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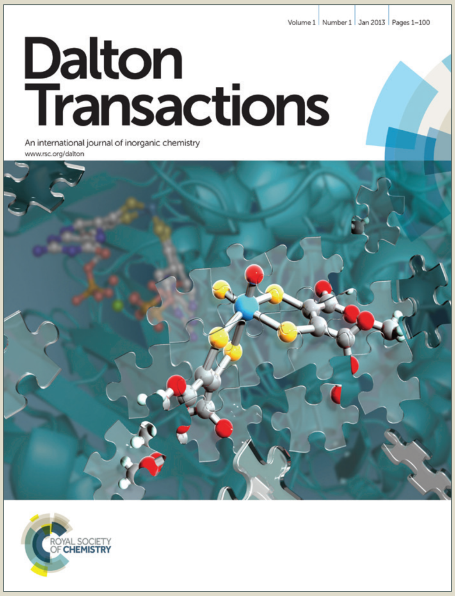

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Alkylfluorenyl substituted *N*-Heterocyclic Carbenes in Copper(I) catalysed Hydrosilylation of Aldehydes and Ketones †

Matthieu Teci,[a] Nicolas Lentz,[a] Eric Brenner,*[a] Dominique Matt,*[a] and Loïc Toupet[b]

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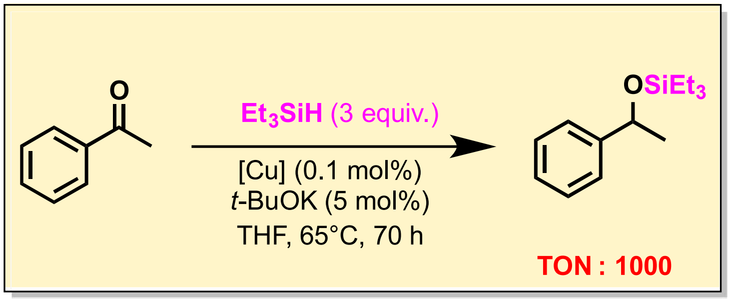
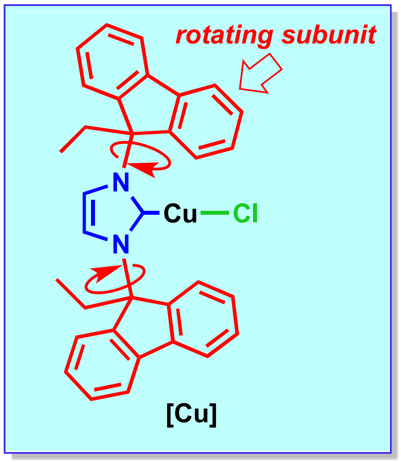
An alkylfluorenyl-substituted imidazolylidene copper complex efficiently catalyses the hydrosilylation of functionalized and/or sterically demanding carbonyl compounds, using triethylsilane as cost-effective hydride source; the catalyst displays remarkable stability as a result of the steric properties of the NHC ligand.





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ARTICLE

Alkylfluorenyl substituted *N*-Heterocyclic Carbenes in Copper(I) catalysed Hydrosilylation of Aldehydes and Ketones†

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Matthieu Teci,[a] Nicolas Lentz,[a] Eric Brenner,*[a] Dominique Matt,*[a] and Loïc Toupet[b]

Copper(I) complexes featuring N-heterocyclic carbenes (NHCs) in which the nitrogen atoms are substituted by a 9-ethyl-9-fluorenyl group (EF) have been synthesised and tested in the hydrosylilation of functionalized and/or sterically demanding ketones and aldehydes. These reactions, carried out with triethylsilane as hydride source, were best achieved with the imidazolylidene copper complex 2 in which the EF substituents can freely rotate about the corresponding N-CEF bonds. The remarkable stability of the active species, which surpasses that of previously reported Cu-NHC catalysts is likely to rely on the ability of the NHC side arms to protect the copper centre during the catalytic cycle by forming sandwich-like intermediates, but also on its steric flexilbility facilitating approach of encumbered substrates. TONs up to 1000 were reached.

Introduction

Hydrosilylation of ketones and subsequent hydrolysis of the resulting silyl ethers is a well-established method for the preparation of a variety of alcohols, including chiral ones.[1] Current research in this area focuses on the development of new, cost-effective catalysts with the hope to move away from the expensive Rh- or Ru-catalysts traditionally employed for these reactions.[2] Efforts to achieve this goal, logically, also require the concomitant development of appropriate ligands.

As part of a program aimed at exploring the catalytic properties of N-heterocyclic carbenes (NHCs) bearing expanded alkylfluorenyl (AF) substituents, we have examined the hydrosylilation of ketones and aldehydes with copper(I) complexes based on such ligands. Previously, we had shown that in their complexes AF-substituted NHCs derived from benzimidazolium salts display a preorganised structure in which the akyl groups are turned towards the metal centre, so as to promote a terdentate, clamp-like bonding mode of the ligand, involving the carbenic C atom and two weakly coordinating CH atoms of the alkyl side groups.[3] Ligands of this type, which combine a strong coordination bond with two non covalent bonds have been termed bimodal pincers. In analogs in which the benzannulated moiety has been replaced by smaller imidazolinylidene or imidazolylidene rings, rotation of the AF unit about the N–CAF bond may occur, this enabling the ligand to adapt to the steric requirements of the metal environment. It is worth mentioning that copper complexes containing other bulky NHCs have recently been used in the hydrosylilation of carbonyl compounds.[4]

Results and discussion

Synthesis of the complexes

The complexes used in this study (**2a-d**) were obtained by reacting the appropriate azolium precursor (**1a-d**) with CuCl in CH_2Cl_2 in the presence of K_2CO_3 (Scheme 1).

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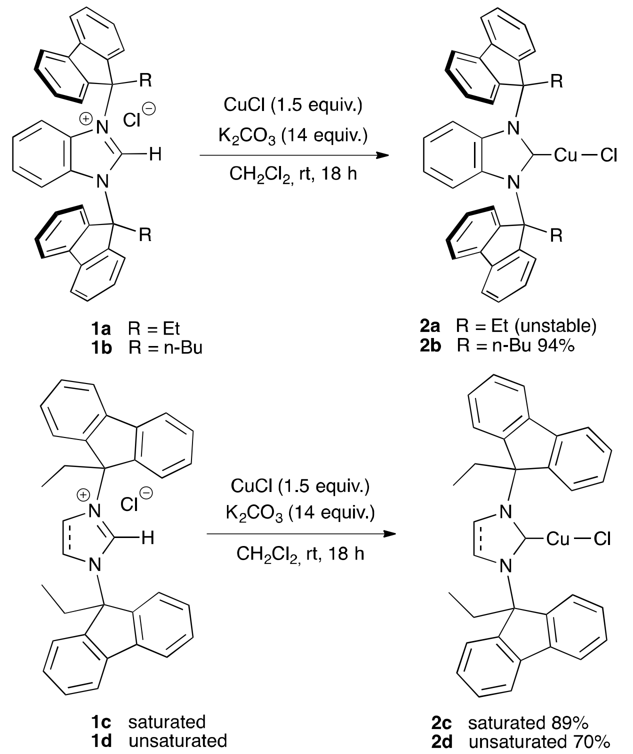
† Electronic supplementary information (ESI) available: Experimental details, NMR spectra. For ESI or other electronic format see DOI: XXXXXX



Scheme 1 Synthesis of copper complexes **2a-d**

Complex **2d** has been briefly described in a previous report.[5] As complex **2a** underwent rapid oxidation in air, both in solution and in the solid state (colour change from white to blue), this complex was not considered for hydrosylilation tests. In contrast, complexes **2b** and **2c** were found stable in air up to ca. 150° over long periods. The most stable complex is **2d**, which is fully air stable at temperatures up to 220°. The relative stability of complexes **2a**-**2d** is likely controlled by the ability of the N-substituents to sterically protect or not the metal centre (*vide infra*).

In keeping with the freely rotating AF groups of **2c** and **2d**,[6] the 2D ROESY spectra of these complexes, measured at room temperature, showed strong through-space correlations between the NCCH_2 hydrogen atoms (termed hereafter α-CH_2 protons) and the CH atoms of the NHC ring (see ESI. Such correlations were not observed for **2b**, as the corresponding α-CH_2 protons remain here permanently[3] directed towards the metal centre.[7] We further noted that while the α-CH_2 protons of **2c** appear at nearly the same chemical shift as that of their precursor salt, those of **2d** have undergone a significant upfield shift (0.42 ppm) with respect to those of **1d**. This could merely reflect a shielding effect of the pi electrons of the NC=C double bond of **2d** on the α-CH_2 protons, which may temporarely approach the backside of the NHC ring.

Palladium and silver complexes containing the carbene ligands derived from **1b**-**1d** have been crystallographically characterised in previous studies.[3, 6] These revealed that the corresponding ligands may have the fluorenylidene planes either turned towards the metal or folded back to the CC bond of the NHC ring, this leading to % buried volumes (pbv) of ca. 58% for the former carbenes and of 36% for the latter (Fig. 1). Thus, when AF groups can freely rotate (as in **1c** and **1d**), the pbv of the corresponding carbenes must be regarded as a time-dependent variable.

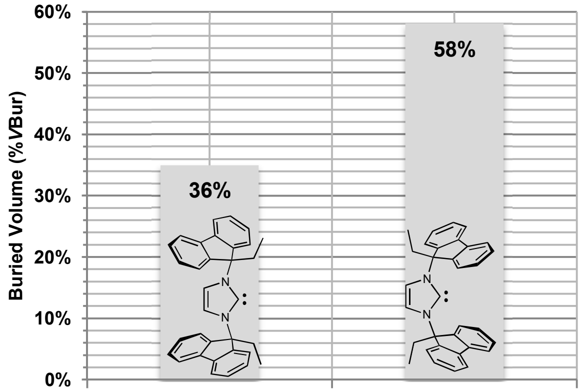
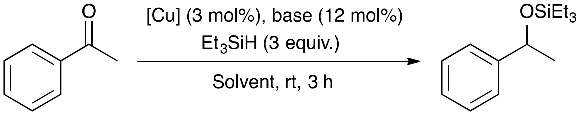


Fig. 1 Percent buried volume (%*V*bur) for the two extreme ligand conformations of **2d** calculated from previously reported X-ray studies. Parameters used for the calculations: C-M distance: 2.1 Å; sphere radius: 3.5 Å

Catalysis

We began the catalytic investigations by examining the properties of **2b**-**d** in the hydrosilylation of acetophenone (taken as the model substrate), using either THF or toluene as solvent, and *t*-BuOK or *t*-BuONa as the base. The runs were carried out applying a slight modification of a procedure described by Nolan et al. (Table 1).[8] Triethylsilane was chosen as a mild and economical hydride source. Optimal conditions consisted in carrying out 3h runs in toluene at room temperature, with 3 equivalents of silane, 3 mol% of copper catalyst, and 12 mol% of *t*-BuONa. Complex **2d** proved to be the most efficient catalyst, the corresponding runs affording 93% of the silyl ether after 3h. In comparaison, under similar conditions the complex [CuCl(IPr)], which is regarded as a very performing NHC-copper catalyst for this reaction,[8] resulted in 97% yield (Table 1 entries 6 and 7). Control experiments showed that no reaction takes place in the absence of catalyst, nor in the presence of ligand free copper(I) chloride (Table 1, entries 1 and 2). Complex **2b** displayed significantly lower activities than **2d** (Table 1, entry 8), seemingly because of gradual degradation of the active species. This likely arises from a lower steric protection of the metal by the carbene ligand of **2b** than that provided by the (time-averaged) sterically bulkier carbene ligand of **2d**, the fluorenylidene planes of which may be bent towards the metal atom, so as to sandwich it. Interestingly, complex **2d** proved also to be more efficient than **2c** in the hydrosilylation of acetophenone (Table 1, entry 9). Note that the corresponding carbenes do note differ by their steric properties, only by their electronic ones, the carbene ligand in **2d** being a weaker donor. This finding is consistent with a recently reported theoretical study by Leyssens et al., who showed that as a general trend Cu-catalysed hydroslylilation is facilitated with electronically poorer NHCs.[9]

Table 1 Catalytic hydrosilylation of acetophenone with Et_3SiH using complexes **2b-d** or [CuCl(IPr)] : influence of the base and the solvent[a]



Entry	Complex	Base	Solvent	Conv. (%)[b]
1	–	*t*-BuOK	THF	0
2	CuCl	*t*-BuOK	THF	0[c]
3	**2d**	*t*-BuOK	THF	15
4	**2d**	*t*-BuONa	THF	10
5	**2d**	*t*-BuOK	toluene	29
6	**2d**	*t*-BuONa	toluene	93
7	IPrCuCl	*t*-BuONa	toluene	97
8	**2b**	*t*-BuONa	toluene	26
9	**2c**	*t*-BuONa	toluene	29

[a] General conditions: complex (3 mol%), base (12 mol%), Et_3SiH (6 mmol), solvent (2 mL), acetophenone (2 mmol), 25°C, 3 h. [b] Conversion determined by ^1H NMR. [c] 9 mol% of CuCl.

In order to assess the scope of the reaction, tests were then run with 14 other ketones (Table 2) applying conditions similar to those described above. We observed that neither with *t*-BuOK nor with *t*-BuONa were aldolisation products observed (Table 2, entries 1-13). As expected, the reaction rates were higher with sterically non demanding as well as with activated ketones. In these cases, hydrosilylation could be carried out efficiently at room temperature within 2-3 h (Table 2, entries 1-3, 6-7, 9 and 12). For sterically bulkier ketones and also with non-activated ones, longer reaction times and/or higher temperatures were required (Table 2, entries 4, 5, 8, 10 and 11).

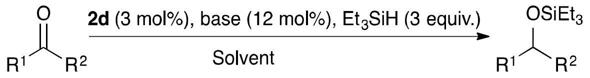
For the reactions carried out at 65°C, the use of *t*-BuOK/THF gave significantly better results than with *t*-BuONa-toluene (Table 2, entries 8, 11, 13 and14).

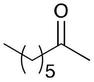
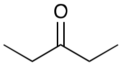
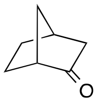
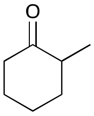
The hydrosilylation of norcamphor, which was achieved at room temperature, gave a 80:20 mixture of endo:exo products (Table 2, entry 3). The observed diastereoselectivity is consistent with a preferential attack of the hydride on the less encumbered exo face. The hydrosilylation of 2-methylcyclohexanone (Table 2, entry 4), which was best achieved at 65°C, afforded the expected silylated alcohol as a mixture of syn/anti diastereomers (45:55). Starting from the bulkier menthone (Table 2, entry 5) did not increase the selectivity (syn:anti ratio = 40:60; configuration with respect to the C-O/C-*i*Pr bonds).

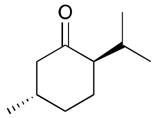
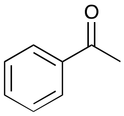
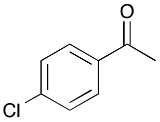
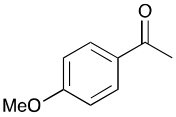
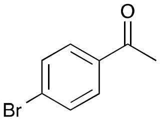
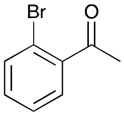
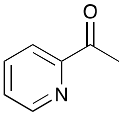
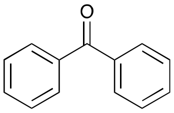
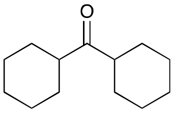
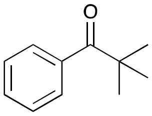
Full conversion to the corresponding silylether was achieved at room temperature with benzophenone as substrate (Table 2, entry 12). Remarkably, bromo- and chloroacetophenone derivatives were fully converted without dehalogenation (Table 2, entries 7, 9 and 10). The deactivated *para*-methoxyacetophenone was also readily hydrosilylated (at 65°C) (Table 2, entry 8). Other successful hydrosilylations include that of acetylpyridine (using *t*-BuOK as base in THF; (Table 2, entry 11), as well as those of the sterically demanding ketones dicyclohexylketone and 2,2-dimethylpropiophenone and (Table 2, entries 13 and 14).

Notably, *para*-cyano or *para*-nitro substituted acetophenone (not drawn) could not be hydrosilylated under conditions similar to the ones reported above. The electron-withdrawing cyano and nitro groups supposed to inductively activate the the conjugated ketone did in fact not result in the expected effect. Lipshutz *et al*. have already made similar observations for 3-acetyl-benzonitrile.[10] Possibly, the nitrile and nitro groups coordinate strongly to the copper atom so as to prevent binding of the keto groups.

Table 2 Hydrosilylation of ketones catalysed by complex **2d**[a]



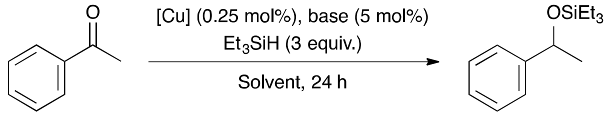
Entry	Substrate	Base/Solvent	Temperature (°C)	Time (h)	Conv. (%)[b]	Yield (%)[c]
1		*t*-BuONa / toluene	25	2	> 99	96
2		*t*-BuONa / toluene	25	2	> 99	94
3		*t*-BuONa / toluene	25	2	> 99	94 (endo : exo / 80 : 20)
4		*t*-BuONa / toluene	65	2	> 99	97 (syn : anti / 45 : 55)

5		*t*-BuONa / toluene	65	2	> 99	96 (syn : anti / 40 : 60)
6		*t*-BuONa / toluene	25	3	93	90
7		*t*-BuONa / toluene	25	3	98	97
8		*t*-BuONa / toluene *t*-BuOK / THF	25 65	2 2	10 92	- 87
9		*t*-BuONa / toluene	25	3	> 99	97
10		*t*-BuONa / toluene	65	6	> 99	92
11		*t*-BuONa / toluene *t*-BuOK / THF	65 65	18 4	> 99 > 99	- 95
12		*t*-BuONa / toluene	25	1	> 99	97
13		*t*-BuONa / toluene *t*-BuOK / THF	65 65	2 4	4 > 99	 98
14		*t*-BuONa / toluene *t*-BuOK / THF	65 65	2 2	50 > 99	- 94

[a] *General conditions:* complex **2d** (3 mol%), base (12 mol%), Et_3SiH (6 mmol), solvent (2 mL), ketone (2 mmol). [b] Conversion determined by ^{1}H NMR. [c] Isolated yields.

In order to test the endurance of **2d** under catalytic conditions, additional hydrosylilation runs were carried out for acetophenone over longer reaction periods (Table 3), these runs being performed at 65°C with only 0.25 mol% of catalyst (a lower catalyst concentration being required for monitoring reaction progress). At the applied temperature, the best conversions were obtained with the couple *t*-BuOK/THF. Under these conditions, the conversion reached 97 % after 24 h (TON = 388) (Table 3, entry 10). In comparison, for the same experiment, [CuCl(IPr)] resulted in a yield of only 35% (TON = 140), this being indicative of a higher stability of the **2d** catalyst (Table 3, entry 9). Note that, consistent with the observations made for the low-temperature experiments (see above), catalysts **2b** and **2c** displayed lower activities at 65°C then **2d** and [CuCl(IPr)] (Table 3, entries 12 and 13). In order to test catalyst **2d** over a still longer period, the runs (at 65°C) were then repeated with only 0.1 mol% of catalyst. In this case, no catalyst deactivation occurred and the reaction was completed after 70 h (Table 3, entry 14), this corresponding to one of the highest TONs (TON = 1000) ever reported for NHC-copper catalysts containing a five-membered diaminocarbene. Low-charge hydrosylilation reactions using 0.25 or 0.5 mol% of **2d** was also successfully applied to all the ketones discussed above (Table 4).

Table 3 Hydrosilylation of acetophenone catalysed by complexes **2b-d** and [IPrCuCl] (0.25 mol%) in the presence of Et_3SiH: influence of the base and the solvent[a]



Entry	Complex	Base / Solvent	Temp. (°C)	Conv. (%)[b]
1	–	*t*-BuOK / THF	65	0
2	CuCl	*t*-BuOK / THF	65	0[c]
3	IPrCuCl	*t*-BuONa / toluene	RT	10
4	**2d**	*t*-BuONa / toluene	RT	23
5	IPrCuCl	*t*-BuONa / toluene	65	23
6	**2d**	*t*-BuONa / toluene	65	41
7	IPrCuCl	*t*-BuOK / THF	RT	5
8	**2d**	*t*-BuOK / THF	RT	11
9	IPrCuCl	*t*-BuOK / THF	65	35
10	**2d**	*t*-BuOK / THF	65	97
11	**2d**	*t*-BuONa / THF	65	23
12	**2b**	*t*-BuOK / THF	65	12
13	**2c**	*t*-BuOK / THF	65	13
14	**2d**	*t*-BuOK / THF	65	>99[d]

[a] General conditions: complex (0.25 mol%), base (5 mol%), Et_3SiH (6 mmol), acetophenone (2 mmol), solvent (2 mL), RT, 24 h. [b] Conversion determined by ^1H NMR. [c] 9 mol% of CuCl. [d] Reaction performed with 0.1 mol% of **2d**, 70 h.

The considerable longer lifetime of catalyst **2d** *vs.* [CuCl(IPr)] is best explained by the steric differences between the corresponding carbenes. In fact, the steric protection of the Cu atom is significantly better in **2d** than in[CuCl(IPr)]. This can be seen, *e.g.*, by comparing the % buried volumes of the ligands, namely 37%-59% for the sterically flexible carbene ligand of **2d** (noted **NHC^{2d}**), vs. 29% for that of [CuCl(IPr)]. The recently reported solid state structure of [AgCl(**NHC^{2d}**)] (Fig. 2) provides proof that both fluorenylidene planes of **NHC^{2d}** may be turned simultaneously towards the bound metal centre, this resulting then in an efficient steric protection of the metal (sandwich type structure) in possible Pd(0) intermediates. A similar protection is not provided by ligands such as in **2a**/**2b**, in which the AF groups do not rotate and where the fluorenylidene planes are folded back away from the metal.

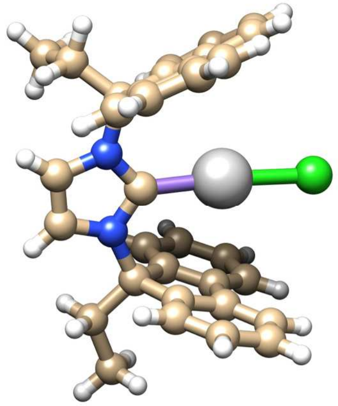
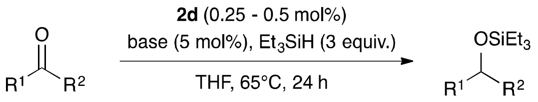
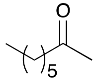
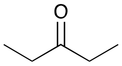
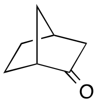
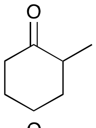
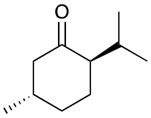
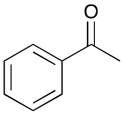
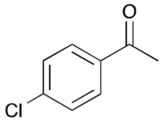
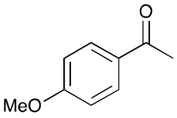
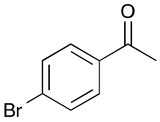
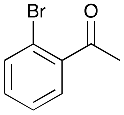
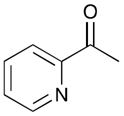
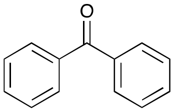
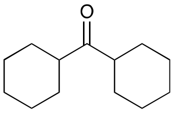
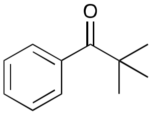


Fig. 2 Solid state structure of of the silver analogue of **2d** [AgCl(**NHC^{2d}**)],[6] showing the flexible carbene ligand **NHC^{2d}** when it displays its highest possible encumbrance

Table 4 Hydrosilylation of ketones using complex **2d**[a]



Entry	Substrate	Conv. (%)[b]	Yield (%)[c]
1		> 99	97
2		> 99	93
3		> 99	96
4		> 99	94
5		> 99	94
6		97	93
7		> 99	95
8		> 99	96[e]
9		> 99	93
10		> 99	94[e]
11		> 99	96[e]
12		> 99	97[d]

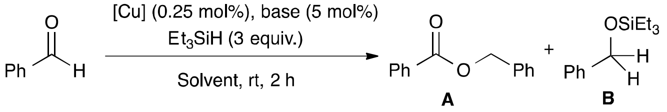
13		> 99	95[e]
14		> 99	94

[a] General conditions: complex **2d** (0.25 mol%), *t*-BuOK (5 mol%), Et$_3$SiH (6 mmol), ketone (2 mmol), THF (2 mL), 65°C, 24 h. [b]Conversion determined by ^{1}H NMR. [c] Isolated yields. [d] Reaction performed at RT, 18 h. [e] Reaction performed with 0.5 mol% of **2d**.

The reactivity of aldehydes was also examined (Table 6). Benzaldehyde was first studied (Table 5). Surprisingly, independently of the solvent used, hydrosilylation with **2d** proceeded with concomitant formation of benzyl benzoate (**A**) (Table 5, entries 1-4). In fact, the formation of this homoester arose from a competitive Tishchenko-type reaction, known to operate without copper.[11] The amount of Tischenko product could be kept at his lowest level when using *t*-BuONa instead of *t*-BuOK (Table 5, entries 1-4). Of further advantage was to use THF as the solvent rather than toluene (Table 5, entry 3).

It is noteworthy that when using *t*-BuONa/THF with Et$_3$SiH in the absence of any copper catalyst, no reaction took place (Table 5, entry 6). Repeating this reaction with *t*-BuOK instead of *t*-BuONa, led selectively and quantitatively to the homoester **A** within 2 h at room temperature (Table 5, entry 5). The superiority of the potassium vs. the sodium salt is consistent with observations made by Berke.[11] Furthermore, in the absence of silane, no Tishchenko reaction occurred, demonstrating that the silane may function as a hydride transfer catalyst.

Table 5 Hydrosilylation of benzaldehyde catalysed by **2d** using Et$_3$SiH: influence of the base and the solvent[a]



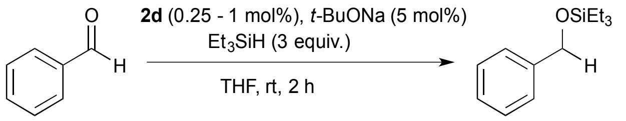
Entry	Complex	Base / Solvent	Conv. (%)[b]	A:B
1	**2d**	*t*-BuOK / THF	98	50:50
2	**2d**	*t*-BuOK / toluene	95	55:45
3	**2d**	*t*-BuONa / THF	88	7:93
4	**2d**	*t*-BuONa / toluene	100	15:85
5	-	*t*-BuOK / THF	100	100:0
6	-	*t*-BuONa / THF	0	-
7	**CuCl**	*t*-BuONa / THF	0[c]	-

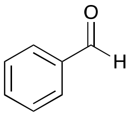
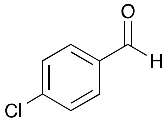
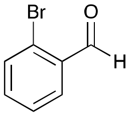
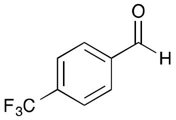
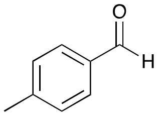
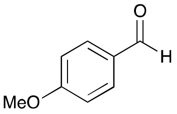
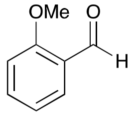
[a] General conditions: **2d** (0.25 mol%), base (5 mol%), Et$_3$SiH (6 mmol), benzaldehyde (2 mmol), solvent (2 mL), RT, 2 h. [b] Conversions determined by ^{1}H NMR. [c] 9 mol% of CuCl.

Overall, effective hydrosylilation of benzaldehyde was best performed with **2d** (0.25 mol%) in THF *at room temperature* with *t*-BuONa as base, this resulting in a PhCH$_2$OSiEt$_3$:PhC(O)OCH$_2$Ph ratio of 93:7 after 2h reaction time (Table 5, entry 3). No Tishchenko products were observed with benzaldehyde derivatives containing electron donating groups, notably *p*-methylbenzaldehyde, *p*-methoxybenzaldehyde and *o*-methoxybenzaldehyde (Table 5, entries 5-7). Note that hydrosilylation of *p*-methoxybenzaldehyde required a reaction temperature of 65°C (Table 5, entry 6), the other two isomers being readily converted at 25°C.

In the presence of 0.25 mol% of catalyst and with *t*-BuONa/THF, the hydrosilylation of benzaldehyde derivatives bearing electronwithdrawing groups, led again to mixtures of silylether and homoester, the proportion of ester being here higher than in the case of benzaldehyde. Obviously, the competitive Tishchenko reaction occurred faster than in the case of benzaldehyde. Thus, in order to favor the hydrosilylation process over the Tishchenko reaction, the 2d:*t*-BuONa ratio was increased to 1:5 instead of 0.25:5. In that case no ester formed (Table 6, entry 2-4). It should also be mentioned that with the chloro- and bromo- substrates, the reaction took place without dehalogenation.

Table 6 Hydrosilylation of aromatic aldehydes catalysed by complex **2d**.



Entry	Substrate	Conv. (%)[b]	Yield (%)[c]
1		> 99[e]	95
2		> 99[e]	94
3		> 99[e]	92[f]
4		> 99[e]	94
5		> 99	96
6		> 99[d]	91
7		> 99	91

[a] General conditions: Activation of complex **2d** (0.25 mol%) with *t*-BuONa (5 mol%) and Et$_3$SiH (6 mmol) in THF (2 mL) at room temperature, then addition of the aldehyde (2 mmol). Reaction mixture stirred at room temperature for 2 h. [b] Conversion to product based on starting material determined by ^{1}H NMR. [c] Isolated yields. [d] Reaction performed at 65°C for 1 h. [e] Reaction performed with 1 mol% of **2d**. [f] Reaction mixture stirred at room temperature for 4 h.

Experimental

All commercial reagents were used as supplied, except liquid aldehydes, which were treated with a $NaHCO_3$(aq.)/CH_2Cl_2 mixture prior to use. The syntheses and catalytic tests were performed in Schlenk-type flasks under dry nitrogen. Solvents were used as received except for tetrahydrofuran (THF) (distilled from sodium/benzophenone) and toluene (distilled from sodium). Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a FT Bruker AVANCE 300 instrument (^1H: 300.1 MHz, ^{13}C: 75.5 MHz) at 25°C. ^1H NMR spectral data were referenced to residual protonated solvents ($CHCl_3$, δ 7.26), ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ 77.16). Data are represented in the following order: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*) in Hz, and assignment. In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still *et al.* employing Geduran SI (E. Merck, 0.040-0.063 mm) silica.[12] Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (UMR 7177 CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. Complex **2d**[5] and IPrCuCl[8] were synthetised according to known procedures.

General procedure for copper-catalysed hydrosilylation reactions :
In a Schlenk tube under nitrogen were introduced the copper complex ($3{\cdot}10^{-2}$–10^{-5} mmol) and the appropriate base (0.24 mmol) followed by the solvent (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After activation, the carbonyl compound (2 mmol) was added and the reaction mixture was stirred at room temperature for a period of time indicated in the corresponding Table. The mixture was filtered through a short pad of Celite using CH_2Cl_2 as solvent. The residue was then purified by flash chromatography (SiO_2; AcOEt–petroleum ether) to afford the hydrosilylated product as a colourless oil.

(1,3-bis(9-*n*-butyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene)copper(I) chloride (2b) A suspension of benzimidazolium salt **1b** (0.400 g, 0.67 mmol), finely crushed K_2CO_3 (1.29 g, 9.77 mmol), and CuCl (0.098 g, 0.99 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. The mixture was filtered through a pad of silica gel and the pad was washed with CH_2Cl_2 (*ca.* 3 × 30 mL). The filtrate was concentrated in vacuo to ca. 1 mL. Pentane (10 mL) was added and the resulting white precipitate was decanted. After removal of the supernatant, the solid was washed with pentane (3 × 10 mL) to afford pure complex **2b** as a white solid (0.411 g, 94%); m.p. decomp. 200 °C. ^1H NMR ($CDCl_3$, 500 MHz), δ 7.78 (4H, d, ^3J = 7.3 Hz, ArH of fluorenylidene), 7.42 (4H, dd, $^3J = {}^3J'$ = 7.3 Hz, ArH of fluorenylidene), 7.32-7.27 (4H, m, ArH of fluorenylidene), 6.48 (2H, br signal, NCCCH of benzimidazolylidene unit), 5.98 (2H, br signal, NCCH of benzimidazolylidene unit), 3.77 (4H, br s, $CH_2CH_2CH_2CH_3$), 1.38 (4H, m, $CH_2CH_2CH_2CH_3$), 0.77 (6H, t, ^3J = 7.3 Hz, $CH_2CH_2CH_2CH_3$), 0.67 (4H, m, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), 145.9 (arom. Cq), 140.2 (arom. Cq), 133.8 (arom. Cq), 129.6 (arom. CH), 128.8 (arom. CH), 123.5 (arom. CH), 123.2 (arom. CH), 120.7 (arom. CH), 113.9 (arom. CH), 73.7 (N*C*Bu), 43.4 ($CH_2CH_2CH_2CH_3$), 25.9 ($CH_2CH_2CH_2CH_3$), 22.5 ($CH_2CH_2CH_2CH_3$), 14.1 ($CH_2CH_2CH_2CH_3$), carbene signal not detected. Found C, 74.57; H, 5.79; N, 4.12. Calc. for $C_{41}H_{38}ClCuN_2$ (M_r = 656.20): C, 74.87; H, 5.82; N, 4.26%.

(1,3-bis(9-ethyl-9-fluoren-9-yl)imidazolin-2-ylidene)copper(I) chloride (2c): A suspension of imidazolium salt (**1c**) (0.204 g, 0.42 mmol), finely crushed K_2CO_3 (0.773 g, 5.85 mmol) and CuCl (0.068 g, 0.69 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature overnight. The mixture was filtered through a pad of silica gel and the pad was washed with CH_2Cl_2 (ca. 3 × 20 mL). The filtrate was concentrated in vacuum to ca. 1 mL. Pentane (6 mL) was added and the resulting white precipitate was decanted. After removal of the supernatant, the solid was washed with pentane (3 × 20 mL) to afford pure complex **2c** as a white solid (0.161 g, 69%); m.p. > 220 °C. ^1H NMR ($CDCl_3$, 500 MHz), δ 7.68 (4H, d, ^3J = 7.3 Hz, ArH), 7.48 (4H, d, ^3J = 7.2 Hz, ArH), 7.42 (4H, dd, $^3J = {}^3J'$ = 7.3 Hz, ArH), 7.35 (4H, dd, $^3J = {}^3J'$ = 7.4 Hz, ArH), 3.10 (4H, q, ^3J = 6.2 Hz, CH_2CH_3), 3.04 (4H, s, NCH_2), 0.44 (6H, t, ^3J = 6.2 Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 196.4 (NCN), 145.4 (arom. Cq), 140.6 (arom. Cq), 129.3 (arom. CH), 128.4 (arom. CH), 123.6 (arom. CH), 120.5 (arom. CH), 73.2 (N*C*Et), 46.2 (NCH_2), 33.5 (CH_2CH_3), 8.4 (CH_2CH_3). Found C, 71.56; H, 5.44; N, 4.94. Calc. for $C_{33}H_{30}ClCuN_2$ (M_r = 552.14) C, 71.60; H, 5.46; N, 5.06%.

Conclusions

We have shown that the AF-substituted imidazolylidene copper complex **2d** efficiently catalyses the hydrosilylation of functionalized and/or sterically demanding carbonyl compounds, using triethylsilane as cost-effective hydride source. Its intrinsic activity compares with that of [CuCl(IPr)], presently considered as the most performing copper-based NHC complex based on a five-membered NHC. Remarkably, the activity of **2d** was not altered after 70 h reaction time (TONs up to 1000), thereby contrasting with its less stable IPr analogue. The high stability of complex **2d** is likely to arise from the capacity of its imidazolylidene ligand to sterically protect, when necessary, the metal centre by forming intermediates with a sandwiched metal atom, this being not possible with benzimidazolylidene analogues. On the other hand, the steric flexibility of the ligand related to rotational freedom of the ethylfluorenyl groups facilitates conversion of encumbered substrates. Overall, the reported results constitute a new illustration of the catalytic potential of NHCs displaying *variable* steric encumbrance.

Acknowledgements

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1. B. Marciniec, *in* B. Cornils, W. A. Herrmann (eds.), Applied Hogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996, Chapter 2.6.
2. a) S. Diez-Gonzalez and S. P. Nolan, *Acc. Chem. Res.*, 2008, **41**, 349-358; b) L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J. B. Sortais and V. Ritleng, *Adv. Synth. Catal.*, 2012, **354**, 2619-2624; c) D. Kumar, A. P. Prakasham, L. P. Bheeter, J. B. Sortais, M. Gangwar, T. Roisnel, A. C. Kalita, C. Darcel and P. Ghosh, *J. Org. Chem.*, 2014, **762**, 81-87.

3. a) M. Teci, E. Brenner, D. Matt and L. Toupet, *Eur. J. Inorg. Chem.*, 2013, 2841-2848; b) M. Teci, E. Brenner, D. Matt, C. Gourlaouen and L. Toupet, *Dalton Trans.*, 2014, **43**, 12251-12262.
4. a) B. H. Lipshutz, J. M. Servesko, T. B. Petersen, P. P. Papa and A. A. Lover, *Org. Lett.*, 2004, **6**, 1273-1275; b) S. Diez-Gonzalez, H. Kaur, F. K. Zinn, E. D. Stevens and S. P. Nolan, *J. Org. Chem.*, 2005, **70**, 4784-4796; c) S. Diez-Gonzalez, N. M. Scott and S. P. Nolan, *Organometallics*, 2006, **25**, 2355-2358.
5. M. Teci, E. Brenner, D. Matt, C. Gourlaouen and L. Toupet, *Chem. Eur. J.,* DOI: 10.1002/chem.201500840.
6. M. Teci, E. Brenner, D. Matt, C. Gourlaouen and L. Toupet, *Dalton Trans.*, 2015, **44**, 9889-9898.
7. Rotating AF groups as in **2c** and **2d** provide better complex stabilisation than the non-rotating ones present in benzimidazolium derivatives such as **2a** and **2b**. In the latter complexes, the fluorenylidene planes are permanently turned away from the metal centre.
8. H. Kaur, F. K. Zinn, E. D. Stevens and S. P. Nolan, *Organometallics*, 2004, **23**, 1157-1160.
9. T. Vergote, F. Nahrar, A. Merschaert, O. Riant, D. Peeters and T. Leyssens, *Organometallics*, 2014, **33**, 1953-1963.
10. B. H. Lipshutz, K. Noson, W. Chrisman and A. Lower, *J. Am. Chem. Soc.*, 2003, **125**, 8779-8789.
11. K. Rajesh and H. Berke, *Adv. Synth. Catal.*, 2013, **355**, 901-906.
12. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923-2925.