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Inter- and Intramolecular Hydroamination of Unactivated Alkenes Catalysed by a Combination of Copper and Silver Salts: The Unveiling of a Brønstedt 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: alkenes; Brønsted acid; copper; hydroamination; silver salts

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 route to secondary and tertiary amines. This atom-economic reaction can be performed on unactivated alkenes according to three methods: radical transfer,[2], metal catalysis[1,3,4] and acid catalysis.[4,5,6] The last-mentioned method can imply a pure Brønstedt 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 is where the hydroamination challenge seems to be. Moreover, the development of recoverable catalysts may favour group 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 the 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 vinylarenes 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 alkoxide 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-back-donation 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

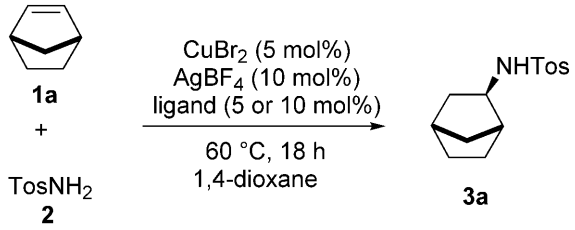
Reactivity Studies

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 $AgBF_4$ 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).

Screening of silver(I) salts confirmed that the less coordinating the anion was, the higher were the conversions (Table 2). Activity decreased according to the order: $SbF_6^- > TfO^- \gg PF_6^- > NTf_2^- \gg ClO_4^- > BF_4^- \gg BARF^-$. Surprisingly, $BARF^-$ salts led to poor conversions (entries 9 and 10). The silver cation confirmed to be the most appropriate as compared to alkaline-earth salts (entries 2 and 9). As expected, no conversion was observed using silver benzoate (entry 7), the benzoate anion coordinating most probably to copper.[21]

Among the various solvents screened (Table 3), 1,1′,2,2′-tetrachloroethane (entries 5 and 6) showed to

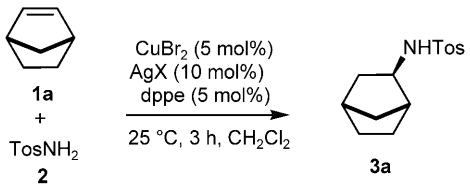
Table 1. Phosphane ligand screening.



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	$P(C_6H_4F)_3$	10	18
9	$P(C_6F_5)_3$	10	16
10	Xantphos	5	34
11	Davephos	5	0

[a] Conversion determined by GC.

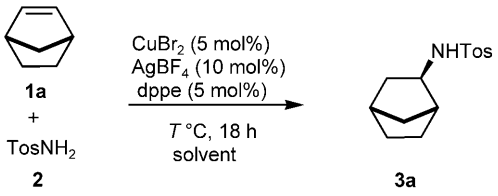
Table 2. Silver and related salts screening.



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.

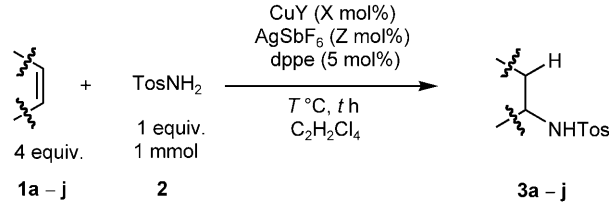
Table 3. Solvent screening.

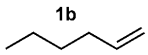
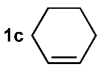
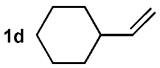
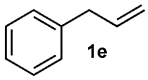
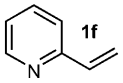
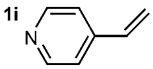
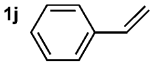


Entry	Solvent	T [°C]	Conversion[a] [%]
1	toluene	60	90
2	toluene	25	70
3	1,2-dichloroethane	60	95
4	1,2-dichloroethane	25	85
5	1,1′,2,2′-tetrachloroethane	25	>95
6	1,1′,2,2′-tetrachloroethane	60	>95
7	dichloromethane	25	>95
8	chloroform	25	25
9	diethyl ether	25	–
10	THF	60	5
11	DME	60	30
12	CH_3CN	60	70
13	1,4-dioxane	60	80

[a] Conversion determined by GC.

Table 4. Olefin reactivities with tosylamine.



Entry	Alkene (**1a–j**)	Copper salt (mol%)	Silver salt (mol%)	Time [h]	Temperature [°C]	Isolated yield[a] [%] of **3a–j**
1		$CuBr_2$ (5)	$AgSbF_6$ (10)	3	25	95 (*exo*)[b]
		CuBr (5)	$AgSbF_6$ (5)	20	100	95 (*exo*)[b]
2		$CuBr_2$ (5)	$AgSbF_6$ (10)	20	100	90 (4/6)[c]
		CuBr (5)	$AgSbF_6$ (5)		100	2
					150	< 5
3		$CuBr_2$ (5)	$AgSbF_6$ (10)	20	100	96
		CuBr (5)	$AgSbF_6$ (5)		100	57
					150	82
4		$CuBr_2$ (5)	$AgSbF_6$ (10)	30	100	50 (branched)[d]
		CuBr (5)	$AgSbF_6$ (5)	20	100	14 (branched)[d]
					150	20 (branched)[d]
5		$CuBr_2$ (5)	$AgSbF_6$ (10)	48	100	88 (branched)[d]
		CuBr (5)	$AgSbF_6$ (5)	20	100	21 (branched)[d]
					150	25 (branched)[d]
6		$CuBr_2$ (5)	$AgSbF_6$ (10)	20	100	16 (linear)[e]
		CuBr (5)	$AgSbF_6$ (5)		100	10 (linear)[e]
					150	0
7		$CuBr_2$ (5)	$AgSbF_6$ (10)	24	100	0
		CuBr (5)	$AgSbF_6$ (5)		100	0
					150	0
8		$CuBr_2$ (5)	$AgSbF_6$ (10)	30	100	0
		CuBr (5)	$AgSbF_6$ (5)	20	150	0
9		$CuBr_2$ (5)	$AgSbF_6$ (10)	20	100	0
10		$CuBr_2$ (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 $TosNH_2$ addition on position 3 of *n*-hexene).
[d] Branched product from Markovnikov addition.
[e] Linear product from anti-Markovnikov addition.

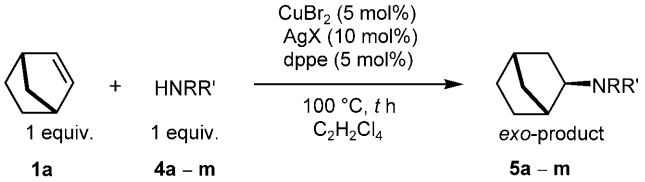
be the most interesting considering its polarity and high boiling point. Other chlorinated solvents were also suitable (entries 3, 4, 7, 8) with the exception of chloroform. Toluene (entries 1 and 2) and 1,4-dioxane (entry 13) led to good conversions as well.

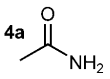
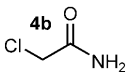
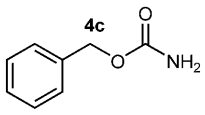
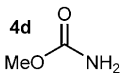
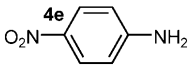
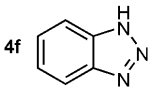
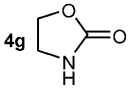
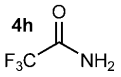
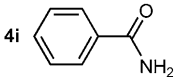
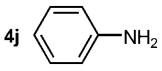
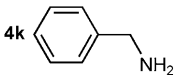
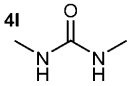
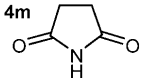
Next, various olefins were allowed to react with tosylamine in the presence of either copper(I) or copper(II) bromide in combination with $AgSbF_6$ and dppe (Table 4). As a general trend, copper(II) bromide proved to be more reactive than copper(I) bro-

mide 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 the linear "anti-Markovnikov" product (entry 6), conjugated olefins (e.g., styrene, 1,3-cyclohexadiene, 4-vinylpyridine) did not 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 and 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) did not react, nor did phthalimide and hydrazones. Moreover, stronger nucleophiles like morpholine, di-*n*-propylamine or butylamine did not react with any screened olefins. Finally, weak basic amines did not react with cyclohexene (see the Supporting Information). Hence, the range of reacting nucleophiles and olefins proved to be quite narrow using such catalysts.

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[d]

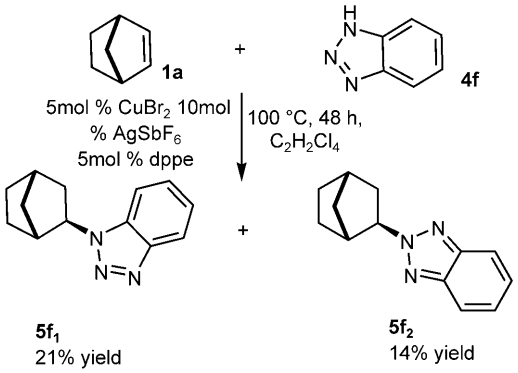
[a] Isolated yield, average of 2 runs.
[b] Hydroamination product **5f₁**.
[c] Rearranged product **5f₂**.
[d] At 150 °C.
[e] Hydroamination product **5j₁**.
[f] Arylation product **5j₂**.

Mechanistic Investigations

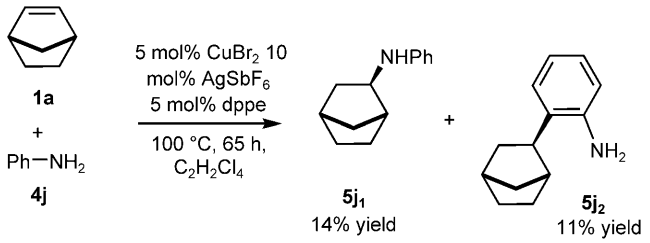
We were particularly interested by two other results. First, benzotriazole reacted with norbornene to afford, in moderate yields, two hydroamination products **5f₁** and **5f₂** (Table 5-entry 6 and Scheme 1). Such a reaction implying triazole derivatives is usually performed by an acid catalysis.[22]

Second, the reaction between aniline and norbornene led 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,f–g] catalyst. At that point, we started suspecting the generation of an acid along our hydroamination reactions and performed control experiments.

Table 6 shows the effects of additives on the hydroamination reaction of norbornene with tosylamine catalysed by a combination of copper(II) bromide and $AgBF_4$. The 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-bis(*tert*-butyl)pyridine (entry 2).



Scheme 1. Reactivity of benzotriazole with norbornene.



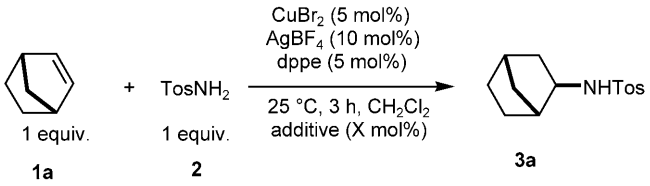
Scheme 2. Reactivity of aniline with norbornene.

The use of a weak Lewis and Brønstedt base like phenothiazine decreased the yield to 29% (entry 5). Phenothiazine is also known as a radical polymerisation inhibitor[24a] but such a 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 did not proceed well in THF (5% conversion, Table 3-, entry 10) 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. 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 10) stopped the reaction and confirmed the presence of free protons in the reaction medium. It is worthy of note that the reaction proceeded well in the presence of 5 mol% $HBF_4{\cdot}O(Me)_2$ with (92% yield, entry 11) or without (75% yield, entry 12) 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 $AgSbF_6$ was also stopped by the addition of an inorganic or organic base (entries 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%.

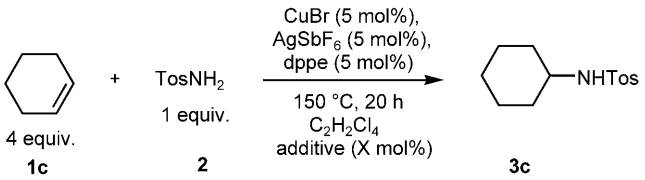
Table 6. Additive effects on copper(II) and silver(I) salts-catalysed reaction of norbornene with tosylamine.



Entry	Additive (mol%)	Conversion[a] [%]
1	no additive	47
2	2,6-bis(*tert*-butyl)pyridine (5.5)	0
3	Cs_2CO_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 equiv.)	0
11	$HBF_4{\cdot}OMe_2$ (5)	92
12	$HBF_4{\cdot}OMe_2$ (5)[b]	75[b]

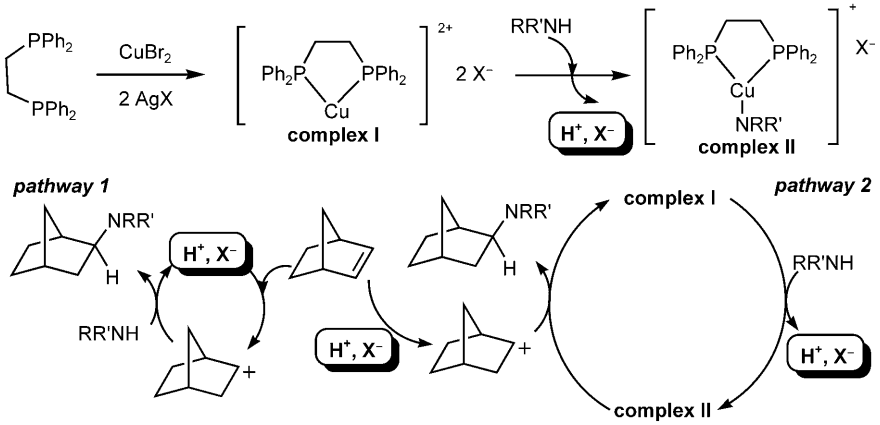
[a] Measured by GC, average of 2 runs.
[b] Conversion with 5 mol% HBF_4 alone, without use of [$CuBr_2$ + $AgBF_4$ + dppe].

Table 7. Additive effects on copper(I) and silver(I) salts-catalysed reaction of cyclohexene with tosylamine.



Entry	Additive (loading mol%)	Isolated yield[a] [%]
1	none	82
2	Cs_2CO_3 (5)	0
3	2,6-bis(*tert*-butyl)pyridine (5.5)	0
4	phenothiazine (25)	0
5	TEMPO (5)	0
6	CaH_2 (10)	32
8	hydroquinone (5)	23
9	benzoquinone (5)	0
10	$PhSi(Me)_3$ (1 equiv.)	0
11	$HBF_4{\cdot}OMe_2$ (5)	90
12	$HBF_4{\cdot}OMe_2$ (5)[b]	50[b]

[a] Average of 2 runs.
[b] Reaction with 5 mol% HBF_4 alone, without use of [$CuBr_2$ + $AgBF_4$ + dppe].



Scheme 3. Proposed reaction pathways for intermolecular hydroamination reactions.

TEMPO (entry 5), benzoquinone (entry 9) and $PhSi(Me)_3$ (entry 10) inhibited the reaction. The reaction proceeded well in presence of 5 mol% $HBF_4{\cdot}O(Me)_2$ with (90% yield, entry 11) and without copper-silver salts (50% yield, entry 12). 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,g,6c,d,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 species.

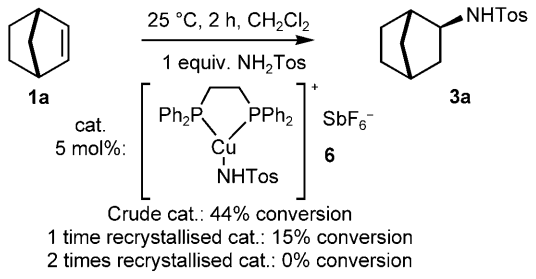
Pathway 2 would allow the amine from copper complex **II** to react with the protonated olefin releasing the hydroamination product and the dicationic copper complex **I**.

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).

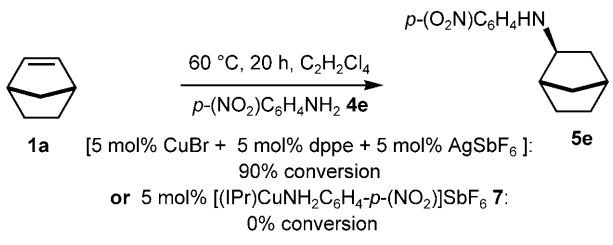
When a crude batch of **6** was used, a 40% conversion was obtained. Repeated recrystallisations of **6** led to complete deactivation of the catalyst without any decomposition.

In a second control experiment, norbornene reacted with *para*-nitroaniline using two types of catalysts (Scheme 5). Whereas the hydroamination reaction proceeded well using a one-pot combination of $CuBr$-$AgSbF_6$-dppe, the use of isolated NHC-Cu(I) complex **7** was not successful. Hence, the involvement of such an 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 $CuBr_2$-$AgBF_4$-dppe or simply by HBF_4. For both catalysts, rates of conversion were quite similar when followed by NMR and GC (see the Supporting Information). Hence, according to all these observations, these intermolecular hydroamination reactions may proceed by following ***pathway 1*** (Scheme 3), a 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



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

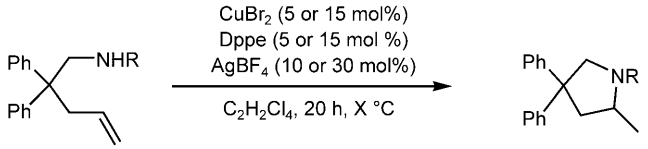


Scheme 5. Comparison of catalytic activities of *in-situ* generated and isolated Cu(I) catalysts.

(see the Supporting Information). Obviously, these catalyses were not likely to allow any asymmetric induction as far as they involve 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, 12 and 14) and a methylcyclohexane moiety (**8e**, entries 15 and 16). These reactions required long heating (20–30 h) at high temperatures (130–150 °C). No reactivity was observed for a primary amine derivative (**8a**, entries 1 and 2) as well as for amides, for example, electron-poor substrates like tosyl (entries 17 and 18), acetyl (entries 19 and 20), benzoyl (entries 21 and 22) and benzyl carbamate derivatives (entries 23 and 24). Acid catalysis using $HBF_4{\cdot}O(Me)_2$ 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 the work of Ackermann et al.,[6c,d] our acid-catalysed reactions for compound **8b** (entries 3–6) gave quite similar results at a 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).

Table 8. Intramolecular reaction screening.



8a – i **9a – i**

Entry	R, Reagent **8a–i**	Conditions[a]	Temp. [°C]	Conversion [%][b] [isolated yield (%)] **9a–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*-Bu, **8d**	A	100	10
12	*i*-Bu, **8d**	A	130	62
13	*i*-Bu, **8d**	D	130	82
14	*i*-Bu, **8d**	A	150	100 [93]
15	CH_2Cy, **8e**	A	130	41
16	CH_2Cy, **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% $CuBr_2$, 5 mol% dppe, 10 mol% $AgBF_4$. *Conditions B:* 15 mol% $CuBr_2$, 15 mol% dppe, 30 mol% $AgBF_4$. *Conditions C:* 5 mol% $CuBr_2$, 5 mol% dppe, 10 mol% $AgSbF_6$. *Conditions D:* 5 mol% $HBF_4{\cdot}O(Me)_2$

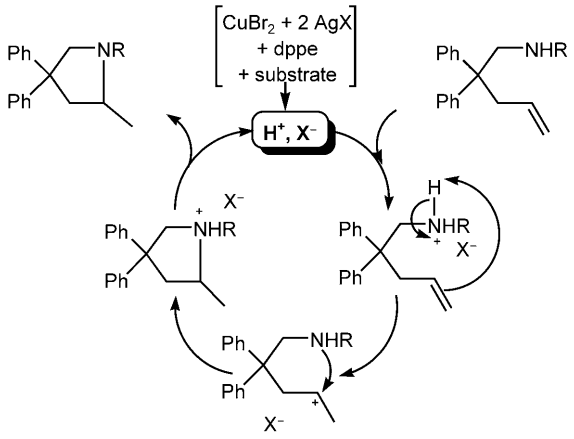
[b] Average of 2 runs. Measured by ^1H NMR with 1,3,5-$(MeO)_3C_6H_3$ as internal standard.

[c] 30 h reaction time.

Coordination of the nitrogen substrate to a cationic Cu(II) complex would liberate an inorganic acid. Amine would then be protonated; and a proton-exchange with the olefin would operate allowing the cyclisation 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 $[dppeCu][SbF_6]_2$ and norbornene in dichloromethane with pentane afforded highly sensitive colourless single crystals. X-ray diffraction analysis showed that the norbornene-dppeCuSbF$_6$ 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.

As demonstrated previously by EPR,[24b] the present X-ray diffraction analysis confirmed that norbornene could reduce copper(II) to copper(I), the standard reduction potential of (Cu^{2+}/Cu^{+}) being low ($E^0 = +0.159$ V). The C=C double bond C3/C8 was lengthened [1.375(5) Å] as compared to the free nor-



Scheme 6. Proposed mechanism for intramolecular hydroamination reactions.

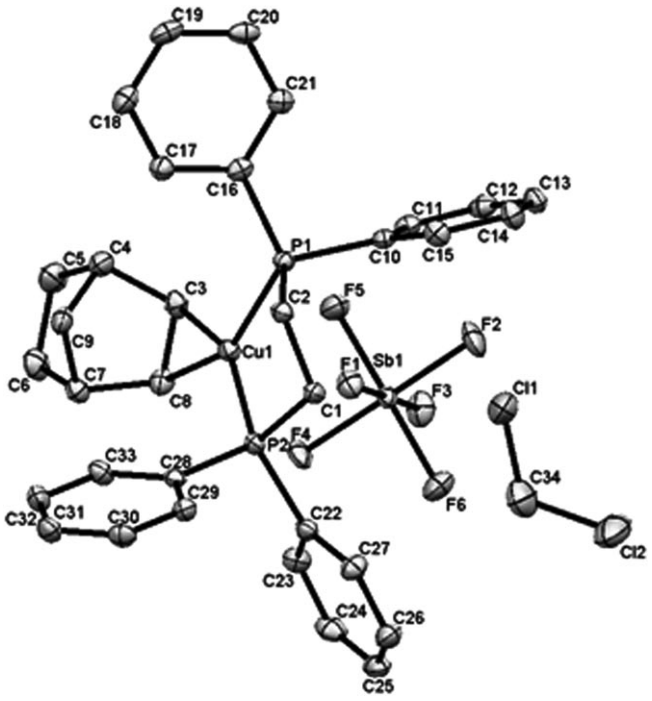


Figure 1. Compound **10** [(dppe)Cu(norbornene)]SbF_6 CH_2Cl_2. Thermal ellipsoids are shown at 50% level and hydrogen atoms are omitted for clarity.[26] Selected bond lengths (Å) and angles (°): Cu–C3 2.097(3), Cu–C8 2.108(3), Cu–P1 2.2876(8), Cu–P2 2.2834(8), C3–C8 1.375(5), P1–Cu–P2 90.71(3), C3–Cu–C8 38.18(13), P1–P2–C3–C8 0.63(5), P1–C2–C1–P2 60.2(2).

bornene[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 *ca.* 78° usually being 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 characterisation attempts.

Otherwise, the diffusion of an equimolar solution of $[dppeCu][SbF_6]_2$ and tosylamine in dichloromethane with pentane afforded colourless single crystals. X-ray diffraction analysis showed no amido-copper species but rather a $Cu(dppe)_2SbF_6$ complex **11**[26] (Figure 2). Similar complexes with different anions[28] were already characterised 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.

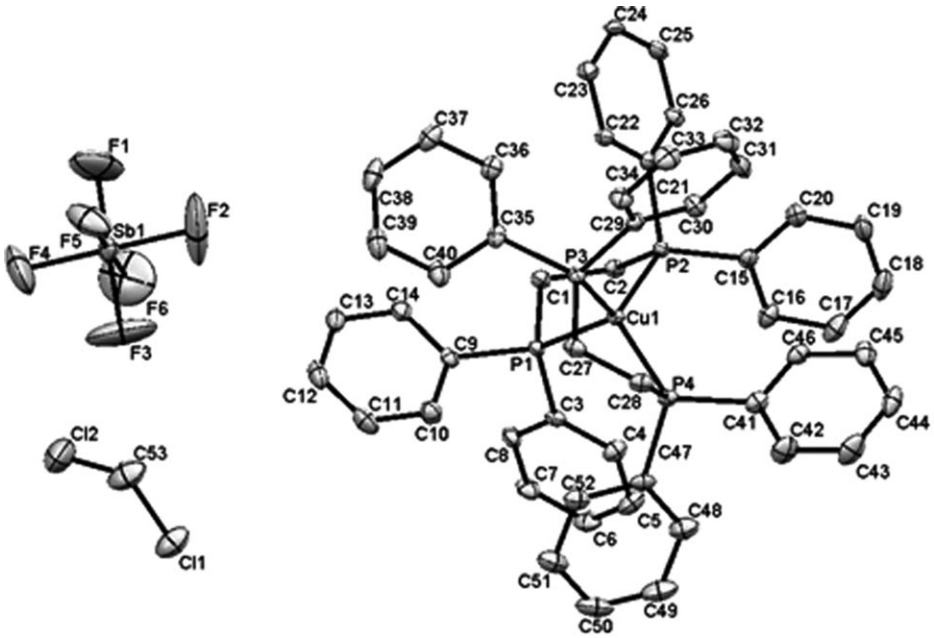


Figure 2. Compound **11** $[(dppe)_2Cu]SbF_6$ CH_2Cl_2. Thermal ellipsoids are shown at 50% level and hydrogen atoms are omitted for clarity.[26] Selected bond lengths (Å) and angles (°): Cu–P1 2.2906(8), Cu–P2 2.2902(8), Cu–P3 2.2863(8), Cu–P4 2.2940(8), P1–Cu–P2 89.22(3), P1–Cu–P3 115.83(3), P2–Cu–P3 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).

Conclusions

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 CaH_2 and stored over molecular sieves (4 Å). Norbornene was sublimed under vacuum and stored in a glove-box. Amine substrates were placed under vacuum during one hour before use, or distilled over CaH_2 if they were liquid. All silver salts, copper salts and ligands were weighed in a glove-box. 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/UV_{254} plates. Flash chromatography was carried out with Macherey silica gel 60 M. ^{1}H (300 MHz), ^{13}C (75 MHz) and ^{31}P (121 MHz) NMR spectra were acquired on a Bruker Avance spectrometer. Chemical shifts are reported downfield of Me_4Si 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 an Alltech EconoCap EC-5™ 30 m column with program (5 °C min^{-1}, 100–230 °C, 36 min) 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. HR-MS 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 the Supporting Information for other details.

General Procedure (Olefin Reactivities)

To a Schlenk flask were added 1 mmol of toluenesulfonamide, 0.05 mmol of $CuBr_2$ (or CuBr), 0.1 mmol of $AgSbF_6$ in case of $CuBr_2$ (or 0.05 mmol of $AgSbF_6$ in case of CuBr), and 0.05 mmol of 1,2-bis(diphenylphosphino)ethane in a glove-box. Then 1.5 mL of 1,1′,2,2′-tetrachloroethane and 4 mmol of the corresponding alkene were added under a 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 for one hour under vacuum (except for aniline which was added at the end of the procedure). Then, 1 mmol of norbornene, 0.05 mmol of $CuBr_2$, 0.1 mmol of $AgSbF_6$, and 0.05 mmol of 1,2-bis(diphenylphosphino)ethane were added in a glove-box. 1.5 mL of 1,1′,2,2′-tetrachloroethane were added under a 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:ethyl acetate 8:2, $R_f = 0.1$) as a colourless oil (from 1 mmol); yield: 252 mg (0.87 mmol, 88%). ^{1}H NMR ($CDCl_3$): $\delta = 1.10$ (d, $J = 6.5$ Hz, 3H), 2.43 (s, 3H), 2.69 (dd, $J = 4.5$ Hz, 2H), 3.53 (sep, $J = 6.5$ Hz, 1H), 4.58 (d, $J = 6.5$ Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 2H), 7.24 (m, 5H), 7.64 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 21.3$ (CH_3), 21.5 (CH_3), 43.4 (CH_2), 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 (KBr): $\nu = 3323$, 2965, 2927, 1313, 1157 cm^{-1}; HR-MS (ESI): $m/z = 290.12080$, calcd. for $C_{16}H_{20}O_2NS$ (MH^+): 290.12093.

***N*-2-(Pyridin-2-yl)ethyl-*p*-toluenesulfonamide (3f):** Isolated after flash chromatography (petroleum ether:ethyl acetate 1:1, $R_f = 0.1$) as a white solid (from 1 mmol); yield: 44 mg (0.16 mmol, 16%); mp 120–122 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.41$ (s, 3H), 2.93 (t, $J = 6.3$ Hz, 2H), 3.35 (q, $J = 6.3$ Hz, 2H), 6.23 (t, $J = 5.7$ Hz, 1H), 7.07 (dd, $J = 7.5$, $J = 4.8$ Hz, 1H), 7.14 (t, $J = 8.3$ Hz, 1H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.58 (td, $J = 7.8$, $J = 1.8$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 2H), 8.46 (d, $J = 4.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 21.3$ (CH_3), 36.3 (CH_2), 42.3 (CH_2), 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 (KBr): $\nu = 3063$, 2956, 2864, 1324, 1155 cm^{-1}; HR-MS (ESI): $m/z = 277.1003$, calcd. for $C_{14}H_{17}O_2N_2S$ (MH^+): 277.1005; anal. calcd. (%) for $C_{14}H_{16}O_2N_2S$: 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:ethyl acetate 8:2) as a white solid (from 1 mmol); yield: 135 mg (0.72 mmol, 72%); mp 123–125 °C; ^{1}H NMR ($CDCl_3$): $\delta =$ 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, $J = 3.5$, $J = 7.8$ Hz, 1H), 3.95 (s, 2H), 6.34 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): $\delta = 26.4$ (CH_2), 28.1 (CH_2), 35.6 (CH_2), 35.7 (CH), 40.2 (CH_2, C), 42.2 (CH), 42.6 (CH_2), 53.1 (CH), 164.9 (CO); IR (KBr): $\nu = 3291$, 2870, 1655, 1549 cm^{-1}; anal. calcd. (%) for $C_9H_{14}ClNO$: 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:ethyl acetate 8:2, $R_f = 0.6$) as a white solid (from 1 mmol); yield: 195 mg (0.80 mmol, 80%; mp 148–150 °C; ^{1}H NMR ($CDCl_3$):

$\delta = 1.05–1.40$ (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, CH_2), 7.30–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$): $\delta = 26.3$ (CH_2), 28.1 (CH_2), 35.3 (CH_2), 35.6 (CH), 40.4 (CH_2), 42.5 (CH), 54.3 (CH), 66.5 (CH_2), 128.1 (2CH), 128.2 (CH), 128.5 (2CH), 136.6 (C), 155.6 (C); IR (KBr): $\nu = 3299$, 2956, 2870, 1682, 1545, 1256 cm^{-1}; HR-MS (ESI): $m/z = 246.1487$, calcd. for $C_{15}H_{20}O_2N$ (MH^+): 246.1489; anal. calcd. (%) for $C_{15}H_{19}O_2N$: 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 ($5f_1$):** Isolated by flash chromatography (petroleum ether:ethyl acetate 80:20, $R_f = 0.7$) as a white solid (from 1 mmol); yield: 30 mg (0.14 mmol, 14%); mp 45–47 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.20–1.80$ (m, 7H), 2.50–2.85 (m, 3H), 4.88 (dd, $J = 4.2$ Hz, $J = 8.5$, 1H), 7.39 (m, 2H), 7.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.1$ (CH_2), 28.5 (CH_2), 35.8 (CH_2), 36.1 (CH), 38.2 (CH_2), 44.1 (CH), 69.4 (CH), 118.0 (2CH), 126.0 (2CH), 143.9 (2C); IR: $\nu = 2955$, 2870, 1277 cm^{-1}; HR-MS (ESI): $m/z = 214.13374$, calcd. for $C_{13}H_{16}N_3$ (MH^+): 214.13387; anal. calcd. (%) for $C_{13}H_{15}N_3$: 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 ($5f_2$):** Isolated by flash chromatography (petroleum ether:ethyl acetate 80:20, $R_f = 0.3$) as a white solid (from 1 mmol); yield:, 46 mg (0.21 mmol, 21%); mp 75–77 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.30–2.10$ (m, 7H), 2.50–2.80 (m, 3H), 4.60 (dd, $J = 3.8$, $J = 8.4$ 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); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.1$ (CH_2), 28.7 (CH_2), 35.9 (CH_2), 36.0 (CH), 37.3 (CH_2), 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: $\nu = 2963$, 2868, 1454 cm^{-1}; HR-MS (ESI): $m/z = 214.1338$, calcd. for $C_{13}H_{16}N_3$ (MH^+): 214.13387; anal. calcd. (%) for $C_{13}H_{15}N_3$: 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, $R_f = 0.6$) as colourless oil (from 1 mmol); yield:173 mg (0.95 mmol, 95%); ^1H NMR ($CDCl_3$): $\delta = 1.30$ (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, $J = 8$, $J = 5$ Hz, 1H), 4.20–4.35 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 27.7$ (CH_2), 28.0 (CH_2), 36.0 (CH), 36.6 (CH_2), 36.7 (CH_2), 40.5 (CH), 42.1 (CH_2), 56.4 (CH), 61.8 (CH_2), 158.2 (CO); IR (KBr): $\nu = 2870$, 1743, 1263 cm^{-1}; HR-MS (ESI): $m/z = 182.1177$, calcd. for $C_{10}H_{16}O_2N$ (MH^+): 182.1176.

[Diphenylphosphinoethano][4-methylbenzenesulfonamidato-κ-*N*-]copper(I) Hexafluoroantimonate [dppeCuNHTos][SbF_6] (6)

$CuBr_2$ (0.052 g, 0.23 mmol), 1,2-bis(diphenylphosphino)-ethane (0.093 g, 0.23 mmol) and $AgSbF_6$ (0.16 mg, 0.46 mmol) were dissolved in 5 mL dichloromethane. After stirring for 3 h under nitrogen at room temperature, AgCl was removed by filtration through Celite™ under nitrogen and the filtrate was allowed to react for 20 min (10 min ultrasonic bath + 10 min stirring at room temperature) with tosylamine (0.04 g, 0.23 mmol). Evaporation to dryness afforded a grey solid which was recrystallised two times using CH_2Cl_2 and pentane then dried affording a white solid; yield: 0.08 g (40%); ^1H NMR (CD_2Cl_2): $\delta = 2.16$ (s, 2H, CH_2), 2.47 (s, 3H, Me), 4.87 (s broad, 1H, NH), 7.22 (m, 2H), 7.36 (d, 2H, $^3J = 8.1$ Hz, H_{Tos}), 7.48 (m, 4H), 7.69 (m, 4H), 7.81 (d, 2H, $^3J = 8.1$ Hz, H_{Tos}); ^{31}P NMR (CD_2Cl_2): $\delta = 50.04$; ^{13}C NMR (CD_2Cl_2): $\delta = 21.2$, 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 (KBr, inert cell): $\nu = 3360$ (s), 3260 (s), 1304 (vs), 1160 cm^{-1} (s); anal. calcd. (%) for $C_{33}H_{32}F_6O_2P_2NSCuSb$: 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-isopropylphenyl)imidazol-2-ylidene][4-nitroaniline-κ-*N*-]copper(I) Hexafluoroantimonate [(IPr)Cu($NH_2C_6H_4NO_2$)][SbF_6] (7)

(IPr)CuCl (0.05 g, 0.1 mmol) was combined with $AgSbF_6$ (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 under vacuum 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; yield: 0.074 g (90%); ^1H NMR (CD_2Cl_2): $\delta = 1.17$ [d, $^3J = 7.0$ Hz, 12H, $CH(CH_3)_2$], 1.24 [d, $^3J = 7.0$ Hz, 12H, $CH(CH_3)_2$], 2.47 (sept, $^3J = 7.9$ Hz, 4H, $CH(CH_3)_2$], 5.08 (s, 2H, NH_2), 6.70 (d, $^3J = 9.2$ Hz, 2H, CH 4-nitroaniline), 7.32 (m, 6H, NCH + CH IPr *p*-phenyl), 7.57 (t, $^3J = 7.7$ Hz, 2H), 7.99 (d, $^3J = 9.2$ Hz, 2H, CH 4-nitroaniline); ^{13}C NMR (CD_2Cl_2): $\delta = 176.5$ (N*C*N), 145.5, 144.3, 133.9, 130.9, 125.7, 124.4(2C), 124.2, 120.1, 29.7 [$CH(CH_3)_2$], 24.6 [$CH(CH_3)_2$], 23.6 [$CH(CH_3)_2$]; anal. calcd. (%) for $C_{33}H_{43}F_6N_4O_2CuSb$: 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 [$(dppe)_2Cu$][SbF_6] (11)

CuBr (0.067 g, 0.47 mmol), diphenylphosphinoethane (0.37 g, 0.94 mmol) and $AgSbF_6$ (161 mg, 0.47 mmol) were dissolved in 5 mL dichloromethane. After stirring for 3 h 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; yield: 0.486 g (95%); ^1H NMR (CD_2Cl_2): $\delta = 2.48$ (m, 8H, CH_2), 7.25 (m, 29H, H_{Ar}), 7.41 (m, 10H, H_{Ar}); ^{31}P NMR (CD_2Cl_2): $\delta = 7.24$ (very broad singlet), 4.17 (d, $J = 17.8$ Hz), 2.11 (d, $J = 17.7$ Hz); anal. calcd. (%) for $C_{52}H_{48}F_6P_4CuSb$: C 56.98, H 4.41; found: C 56.90, H 4.30.

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