Elemental analyses on sensitive samples were performed at London Metropolitan University, UK. Elemental analyses on other samples were performed at UCCS, University Lille Nord de France, France. See supporting information for other details.

General procedure (olefin reactivities)

To a Schlenk flask was added 1 mmol of toluenesulfonamide, 0.05 mmol of CuBr₂ (or CuBr), 0.1 mmol of AgSbF₆ in case of CuBr₂ (or 0.05 mmol of AgSbF₆ in case of CuBr), and 0.05 mmol of 1,2-bis(diphenylphosphino)ethane in a glovebox. Then 1.5 mL of 1,1',2,2'-tetrachloroethane and 4 mmol of the corresponding alkene were added under nitrogen atmosphere. After stirring at 100 or 150°C, the mixture was filtered over Celite™, and the corresponding product was isolated by flash chromatography.

General procedure (amine reactivities)

In a Schlenk flask, 1 mmol of the corresponding amine was dried one hour under vacuum (except aniline which was added at the end of the procedure). Then, 1 mmol of

norbornene, 0.05 mmol of CuBr₂, 0.1 mmol of AgSbF₆, and 0.05 mmol of 1,2-bis(diphenylphosphino)ethane were added in a glovebox. 1.5 mL of 1,1',2,2'-tetrachloroethane was added under nitrogen atmosphere. After stirring at 100°C, the mixture was filtered over Celite™, and the corresponding product was isolated by flash chromatography.

***N*-1-phenylpropan-2-yl-*p*-toluenesulfonamide 3e.**

Isolated after flash chromatography (petroleum ether:ethylacetate 8:2, Rf = 0.1) as a colourless oil (from 1 mmol, 0.87 mmol-252 mg, 88 % yield). ¹H NMR (CDCl₃) δ 1.10 (*d*, *J* = 6.5, 3H), 2.43 (*s*, 3H), 2.69 (*dd*, *J* = 4.5, 2H), 3.53 (*sep*, *J* = 6.5, 1H), 4.58 (*d*, *J* = 6.5, 1H), 7.04 (*d*, *J* = 8.0, 2H), 7.24 (*m*, 5H), 7.64 (*d*, *J* = 8.0, 2H); ¹³C NMR (CDCl₃) δ 21.3 (CH₃), 21.5 (CH₃), 43.4 (CH₂), 50.9 (CH), 126.6 (CH), 127.0 (2CH), 128.5 (2CH), 129.4 (2CH), 129.6 (2CH), 137.1 (C), 137.6 (C), 143.1 (C); IR ν (KBr, cm⁻¹) 3323, 2965, 2927, 1313, 1157; HMRS (ESI) *m/z* calcd for C₁₆H₂₀O₂NS, 290.12093 (MH⁺), found 290.12080.

***N*-(2-(pyridin-2-yl)ethyl)-*p*-toluenesulfonamide 3f.**

Isolated after flash chromatography (petroleum ether:ethylacetate 1:1, Rf = 0.1) as a white solid (from 1 mmol, 0.16 mmol-44 mg, 16 % yield). M.p. 120-122°C; ¹H NMR (CDCl₃) δ: 2.41 (*s*, 3H), 2.93 (*t*, *J* = 6.3, 2H), 3.35 (*q*, *J* = 6.3, 2H), 6.23 (*t*, *J* = 5.7, 1H), 7.07 (*dd*, *J* = 7.5, *J* = 4.8, 1H), 7.14 (*t*, *J* = 8.3, 1H), 7.26 (*d*, *J* = 8.2, 2H), 7.58 (*td*, *J* = 7.8, *J* = 1.8, 1H), 7.72 (*d*, *J* = 8.2, 2H), 8.46 (*d*, *J* = 4.5, 1H); ¹³C NMR (CDCl₃) δ 21.3 (CH₃), 36.3 (CH₂), 42.3 (CH₂), 121.8 (CH), 123.5 (CH), 127.0 (2CH), 129.7 (2CH), 136.8 (CH), 137.1 (C), 143.2 (C), 149.1 (CH), 158.9 (C); IR ν (KBr, cm⁻¹): 3063, 2956, 2864, 1324, 1155; HMRS (ESI) *m/z* calcd for C₁₄H₁₇O₂N₂S, 277.1005 (MH⁺), found 277.1003; Anal. calcd (%) for C₁₄H₁₆O₂N₂S: C, 60.85; H, 5.84; N, 10.14; S, 11.60; found: C, 60.90; H, 5.81; N, 10.78; S, 11.13.

***N*-Bicyclo[2.2.1]hept-2-yl-2-chloroacetamide 5b.**

Isolated after flash chromatography (petroleum ether:ethylacetate 8:2) as a white solid (from 1 mmol, 0.72 mmol-135 mg, 72 % yield). M.p. 123-125°C; ¹H NMR (CDCl₃) δ 1.00-1.30 (*m*, 5H), 1.35-1.55 (*m*, 2H), 1.85 (*m*, 1H), 2.17 (*m*, 1H), 2.25 (*m*, 1H), 3.66 (*td*, *J* = 3.5, *J* = 7.8, 1H), 3.95 (*s*, 2H), 6.34 (*s*, 1H, NH); ¹³C NMR (CDCl₃) δ 26.4 (CH₂), 28.1 (CH₂), 35.6 (CH₂), 35.7 (CH), 40.2 (CH₂, C), 42.2 (CH), 42.6 (CH₂), 53.1 (CH), 164.9 (CO); IR ν (KBr, cm⁻¹) 3291, 2870, 1655, 1549; Anal. calcd (%) for C₉H₁₄ClNO: C, 57.60; H, 7.52; N, 7.46; found: C, 57.15; H, 7.21; N, 7.10.

***N*-Bicyclo[2.2.1]hept-2-yl-carbamic acid benzyl ester 5c.**

Isolated after flash chromatography (petroleum ether:ethylacetate 8:2, Rf = 0.6) as a white solid (from 1 mmol, 0.80 mmol-195 mg, 80 % yield). M.p.: 148-150°C; ¹H NMR (CDCl₃) δ 1.05-1.40 (*m*, 5H), 1.50 (*m*, 2H), 1.70-1.85 (*m*, 1H), 2.20-2.35 (*m*, 2H), 3.50-3.60 (*m*, 1H), 4.70 (*s*, 1H, NH), 5.1 (*s*, 2H, CH₂), 7.30-7.45 (*m*, 5H); ¹³C NMR (CDCl₃) δ 26.3 (CH₂), 28.1 (CH₂), 35.3 (CH₂), 35.6 (CH), 40.4 (CH₂), 42.5 (CH), 54.3 (CH), 66.5 (CH₂), 128.1 (2 CH), 128.2 (CH), 128.5 (2 CH), 136.6 (C), 155.6 (C); IR ν (KBr, cm⁻¹) 3299, 2956, 2870, 1682, 1545, 1256; HMRS

(ESI) *m/z* calcd for C₁₅H₂₀O₂N, 246.1489 (MH⁺), found 246.1487; Anal. calcd (%) for C₁₅H₁₉O₂N: C, 73.44; H, 7.81; N, 5.71; found: C, 72.91; H, 7.89; N, 5.47.

***N*-Bicyclo[2.2.1]hept-2-yl-2*H*-benzo[d][1,2,3]triazole 5f₁**

Isolated by flash chromatography (petroleum ether:ethyl acetate 80:20, Rf = 0.7) as a white solid (from 1 mmol, 0.14 mmol (30 mg), 14 % yield). Melting point: 45-47°C. ¹H NMR (300 MHz, CDCl₃) δ: 1.20-1.80 (*m*, 7H), 2.50-2.85 (*m*, 3H), 4.88 (*dd*, *J* = 4.2 Hz, *J* = 8.5 Hz, 1H), 7.39 (*m*, 2H), 7.89 (*m*, 2H); ¹³C NMR (75 MHz, CDCl₃) δ: 27.1 (CH₂), 28.5 (CH₂), 35.8 (CH₂), 36.1 (CH), 38.2 (CH₂), 44.1 (CH), 69.4 (CH), 118.0 (2 CH), 126.0 (2 CH), 143.9 (2C). IR ν: 2955, 2870, 1277 cm⁻¹. HMRS (ESI) calcd for C₁₃H₁₆N₃, 214.13387 (MH⁺), found 214.13374; Anal. calcd (%) for C₁₃H₁₅N₃: C, 73.21; H, 7.09; N, 19.70; found: C, 72.69; H, 7.09; N, 20.34.

***N*-Bicyclo[2.2.1]hept-2-yl-1*H*-benzo[d][1,2,3]triazole 5f₂**

Isolated by flash chromatography (petroleum ether:ethyl acetate 80:20, Rf = 0.3) as a white solid (from 1 mmol, 0.21 mmol (46 mg), 21 % yield). Melting point: 75-77°C. ¹H NMR (300 MHz, CDCl₃) δ: 1.30-2.10 (*m*, 7H), 2.50-2.80 (*m*, 3H), 4.60 (*dd*, *J* = 3.8 Hz, *J* = 8.4 Hz, 1H), 7.36 (*m*, H), 7.47 (*t*, H), 7.56 (*d*, *J* = 8.3 Hz, H), 8.07 (*d*, *J* = 8.3 Hz, H); ¹³C NMR (75 MHz, CDCl₃) δ: 27.1 (CH₂), 28.7 (CH₂), 35.9 (CH₂), 36.0 (CH), 37.3 (CH₂), 42.9 (CH), 61.9 (CH), 109.7 (CH), 119.9 (CH), 123.8 (CH), 126.8 (CH), 133.0 (C), 146.3 (C). IR ν: 2963, 2868, 1454 cm⁻¹; HMRS (ESI) calcd for C₁₃H₁₆N₃, 214.13387 (MH⁺), found 214.1338; Anal. calcd (%) for C₁₃H₁₅N₃: C, 73.21; H, 7.09; N, 19.70; found: C, 73.64; H, 7.47; N, 20.14.

***N*-Bicyclo[2.2.1]hept-2-yl-oxazolidin-2-one 5g.**

Isolated after flash chromatography (petroleum ether:acetone 7:3, Rf = 0.6) as colourless oil (from 1 mmol, 0.95 mmol-173 mg, 95 % yield). ¹H NMR (CDCl₃) δ 1.30 (*m*, 4H), 1.50 (*m*, 3H), 1.78 (*m*, 1H), 2.25 (*s*, 1H), 2.31 (*s*, 1H), 3.55 (*m*, 2H), 3.78 (*dd*, *J* = 8, *J* = 5, 1H), 4.20-4.35 (*m*, 2H); ¹³C NMR (CDCl₃) δ 27.7 (CH₂), 28.0 (CH₂), 36.0 (CH), 36.6 (CH₂), 36.7 (CH₂), 40.5 (CH), 42.1 (CH₂), 56.4 (CH), 61.8 (CH₂), 158.2 (CO); IR ν (KBr, cm⁻¹) 2870, 1743, 1263; HMRS (ESI) *m/z* calcd for C₁₀H₁₆O₂N, 182.1176 (MH⁺), found 182.1177.

[Diphenylphosphinoethano][4-methyl-benzene-sulfonamidato-κ-*N*]-copper(I) hexafluoroantimonate: [dppeCuNHTos][SbF₆] 6.

CuBr₂ (0.052 g, 0.23 mmol), 1,2-bis(diphenylphosphino)ethane (0.093 g, 0.23 mmol) and AgSbF₆ (0.16 mg, 0.46 mmol) were dissolved in 5 mL dichloromethane. After stirring for 3 hours under nitrogen at room temperature, AgCl was removed by filtration through Celite™ under nitrogen and the filtrate was allowed to react 20 minutes (10 min. ultrasonic bath+10 min. stirring at R.T.) with tosylamine (0.04 g, 0.23 mmol). Evaporation to dryness afforded a grey solid which was recrystallised two times using CH₂Cl₂ and pentane then dried affording a white solid (0.08 g, 40 % yield). ¹H NMR (CD₂Cl₂) δ: 2.16 (*s*, 2H, CH₂), 2.47 (*s*, 3H, Me), 4.87 (*s* broad, 1H, NH), 7.22 (*m*, 2H), 7.36 (*d*, 2H, ³*J* = 8.1, H_{Tos}), 7.48 (*m*, 4H), 7.69 (*m*, 4H), 7.81 (*d*, 2H, ³*J* = 8.1, H_{Tos}); ³¹P

NMR (CD₂Cl₂) δ : 50.04; ¹³C NMR (CD₂Cl₂) δ : 21.2, 29.7, 126.3, 129.1, 129.6, 129.7, 130.4, 131.0, 131.6, 132.1(2C), 132.7, 138.9, 143.9; IR ν (cm⁻¹) (KBr, inert cell) 3360 (s), 3260 (s), 1304 (vs), 1160 (s); Anal. calcd (%) for C₃₃H₃₂F₆O₂P₂NSCuSb: C, 45.67; H, 3.72; N, 1.61; found: C, 45.44; H, 3.61; N, 1.75.

[1,3-bis(2,6-di-*i*-propyl-phenyl)imidazol-2-ylidene][4-nitroaniline- κ -N-]copper(I) hexafluoroantimonate: [(IPr)Cu(NH₂C₆H₄NO₂)] [SbF₆] 7.

(IPr)CuCl (0.05 g, 0.1 mmol) was combined with AgSbF₆ (0.036 g, 0.1 mmol) in 4 ml THF. After stirring for 1 hour, AgCl was removed by filtration through dry Celite™, and the filtrate was concentrated in vacuo to approximately 2 mL and transferred to a 4 mL THF solution of 4-nitroaniline (0.014 g, 0.1 mmol). The resulting solution was heated to 60°C under nitrogen for one hour. Evaporation to dryness afforded a yellow solid (0.074 g, 90% yield). ¹H NMR (CD₂Cl₂) δ : 1.17 (*d*, ³*J* = 7.0, 12H, CH(CH₃)₂), 1.24 (*d*, ³*J* = 7.0, 12H, CH(CH₃)₂), 2.47 (*sept*, ³*J* = 7.9, 4H, CH(CH₃)₂), 5.08 (*s*, 2H, NH₂), 6.70 (*d*, ³*J* = 9.2, 2H, CH 4-nitroaniline); 7.32 (*m*, 6H, NCH + CH IPr *p*-phenyl); 7.57 (*t*, ³*J* = 7.7, 2H), 7.99 (*d*, ³*J* = 9.2, 2H, CH 4-nitroaniline); ¹³C NMR (CD₂Cl₂) δ : 176.5 (NCN), 145.5, 144.3, 133.9, 130.9, 125.7, 124.4(2C), 124.2, 120.1, 29.7 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 23.6 (CH(CH₃)₂); Anal. calcd (%) for C₃₃H₄₃F₆N₄O₂CuSb: C, 47.93; H, 5.24; N, 6.77; found: C, 47.81; H, 5.11; N, 6.65.

Bis[bis(diphenylphosphino)ethano]copper(I) hexafluoroantimonate: [(dppe)₂Cu] [SbF₆] 11.

CuBr (0.067 g, 0.47 mmol), diphenylphosphinoethane (0.37 g, 0.94 mmol) and AgSbF₆ (161 mg, 0.47 mmol) were dissolved in 5 mL dichloromethane. After stirring for 3 hours under nitrogen at room temperature, AgCl was removed by filtration through dry Celite™ under nitrogen and the filtrate was evaporated to dryness to afford a white solid (0.486 g, 95 % yield). ¹H NMR (CD₂Cl₂) δ : 2.48 (*m*, 8H, CH₂), 7.25 (*m*, 29H, H_{Ar}), 7.41 (*m*, 10H, H_{Ar}); ³¹P NMR (CD₂Cl₂) δ : 7.24 (very broad singlet), 4.17 (*d*, *J* = 17.8), 2.11 (*d*, *J* = 17.7); Anal. calcd (%) for C₅₂H₄₈F₆P₄CuSb: C, 56.98; H, 4.41; found: C, 56.90; H, 4.30.

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