

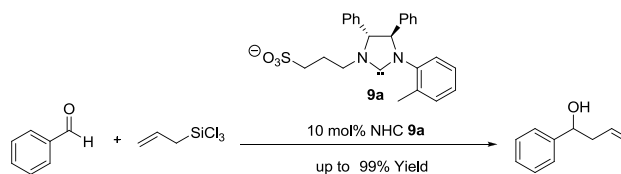
First examples of carbene-catalyzed allylation of benzaldehyde with allyltrichlorosilane

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Abstract We report here first examples of carbene-catalyzed allylation of benzaldehyde. *N*-Heterocyclic carbenes applied here, **9a** and **10a**, were derived from imidazolium zwitterions, and contained sulfonate and sulfamate substituents, respectively. Different reaction conditions such as temperature, organic solvents, additive and bases were used to optimize the reaction. Sulfonate substituted NHC **9a** is found more efficient organocatalyst for the allylation of benzaldehyde (greater than 99 % yield at lower temperature) than sulfamate-based NHC **10a** (a yield of no more than 15 %). These results are justified on the basis of philicity descriptors of the NHCs and their corresponding allyldichlorosilane complexes.

Graphical abstract



Keywords *N*-Heterocyclic carbenes · Imidazolium salts · Zwitterions · Organocatalysis · Allyltrichlorosilane

Introduction

Organocatalysts provide simple operational facility with low level of toxicity compared to metal-based catalysts [1–3]. In this context, carbenes have emerged as efficient organocatalysts and ligands. In carbene family, *N*-heterocyclic carbenes (NHCs) are Lewis-base organocatalysts and offer alternative ways for conventional reactions. For example, NHCs render electrophiles such as carbonyl and Michael systems to acyl anion equivalent and homoenolates, respectively, via umpolung [4–7]. There is a rapid progress in the field of NHC catalysis because NHCs offer efficiency and new reactivity with a range of reactions, such as umpolung reactions of aldehydes [8], conjugate umpolung [8], benzoin condensation [9], Stetter reaction [10], cycloaddition reactions [11, 12], ring opening reactions [13], aza-Morita–Baylis–Hillman reactions [14], addition of silylated nucleophiles to electrophiles [15], transesterification [16], and polymerization [17].

The allylation of carbonyl compounds leads to a carbon–carbon bond formation and the product of the reaction is homoallylic alcohol, an important intermediate/synthon in organic synthesis [18, 19]. In addition to

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Table 1 Allylation of benzaldehyde with *N*-heterocyclic carbenes derived from 10 mol % zwitterion

Entry	Solvent	Base ^a	T (°C)	Time (h)	Zwitterion	Yield (%)
1	THF	NaH	rt	48	9	57
2	THF	NaH	rt	48	10	Traces
3	THF	NaH	rt	65	10	15
4	CH ₂ Cl ₂	NaH	rt	48	9	56
5	Toluene	KHMDS	rt	48	9	45
6	THF	KHMDS	rt	48	9	56
7 ^b	CH ₂ Cl ₂	NaH	rt	24	9	75
8 ^b	THF	NaH	rt	24	9	60
9 ^b	Toluene	NaH	rt	24	9	73
10 ^b	CH ₂ Cl ₂	NaH	−60	24	9	99

^a 9 mol % base was used to generate NHCs^b Diisopropylethylamine was used as an activator

different metal-based allylating agents, allyltrichlorosilane has been proven as an effective allylating agent. The success of the reagent lies in the fact that it can react with Lewis-base catalysts and a hypervalent silicon complex is formed. This silicon complex can efficiently react with different electrophiles and corresponding allylated products are formed [20]. A pioneer work has been done by Kobayashi et al. who reported the allylation to electrophiles catalyzed by a Lewis-base, *N,N*-dimethylformamide [21, 22]. After that, a variety of Lewis-basic molecules have been reported. Examples include dinitrones [23], ureas [24], phosphoramides [25], formamides [26–28], *N*-oxides [29–31] and phosphine oxides [32, 33]. In the ongoing search for new classes of organocatalysts in the allylation of aldehydes, we report here the allylation reactions catalyzed by nucleophilic NHCs derived from the imidazolinium zwitterions. According to our knowledge there is no report about exploitation of NHCs as organocatalysts for the allylation of aldehydes. A comparison of NHCs derived from imidazolinium zwitterions having sulfonate and sulfamate substituents is described. The philicity descriptors such as electrophilic/nucleophilic power calculated by theoretical calculations are used to explain the efficiency of sulfonate substituted imidazolinium NHC.

Experimental

General remarks

NMR spectra were measured on a Bruker AMX 400 (400 MHz) and a Bruker AC 200F (200 MHz) in deuterated solvents as mentioned. Flash column chromatography [34] was performed on Sorbisil C-60. The reactions were monitored by TLC plates of Merck Silica gel 60 F254. The zwitterions **9** and **10** were synthesized and characterized according to our already reported protocol [35].

General procedure for allylation of benzaldehyde using allyltrichlorosilane in the presence of carbene

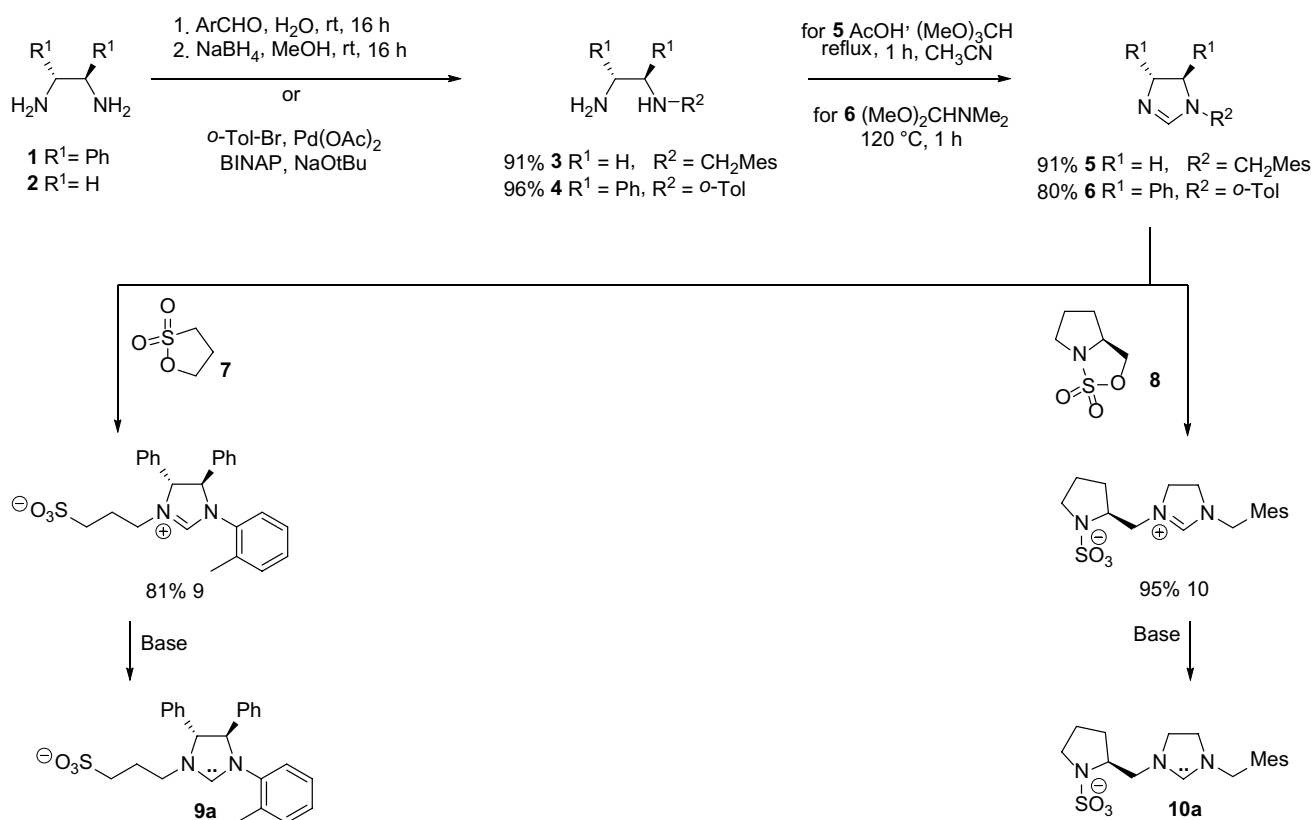
1-Phenylbut-3-en-1-ol

A stirred solution of imidazolinium zwitterion (10 mol %) was treated with 9 mol % base for 0.5–1.5 h at rt to −60 °C according to the entries in the Table 1. Benzaldehyde (0.05 mL, 0.49 mmol, 1 eq) and the additive diisopropylethylamine (0.41 mL, 2.35 mmol, 5.0 eq) were added. Then allyltrichlorosilane (0.105 mL, 0.735 mmol, 1.5 eq) was added dropwise. The reaction was stirred for a fixed time as mentioned in the Table 1. The reaction was carefully quenched with 1 mL of 10 % NaOH and extracted three times with ethyl acetate. The organic layer was washed with 15 mL of 5 % HCl, NaHCO₃ and brine, dried over Na₂SO₄ and concentrated. For the purification of crude product, flash column chromatography (EtOAc/petrol ether 15:85) was performed to yield 1-phenylbut-3-en-1-ol as an oil. The spectral data were consistent with the literature [32].

¹H-NMR (CDCl₃, 400 MHz): δ ppm = 7.38–7.27 (m, 5H), 5.82 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.17 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.74 (dt, *J* = 6.4, 2.4 Hz, 1H), 2.58–2.6 (m, 2H), 2.06 (d, *J* = 2.8 Hz, 1H). ¹³C-NMR (CDCl₃, 100 MHz): δ ppm = 143.9, 134.5, 128.5, 127.6, 125.9, 118.5, 73.5, 44.1.

Theoretical calculation

All calculations were performed with Gaussian 09 [36]. The geometries of the structures were optimized by using a density functional theory (DFT) at hybrid functional (B3LYP) [37] with a basis set 6-31G(d). The method and basis set chosen provided a nice balance between cost and accuracy. The geometries of the optimized structures were plotted with Marvin View [38]. The stationary points were confirmed as true minima through frequency calculations (no imaginary frequency). Geometries and intermolecular



Scheme 1 Synthesis of imidazolinium sulfonate/sulfamate zwitterions

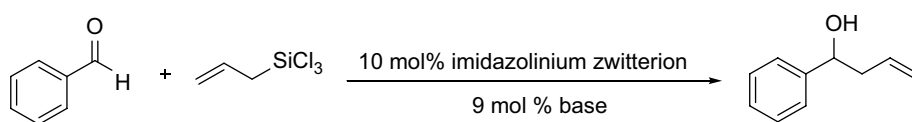
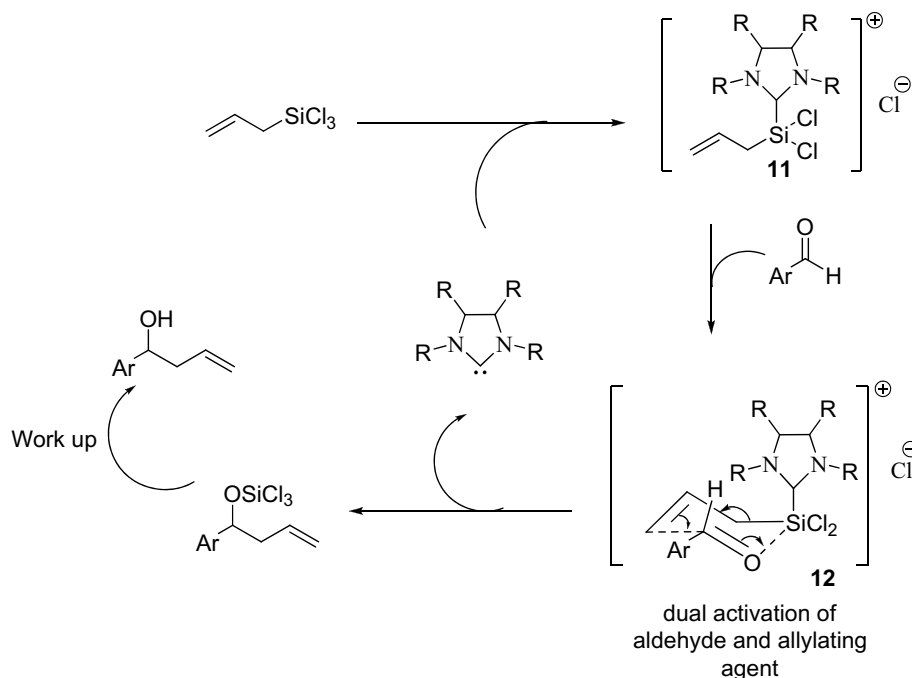
interaction energies such as energy of highest occupied molecular orbital (HOMO), energy of lowest unoccupied molecular orbital (LUMO), band gap, electronic properties (Mulliken and NPA charge analysis), chemical hardness (η), electronic chemical potential (μ), global softness (S), local softness (S_k), Fukui function, global nucleophilicity (N), local nucleophilicity (N_k), global electrophilicity (ω) and local electrophilicity (ω_k) for carbenes and carbene-allyldichlorosilane complexes were calculated at DFT/B3LYP/6-31G(d) level. The negative of HOMO and LUMO values were estimated as ionization potential (I) and electron affinity (A), respectively [37, 39]. For the estimation of Fukui functions, energy calculations of the $N - 1$ and $N + 1$ electronic species were done using unrestricted open shell method at the optimized geometry of the N-electron species at DFT/B3LYP/6-31G(d) level. The condensed Fukui functions were calculated by using Mulliken as well as natural population analysis (NPA) [40].

Results and discussion

Two imidazolinium zwitterions, **9** and **10**, functionalized with alkyl sulphonate and sulphonate substituents,

respectively, were synthesized according to our reported method. (Scheme 1) [35]. First step in the synthesis of imidazolinium zwitterions is the mono-substitution of diamines with mesityl aldehyde or with toluene bromide. The imidazolines were prepared by the reaction of monosubstituted diamines **3** and **4** with an electrophile such as trimethyl-orthoformate [41] and dimethoxy-*N,N*-dimethylformamide, respectively [42, 43], under neat reaction conditions. The imidazoline **5** was quaternized with 1,3-propanesultone **7** and the imidazoline **6** with cyclic sulphonamide **8**. The compound **7** was commercially available, whereas **8** was synthesized by a modified method of Avenoza et al. [44] from easily available, commercial, and cheap prolinol.

The NHCs **9a** and **10a** were generated in situ from their corresponding imidazolinium zwitterions **9** and **10**, respectively, and were applied as organocatalysts in the allylation of benzaldehyde (Scheme 2). In the initial experiments, sodium hydride was used as a base for deprotonation of the imidazolinium salts and the reaction was performed in THF. The alkyl sulfonate substituted NHC **9a** gave encouraging results with a yield of 51 %. The traces of the product were obtained when alkyl sulfamate substituted NHC **10a** generated in situ was applied as catalyst and the maximum yield was obtained to 15 % after a longer reaction

Scheme 2 Allylation of benzaldehyde with 10 mol % NHC**Scheme 3** Mechanism of NHC-catalyzed allylation

time of 65 h (Table 1, entries 2 and 3). Further optimization was performed with the NHC derived from the zwitterion **9**. The yields were comparable when a different base, KHMDS, was used in toluene and THF solvents, respectively (Table 1, entries 5 and 6).

In the allylation reaction it is well established that different catalyst activators can improve the catalytic activity and reduce the reaction time [32, 45]. Diisopropylethylamine was shown to produce excellent results in the allylation of aldehydes when used in combination with tetrabutylammonium iodide [33]. Therefore, we have chosen diisopropylethylamine to evaluate as a catalyst activator. It was observed that the activator shortened the reaction time to 24 h and the yields were improved to 75 % in dichloromethane and 60 % in THF, respectively, (Table 1, entries 7 and 8). As the solvent dichloromethane was giving the higher yield therefore further optimization was done in it and at a lower temperature of $-60\text{ }^\circ\text{C}$, a quantitative yield of the product was obtained. (Table 1, entry 10). A control reaction in the presence of diisopropylethylamine without NHC did not proceed.

The well accepted mechanism for the addition of organosilicon reagents to aldehydes involves the activation of carbon–silicon bond by Lewis-base organocatalysts. Lewis base donates its charge density to silicon atom of

allyltrichlorosilane and its valence shell is expanded. As a result, one of the chlorine silicon bonds is ionized and a positively charged reactive hypervalent silicon complex is formed, which in turn acts as a Lewis acid activator for aldehydes [46, 47]. In our experiments NHCs act as Lewis base organocatalysts, therefore the same mechanism could be rationalized (Scheme 3) which was supported by the subsequent theoretical investigations.

We present here a theoretical explanation for high efficiency of the organocatalyst **9a** over **10a** in catalyzing the allylation of benzaldehyde. To understand chemical reactivity, electron density distribution and electrostatic interactions provide useful information for the explanation of nucleophilic and electrophilic attack. In a catalytic cycle the nucleophilic–electrophilic interactions govern the outcome of the reaction. Before going into the details of theoretical explanation of the mechanism, an introduction of the basic reactivity descriptors is given. According to the Koopmans' theorem for closed-shell molecules, negative energy values of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) express ionization potential (I) and electron affinity (A), respectively [48]. When the values of I and E are known, one can determine the absolute hardness (η), softness (S), and chemical potential (μ): (Hardness

$\eta = E_{\text{LUMO}} - E_{\text{HOMO}}$, softness $S = 1/2\eta$, chemical potential $\mu = (E_{\text{LUMO}} + E_{\text{HOMO}})/2$. Nucleophilicity index N is defined as $N = E_{\text{HOMO}(\text{nu})} - E_{\text{HOMO}(\text{TCE})}$ and tetracyanoethylene (TCE) is used as reference for nucleophilicity scale [49]. Similar to chemical hardness and chemical potential, the concept of electrophilicity (ω) has been introduced by Parr et al. [50]. This reactivity descriptor calculates the stabilization in energy when the system gets an additional electronic charge ΔN from the environment. The electrophilicity is defined as $\omega = \mu^2/2\eta$. In the past few years, the local variants of the global reactivity parameters have been introduced which indicate the most reactive sites intramolecularly and intermolecularly. These local variants are calculated from Fukui function and global parameters [51]. The Fukui functions are used to identify the local reactivity sites (electrophilic or nucleophilic) of molecules in a reaction where the electron transfer is involved. Single-point $N + 1$ and $N - 1$ calculations were carried out for an N

electrons system. The electronic population for an atom k in the molecules has been calculated from natural population analysis (NPA) or Mullikan population analysis (MPA) [52]. The equations showing a condensed form of Fukui functions for an atom k in a molecule for nucleophilic, electrophilic and radical attacks are outlined as:

$$f_k^+ = [q_k(N + 1) - q_k(N)] \text{ for nucleophilic attack}$$

$$f_k^- = [q_k(N) - q_k(N - 1)] \text{ for electrophilic attack}$$

$$f_E^0 = 1/2[q_k(N + 1) - q_k(N - 1)] \text{ for radical attack}$$

where q_k is the electronic population of atom k of the molecule under investigation.

The global philicity index is the sum of philicity over all atoms, but site selectivity is more important to understand a chemical reaction. Although global philicity values execute

Table 2 Ionization potential (I), electron affinity (A), chemical hardness (η), electronic chemical potential (μ), global softness (S), global nucleophilicity (N), Fukui function (f^-) and local nucleophilicity (N_k)

Carbene	I (eV)	A (eV)	η (eV)	μ (eV)	S (eV)	N (eV)	MPA ¹		NPA ¹	
							f^-	N_k (eV)	f^-	N_k (eV)
9a	2.346	−2.205	4.551	−0.070	9.103	6.775	0.118	0.804	0.093	0.632
10a	2.163	−1.943	4.107	−0.109	8.213	6.958	0.0479	0.334	0.056	0.390

¹ Fukui functions, local nucleophilicities were calculated and compared at the carbenic carbon atoms of the corresponding carbenes

for carbenes generated from corresponding zwitterions obtained at the level of BLYP/6-31G(d)

Fig. 1 Optimized geometries of the carbenes and their allyldichlorosilane complexes

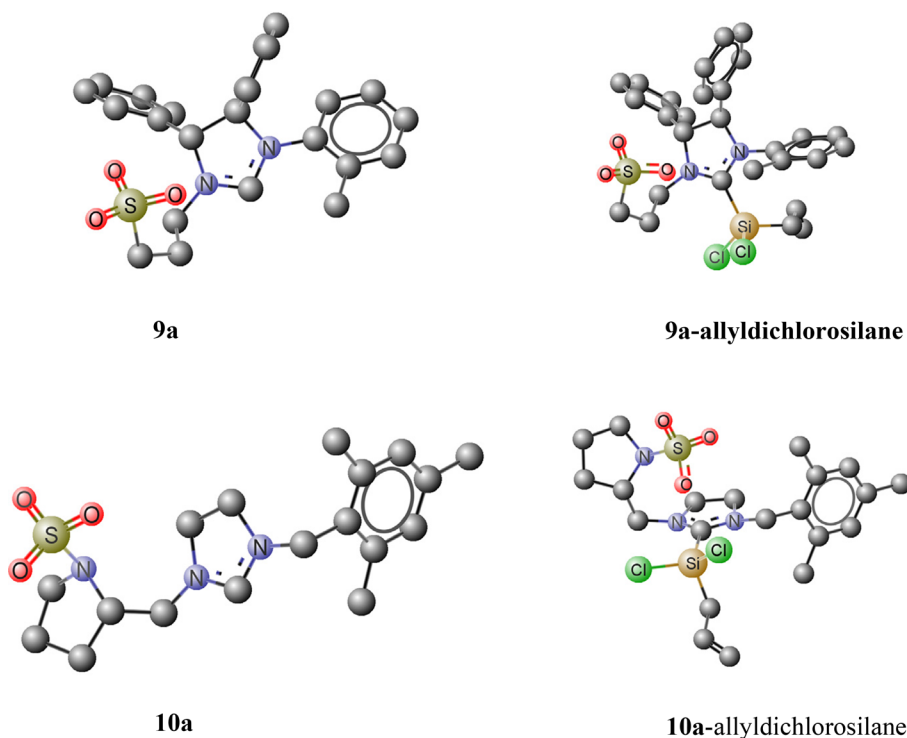


Table 3 Ionization potential (*I*), electron affinity (*A*), chemical hardness (η), electronic chemical potential (μ), global softness (*S*), global electrophilicity (ω), Fukui function (f^+), local electrophilicity (ω_k),and local softness (S_k) for carbene-allyldichlorosilane complexes obtained at BLYP/6-31G(d) level

NHC-silane complex	<i>I</i> (eV)	<i>A</i> (eV)	η (eV)	μ (eV)	<i>S</i> (eV)	ω (eV)	MPA ^a			NPA ^a		
							f^+	ω_k (eV)	S_k (eV)	f^+	ω_k (eV)	S_k (eV)
9a -silane complex	6.24	2.22	4.02	4.23	92.1	2.228	0.123	0.275	11.38	0.253	0.191	7.903
10a -silane complex	5.59	1.45	4.14	3.52	89.4	1.499	0.069	0.104	6.204	0.086	0.099	5.910

^a Fukui functions, local electrophilicities and softness were calculated and compared at silicon atoms of the corresponding carbene-allyldichlorosilane complexes

reliable results yet there are examples in the literature where local indices (i.e., ω_k^α) are more reliable compared to global philicity (ω) [53–55]. Moreover, local philicity expresses combination of information obtained from global to local parameters such as global electrophilicity index, global nucleophilicity index, Fukui function, local softness, or global softness, etc. [56, 57]. Local philicity can be defined as $\omega_k^\alpha = f\omega_k^\alpha$; $\alpha = +, -, 0$. Condensed local nucleophilicity index can be expressed as $N_k = Nf_k^-$ [58]. Local softness describes the reactivity of a specific atom in a molecule and can be defined as $s_k^\alpha = Sf_k^\alpha$; $\alpha = +, -, 0$ [59].

In the proposed mechanism, first step is the nucleophilic attack of carbene generated in situ to allyltrichlorosilane reagent. The more nucleophilic the carbene is, greater is the chance for activated silyl formation and the product in turn. Local nucleophilicity has proven itself a better criterion for explaining the greater nucleophilic power of a certain site in a molecule or between the molecules. It is evident by comparing the values of Fukui function and local nucleophilicity at the carbenic carbons of the corresponding carbenes that the carbene from the zwitterion **9** is more nucleophilic (Table 2). This greater nucleophilicity favors the formation of activated silyl reagent that takes part in the second step. The results are same either calculated from the Mullikan population analysis (MPA) or from the natural population analysis (NPA) (Fig. 1).

The second step involves the activation of the starting material by Lewis acid–base type of interactions. The silicon of the activated allyl reagent acts as Lewis acid for the carbonyl group of benzaldehyde. Again, local electrophilicity and local softness values were calculated at the silicon atom of the proposed Lewis acids made from the NHCs **9a** and **10a**, respectively. The silicon of **9a**-allyldichlorosilane complex shows greater value of Fukui function, local electrophilicity and local softness as compared to the **10a**-allyldichlorosilane complex. Hence it is clear that the **9a**-allyldichlorosilane complex acts effectively as Lewis acid and thus provides higher yield (Table 3).

For the complex leading to poor yield, it can be concluded that silicon of the complex is not electrophilic enough to act as Lewis acid and hence it is not going to catalyze the

reaction. This proposition is also supported by the fact that starting material was recovered after workup in this case. It is pertinent to mention that unlike some of the results reported in the literature [60] the values of Fukui function, local philicity and local softness showed the same trend.

Conclusion

The role of *N*-heterocyclic carbenes as organocatalysts is presented for the first time in the allylation of benzaldehyde. It was found that NHC **9a** generated from the imidazolium zwitterion having alkylsulfonate substituent proved superior catalyst compared to sulfamate substituted **10a**. A quantitative yield of homoallylic alcohol was obtained at low temperature with NHC **9a**. The observed reactivity patterns were justified on the basis of reactivity descriptors calculated from density functional theory.

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