Encapsulated Reactive Groups

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Encapsulated N-Heterocyclic Carbenes in Silicones without Reactivity Modification**

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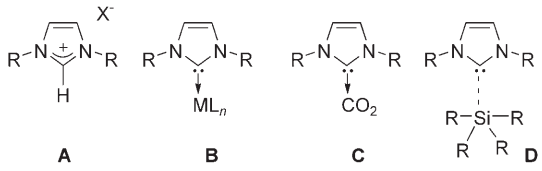
N-heterocyclic carbenes (NHCs)[1] are recognized as powerful tools in organometallic chemistry as ligands for transition metals[2] as well as in organic chemistry as nucleophilic organocatalysts.[3]

The deprotonation of air-stable imidazolium salts **A** using strong bases is the most commonly used method to prepare



air-sensitive NHCs. The development of storable precursors of NHCs[4,5] or of original methods[6] to more easily generate NHCs is an active research area. Herein we describe the first efficient stabilization of NHCs in silicone derivatives, without any significant modification of the reactivity compared to the free species.

To conserve highly reactive species, two types of protection (physical and chemical) can be considered. Physical protection in paraffin oils is the usual method for air-sensitive compounds, such as alkali metals or metal hydrides. Recently, a few encapsulations of reactive species in hydrophobic cages,[7,8] which can be kept even in water without decomposition, have been reported.[9] Bowden et al. reported that Grubbs catalysts occluded in a silicone resin can be used for the metathesis reaction in water.[10] For NHCs, chemical protection using a Lewis acid is also effective. The stability of NHC ligands on transition metals **B** is very well known. Crabtree et al. recently developed an air- and moisture-stable NHC–CO_2 adduct **C** which can be used as a useful precursor for the synthesis of NHC complexes.[5] However, in all these cases, the NHC–Lewis acid interactions are so strong that the release of the NHC requires thermal activation, and, to our knowledge, there are no reports concerning the use of these protected carbenes in organocatalysis.

In this context, we chose the hydrophobic, chemically resistant polydimethylsiloxane (PDMS) as a matrix to protect NHCs. In addition, since silicon compounds show weak Lewis acid character depending on the substituents on silicon, an additional chemical stabilization effect on NHCs can also be expected. In fact, a stable hypervalent NHC–SiR_4 complex **D**, using chlorosilanes with relatively strong Lewis acid character ($SiR_4 = SiCl_4$, $SiPh_2Cl_2$), has been reported.[11]

Silicones containing NHCs were prepared by two methods: either by dissolving the NHC in already prepared PDMS (10 wt%) or through the polymerization of octamethylcyclotetrasiloxane (known as D_4) catalyzed by the NHC[12] itself in the presence of hexamethyldisiloxane (known as M_2) as a blocking agent.

The decomposition of NHCs **1a–d** in different media was monitored by ^{1}H NMR spectroscopy in C_6D_6 (Table 1). The results clearly show that simple physical protection of NHCs by polymeric compounds is not sufficient to conserve the carbene as indicated by the relatively rapid degradation (hydrolysis) of the NHC **1a** into the iminoformamide **2a** in a chemically inert polymer, such as paraffin (Table 1, entry 9). In contrast, using PDMS (Table 1, entry 5), or silicone oligomer MD_4M (Table 1, entry 10), no decomposition was observed after one week, and only a slight amount of hydrolyzed product (**2a**, 5–8%) was observed after one month. However, the NHC **1a** in hexamethyldisiloxane M_2 (Table 1, entry 7), which possesses weaker Lewis acid silicon centers, decomposes more rapidly (complete hydrolysis after one week). These results clearly demonstrate the importance of the chemical protection through a silicon–NHC interaction for the protection of NHCs. Although carbene **1a** is stable to oxidation, carbenes **1b** and **1c** are much more reactive. Particularly, **1c** is a highly reactive oily product, which slowly decomposes at room temperature.[13] In fact, **1c**, the NHC with the smallest substituents, quickly oxidized in PDMS

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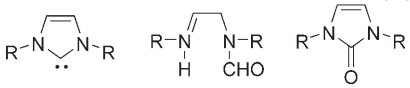
Table 1: Degradation of NHCs **1a–d** in different media (%).[a]



1 **2** **3**

Entry		**2**+**3** [%][b]				
		3 h	20 h	48 h	1 w	4 w
1	**1a**[c]	5	9	84		
2	**1b**[c]	13	23	95		
3	**1c**[c]	58	60	100		
4	**1d**[c]	5	20	100		
5	**1a**-PDMS[d]	0	0	1	2	8
6	**1c**-PDMS	3	15	45	81	
7	**1a**-M_2[e]	0	2	15	100	
8	**1a**-THF	0	2	25	100	
9	**1a**-Paraffin[f]	0	0	7	13	87
10	**1a**-MD_4M[g]	0	0	0	1	5
11	**1a**-$MD_4^{Ph}M$[h]	0	0	0	0	0
12	**1b**-$MD_4^{Ph}M$	1	4	5	6	8
13	**1c**-$MD_4^{Ph}M$[i]	0	0	2	3	8
14	**1d**-$MD_4^{Ph}M$	12	16	25	100	

[a] **1a**: R = *t*Bu, **1b**: R = cyclohexyl, **1c**: R = *i*Pr, **1d**: R = Mes = 2,4,6-$Me_3C_6H_2$. [b] Proportion of decomposed products (**2**+**3**) relative to **1** after the times indicated, determined from the intensity of signals in the ^{1}H NMR spectrum for **1**, **2** and **3**. [c] **1a** (crystals), **1b** (crystals), **1c** (distillated oil), **1d** (crystals). [d] PDMS = polydimethylsiloxane. [e] M_2 = $(Me_3Si)_2O$. [f] In this case, the decomposition estimation by NMR spectroscopy may not be precise because the NHC solution continually separated into two phases over the course of the decomposition. [g] $MD_4M = Me_3SiO(SiMe_2O)_4SiMe_3$. [h] $MD_4^{Ph}M = Me_3SiO(Me_2SiO)_{6.6}(MePhSiO)_{7.1}SiMe_3$. [i] Owing to the high volatility of **1c**, 26% of **1c** was lost in 4 weeks, which was indicated by the gradual decrease of intensity of signals for **1c** compared to that for silicone oligomers as measured by in ^{1}H NMR spectroscopy.

(Table 1, entry 6) to give the corresponding cyclic urea **3c** after one week. Silicones are not only hydrophobic but also highly gas- (and notably oxygen-) permeable polymers, which promotes the oxidation rather than the hydrolysis of NHCs. The situation dramatically changes in the case of the silicone oligomer $MD_4^{Ph}M$, which has more Lewis acidic silicon centers owing to the presence of phenyl substituents. This oligomer strongly protects the more reactive NHCs **1b,c** (Table 1, entries 12 and 13; 8% decomposition after 4 weeks), and NHC **1a** was almost perfectly protected (Table 1, entry 11). Noteworthy is the absence of protection of NHC **1d** in $MD_4^{Ph}M$ (Table 1, entry 14). Complete decomposition of **1d** occurs within only one week, which is probably due to the presence of bulky mesityl groups and the less basic character of **1d** (π-accepting groups on nitrogen atoms), which hamper the silicon–NHC interaction.[12]

To better understand the interaction between NHCs **1** and silicones, we carried out some DFT and ab initio calculations[14,15] on the binding between NHC **1e** and model silicone oligomers with different substituents (**4a**: R = Me, **4b**: R = Ph, Figure 1). The structures of the NHC–silicone complexes **5a**,**b** are shown in Figure 1. As expected, in both complexes **5a**,**b** there is an interaction between the NHC and the silicon center to give a pentacoordinate silicon atom[16] with much longer Si–C_{NHC} distances (1.982 and 1.988 Å, bond orders of 0.58) than that of the reported NHC complex with more

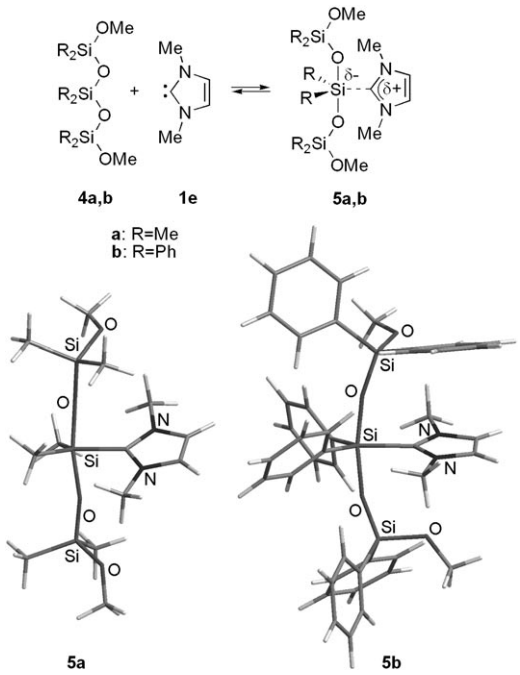
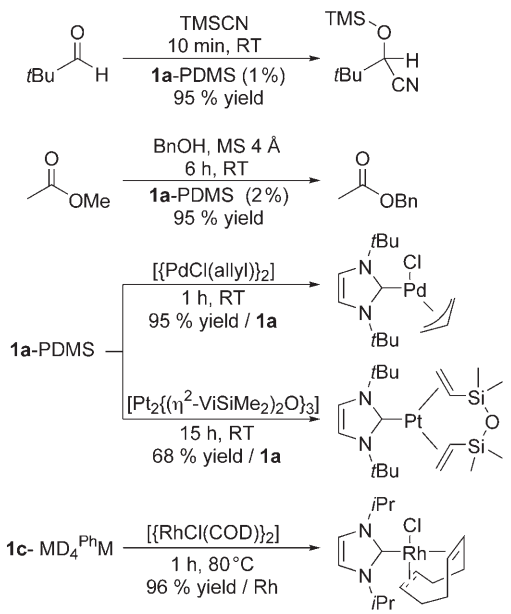


Figure 1. B3LYP/6-31G*-optimized structures of complexes **5a**,**b**. Bond lengths are given in Å.

electrophilic tetrachlorosilane (1.911 Å), indicating a weaker NHC–silicone interaction.[11] Indeed, the theoretical calculations indicate the exothermic formation of complexes (**5a**,**b**) with relatively small stabilization energies of 2.6[17] and 5.4[17,18] kcal mol^{-1}, respectively. The interaction in **5b** is about 2.8 kcal mol^{-1} [18] stronger than that in **5a**, in good agreement with the experimental observations.

Because of the weak Si–C_{NHC} bond energies in the complexes, the easy dissociation of complexes of type **5** in dilute solutions would be expected. In fact, in contrast to the relatively inert NHC complexes,[5,19] the reactivity of NHCs in silicones (**1a**-PDMS, **1c**-$MD_4^{Ph}M$) was found to be almost identical to that of the free NHC **1**. To check the reactivity of **1a**-PDMS as an organocatalyst, several known organic reactions catalyzed by NHCs, namely cyanosilylation,[20] transesterification (Scheme 1),[21] and the polymerization of D_4[12] were tested. In all cases, reaction proceeded smoothly with the conditions previously described, and the resulting products were obtained in high yields. In the same way, the synthesis of NHC–transition-metal complexes of Pd^{II},[22] Pt^0,[23] and Rh^{II}[24] were also successfully achieved with **1a**-PDMS or **1c**-$MD_4^{Ph}M$, indicating that the silicone polymer does not perturb the reaction. Moreover, PDMS appears to be suitable as the protecting media for the preparation of late-transition-metal complexes, since there are only very few reported cases where complexes are known to react with PDMS.[25] In all cases, the silicone matrix was easily removed by washing the resulting complexes with pentane.

The convenience of stable NHCs in silicone derivatives is clear, as the mixture (**1a**-PDMS or **1c**-$MD_4^{Ph}M$) can be introduced into the Schlenk tube using a spatula in air without any problem for all the test reactions.



Scheme 1. Reactions using NHCs in silicones (**1a**-PDMS and **1c**-$MD_4^{Ph}M$). TMS = trimethylsilyl, Bn = benzyl, MS = molecular sieves, Vi = vinyl, COD = cyclooctadiene.

In conclusion, silicone derivatives were found to be an efficient protecting medium for N-heterocyclic carbenes, and these derivatives allow moisture-sensitive NHCs to be handled or stored in air without any special precautions. More interestingly, this encapsulation is efficient for NHCs which are usually not stable at room temperature, such as **1c**. In fact, only a weak carbene–Lewis acid interaction (ca. 3–5 kcal mol^{-1}) stabilizes NHCs enough for them to be stored without significant decomposition. Furthermore, the weakness of this interaction does not inhibit the reactivity of the NHCs.

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