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Uncovering diverse reactivity of NHCs with diazoalkane: C–H activation, C=C bond formation, and access to N-heterocyclic methylenehydrazine†

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N-heterocyclic carbenes (NHCs) have attracted significant attention due to their strong σ -donating capabilities, as well as their transition-metal-like reactivity towards small molecules. However, their interaction with diazoalkanes remains understudied. In this manuscript, we explore the reactivity of a series of stable carbenes, encompassing a wide range of electronic properties, with $\text{Me}_3\text{SiCHN}_2$. 5-SIPr activates the C–H bond of $\text{Me}_3\text{SiCHN}_2$, resulting in the formation of a novel diazo derivative (**1**), while carbenes such as 5-IPr, 6-SIPr, and diamido carbene yield N-heterocyclic methylenehydrazine derivatives (**3**, **4**, and **8**). The reaction of $\text{Me}_3\text{SiCHN}_2$ with 5-*i*Bu unexpectedly leads to the formation of a triazole ring linked with the imidazole moiety *via* a C=C double bond (**6**) alongside the azine product (**7**). Substituting the diazoalkane with diazoester consistently yields azine derivatives (**9–12** and **14**). Only in the case of 5-*i*Bu, an imidazolium salt with tetrazenide anion (**13**) was obtained as a side product. The reaction of **4** with HCl resulted in the desilylprotonation to form a salt, **5a**, which undergoes deprotonation upon using bases such as Et_3N and KHMDS to form N-heterocyclic methylene hydrazine, **5**. Theoretical calculations have been conducted to elucidate the diverse mechanisms underlying product formation.

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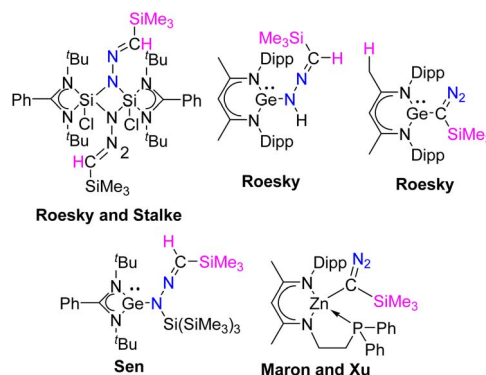
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Introduction

Diazoalkanes have been recognized for over a century and have demonstrated their versatility as significant building blocks in organic synthesis. Over the past two decades, there has been a substantial increase in research focused on the reactions between diazoalkanes and transition metal complexes. By examining these structures, it is conceivable that diazoalkanes engage in reactions with transition metal complexes, by serving as 1,3-dipoles, N-nucleophiles, or C-nucleophiles.¹ In contrast, to this well-explored chemistry, the reactions of diazoalkanes with compounds having low-valent main-group elements are poorly studied (Scheme 1). Roesky and coworkers reported the reaction of silicon(II) species, LSiCl [$\text{L} = \text{PhC}(\text{N}^t\text{Bu})_2$], with $\text{Me}_3\text{SiCHN}_2$.² The same group documented the reactions between β -diketiminate germylene hydride, L_1GeH [$\text{L}_1 = \text{HC}$

$\{(\text{CMe})(\text{NAr})\}_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$] and $\text{Me}_3\text{SiCHN}_2$, which resulted in the end-on insertion of the diazoalkane moiety into the germanium hydride.³ Our group made a similar observation when we studied a reaction involving $\text{PhC}(\text{N}^t\text{Bu})_2\text{GeSi}(\text{SiMe}_3)_3$ and $\text{Me}_3\text{SiCHN}_2$, leading to the insertion of the diazoalkane motif into the Ge–Si bond.⁴ Very recently, the groups of Maron and Xu reported the synthesis of the first example of a well-defined zinc α -diazoalkyl complex by reacting a zinc hydride with $\text{Me}_3\text{SiCHN}_2$.⁵



Scheme 1 Examples of the reactivity of diazoalkane with main-group species.

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It is explicit from the aforementioned discussion that while the reactions of diazoalkane with Si(II), Ge(II) are reported, there is only one paper reported describing the interaction of diazoalkane with stable N-heterocyclic carbene (NHC) resulting in azine formation.⁶ In addition, there is another report on the reaction of 2,2,2-trifluorodiazooethane with the *in situ* generated N-heterocyclic carbenes leading to azine formation.⁷ As a consequence, systematic investigation of the reaction of diazoalkane with NHCs is important. Here, we report the reactions of Me₃SiCHN₂ with a diverse array of NHCs, which resulted in divergent reactivities: (a) 5-IPr, 6-SIPr, and diamido carbene led to N-heterocyclic methylenehydrazine derivatives; (b) 5-SIPr inserts into the C–H bond of Me₃SiCHN₂ reminiscent to Xu's dehydrocoupling reaction of Me₃SiCHN₂ with zinc hydride; (c) 5-I^tBu led to a 1,2,4-triazole ring formation connected to the imidazole unit with a C=C bond; (d) the reaction of 5-IPr and 5-I^tBu with Me₃SiCHN₂ and water led to the formation of novel N-heterocyclic hydrazines, which were structurally unknown so far.

Results and discussion

Case I: reaction with 5-SIPr

Because of the report on the reactivity of 5-IMes with diazoalkanes,⁶ we have initiated our investigation with the more nucleophilic and saturated 5-SIPr to determine whether the reaction proceeds similarly or diverges in reactivity. Interestingly, treatment of 5-SIPr with Me₃SiCHN₂ activated the C–H bond of diazoalkane yielding diazoalkyl compound **1**, accompanied by the formation of compound **2** *via* hydrolysis due to the presence of adventitious water (Scheme 2).⁸ NHCs have shown a remarkable ability to mimic transition metals in activating robust C–H bonds.⁹ Following the seminal work on the C–H activation using 5-SIMes by Arduengo's group in 1999,¹⁰ the groups of Whittlesey,¹¹ Bielawski,¹² Turner¹³ and Bertrand¹⁴ explored various NHCs, including ring-expanded, diamido, and cyclic alkyl amino carbenes for C–H bond activation. However, the insertion of NHC into the C–H bond of diazoalkane is unprecedented, as the C–H bond of diazoalkanes is not highly acidic. To the best of our knowledge, there is only one report published by Roesky and coworkers, where the C–H activation of diazoalkane takes place at the exocyclic double bond of nacnac N-heterocyclic germylene (Scheme 1).¹⁵ Crystallization of the crude reaction mixture in *n*-hexane at room temperature yielded block-shaped yellow crystals. The ¹H NMR spectrum shows a peak at –0.38 ppm for the SiMe₃ groups, and the

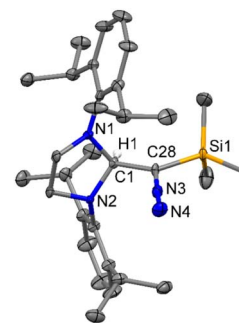
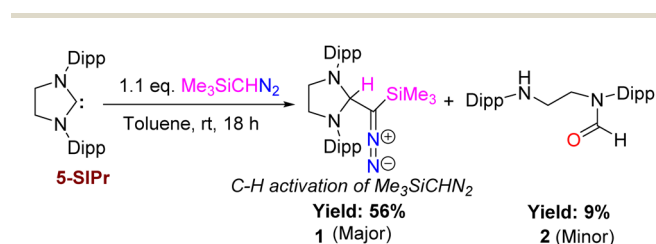


Fig. 1 The molecular structure of **1** with anisotropic displacement parameters are depicted at the 50% probability level respectively. The hydrogen atoms are not shown for clarity. Selected distances (Å) and angles (deg): C1–C28 1.530(4), N3–N4 1.143(4), N3–C28 1.307(4), Si1–C28 1.861(3), N1–C1–N2 102.4(2), N4–N3–C28 178.8(3), N3–C28–C1 117.4(3), N3–C28–Si1 117.8(2).

corresponding peak appears at –2.1 ppm in the ²⁹Si NMR spectrum. The molecular structure of compound **1** reveals a linear geometry of C28–N3–N4 (178.8(3)°) (Fig. 1).

Using density functional theory (DFT) calculations at the PBE0-D3/def2TZVP//PBE-D3/def2TZVP level of theory, incorporating the COSMO solvation model for toluene ($\epsilon = 2.38$), we systematically investigated the formation of compound **1** (see the ESI† for detailed computational methodology). Additionally, we explored the reasons why the putative azine product (**1'**) was not obtained (Fig. 2).

The DFT results reveal that the formation of **1** is exergonic, with a free energy (ΔG_{sol}) release of 10.2 kcal mol^{–1}, attributed to C–H bond activation of the diazoalkane. Conversely, the formation of **1'** is significantly more thermodynamically favorable, releasing 32.1 kcal mol^{–1} of free energy, indicating that **1'** is 21.9 kcal mol^{–1} more stable than **1**. However, kinetic analysis shows that the free energy barrier ($\Delta G_{\text{sol}}^\ddagger$) for the formation of **1'**



Scheme 2 Insertion of NHC into the C–H bond of diazoalkane in the reaction of 5-SIPr with Me₃SiCHN₂.

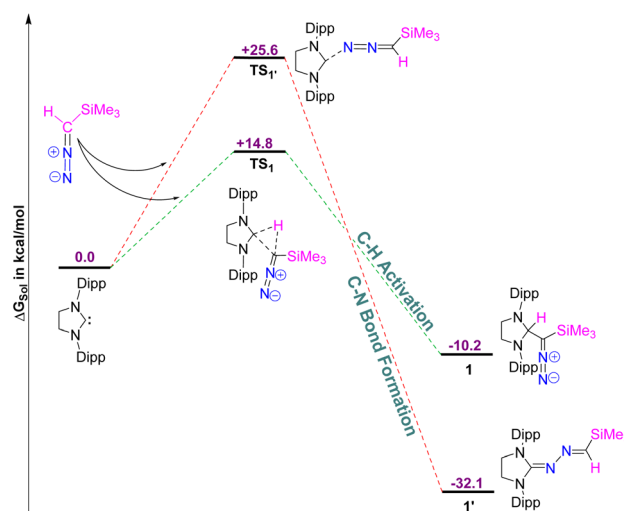


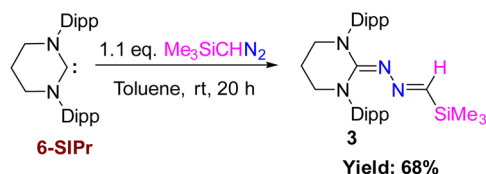
Fig. 2 The free energy profile for the formation of **1** and **1'**. The energy values are in kcal mol^{–1}. Level of theory: PBE0-D3/def2TZVP//PBE-D3/def2TZVP with solvent toluene ($\epsilon = 2.38$).

is 10.8 kcal mol⁻¹ higher than that for **1**. Specifically, the free energy barrier for **1** is calculated to be 14.8 kcal mol⁻¹, whereas for **1'**, it is 25.6 kcal mol⁻¹. Therefore, despite the greater thermodynamic stability of **1'** the reaction favors the formation of **1**, as it proceeds *via* a lower free energy pathway, making **1** the kinetically preferred product.

Case II: reaction with 6-SIPr

Very recently, we employed a six-membered saturated NHC, 6-SIPr, to isolate parent oxoborane,¹⁶ cationic bori-¹⁷ and boronic acid,¹⁸ and investigated their ring-expansion chemistry in the presence of borane¹⁹ and alane.²⁰ The unexpected results obtained from the reaction involving 5-SIPr prompted us to investigate the reaction with 6-SIPr. In contrast to the previously mentioned results, the reaction of 6-SIPr with Me₃SiCHN₂ in toluene for 20 hours yielded a yellow-colored solution. Subsequent workup and characterization confirmed the formation of an unprecedented trimethylsilyl-substituted N-heterocyclic methylene hydrazine (**3**) (Scheme 3). The characteristic peak of Me₃SiCHN₂ appeared as a singlet at 7.40 ppm for C–H and –0.21 ppm for Me₃Si group in the ¹H NMR spectrum, and a resonance at –11.2 ppm in the ²⁹Si NMR spectrum confirmed the presence of the trimethylsilyl group. Compound **3** crystallized in the triclinic *P* $\bar{1}$ space group, and its molecular structure is depicted in Fig. 3. The C=N and N–N bond lengths in **3** are 1.308(3) and 1.389(3) Å, respectively, consistent with the bond lengths observed in azines.

The DFT calculations reveal that the formation of **3** is thermodynamically favored over **3'** by 24.4 kcal mol⁻¹ (Fig. 4).



Scheme 3 Reaction of 6-SIPr with Me₃SiCHN₂ and the formation of trimethylsilyl protected N-heterocyclic methylene hydrazine (**3**).

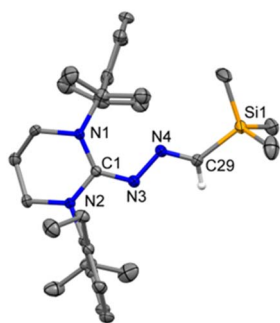


Fig. 3 The molecular structure of **3** with anisotropic displacement parameters are depicted at the 50% probability level respectively. Hydrogen atoms and vibrational atoms are not shown for clarity. Selected distances (Å) and angles (deg): N3–C1 1.308(3), N3–N4 1.389(3), N4–C29 1.288(4), Si1–C29 1.861(3), N1–C1–N2 119.2(2), C1–N3–N4 115.7(2), C29–N4–N3 112.8(2), N4–C29–Si1 122.8(2).

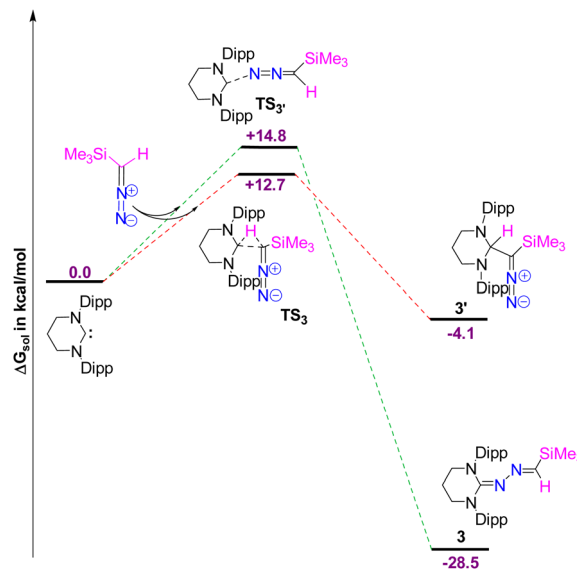


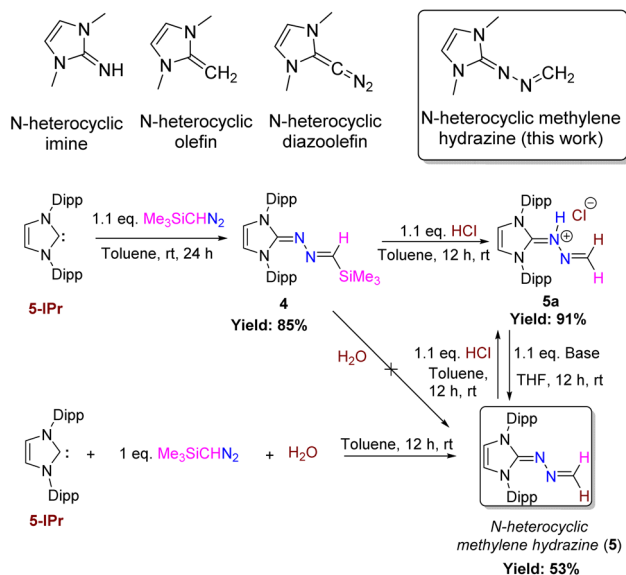
Fig. 4 The free energy profile for the formation of **3** and **3'**. The energy values are in kcal mol⁻¹. Level of theory: PBE0-D3/def2TZVP//PBE-D3/def2TZVP with solvent toluene ($\epsilon = 2.38$).

Although the free energy barrier for forming **3'** is 12.7 kcal mol⁻¹, only 2.1 kcal mol⁻¹ lower than that of **3**, the weakly exergonic C–H bond activation in **3'** (releasing 4.1 kcal mol⁻¹ of free energy) may allow the system to overcome the backward barrier of 16.8 kcal mol⁻¹, potentially reverting to the initial reactants at room temperature. In contrast, the formation of **3** is significantly more exergonic, releasing 28.5 kcal mol⁻¹ of free energy (ΔG_{sol}). Once formed, **3** is unlikely to revert to the initial reactants due to the high backward energy barrier of 43.3 kcal mol⁻¹, which is not surmountable at room temperature. Therefore, **3** is identified as the thermodynamically controlled product.

Case III: reaction with 5-IPr

With these two divergent reactivities in hand, we wondered how Me₃SiCHN₂ would react with unsaturated carbenes. The C–H activation was not expected because Bertrand's group noted no reaction of terminal alkyne with 5-IPr.¹⁴ The reaction of 5-IPr with Me₃SiCHN₂ for 24 h in toluene at room temperature resulted in a deep red-colored solution. The NMR spectrum of the crude mixture reveals the formation of a product (**4**) (Scheme 4), akin to **3**. The ¹H NMR shows a peak at –0.18 ppm for the Me₃Si protons. The corresponding resonance in the ²⁹Si NMR appears at –10.9 ppm. Attempts to hydrolyze the Me₃Si group in compound **4** using methanol and water were unsuccessful. However, treatment with HCl led to the unexpected formation of **5a** *via* desilylprotonation. Our investigation revealed that the reaction consistently yields product **5a** regardless of the equivalence of HCl used (0.5–1.1 equiv.) with a maximum yield of 91% obtained upon using 1.1 equivalents of HCl in toluene. Interestingly, the dehydrohalogenation of **5a** using bases such as Et₃N and KHMDS yielded **5** (Scheme 4). Likewise, the treatment of **5** with HCl gives back **5a**. We have





also noted that the reaction of 5-IPr with $\text{Me}_3\text{SiCHN}_2$ in the presence of a stoichiometric amount of water straightforwardly afforded compound **5** exclusively, presumably *via in situ* generation of CH_2N_2 . Attempts to prepare analogous compound with 6-SIPr led to an intractable mixture of products.

While there are a huge number of azines reported in the literature,²¹ an azine with a terminal methylene group (**5**) is unprecedented, and a new addition to the tapestry of NHC based organic functionalities such as N-heterocyclic imine,²² N-heterocyclic olefin,²³ N-heterocyclic diazoalkene²⁴ *etc.* The molecular structures of **4**, **5**, and **5a** are shown in Fig. 5. Similar

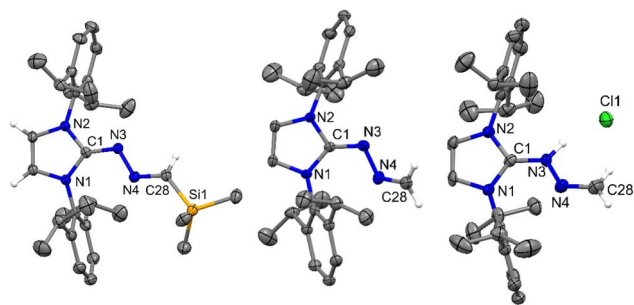


Fig. 5 The molecular structures of **4** (left), **5** (middle), and **5a** (right) with anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except on terminal C) are not shown for clarity. Selected distances (Å) and angles (deg) for **4** (Vibrational atoms are omitted for clarity): N3–C1 1.309(2), N3–N4 1.394(2), N4–C28 1.286(2), Si1–C28 1.871(2), N2–C1–N1 109.85(14), C1–N3–N4 112.62(15), C28–N4–N3 114.07(15), N4–C28–Si1 119.82(14). **5**: N3–C1 1.308(3), N3–N4 1.397(3), N4–C28 1.275(3), N1–C1–N2 105.61(17), C1–N3–N4 112.95(17), C28–N4–N3 112.9(2); **5a** (H_2O molecule is not shown for clarity): N3–C1 1.334(4), N3–N4 1.375(3), N4–C28 1.271(4), N2–C1–N1 107.7(3), C1–N3–N4 116.0(3), C28–N4–N3 116.1(3).

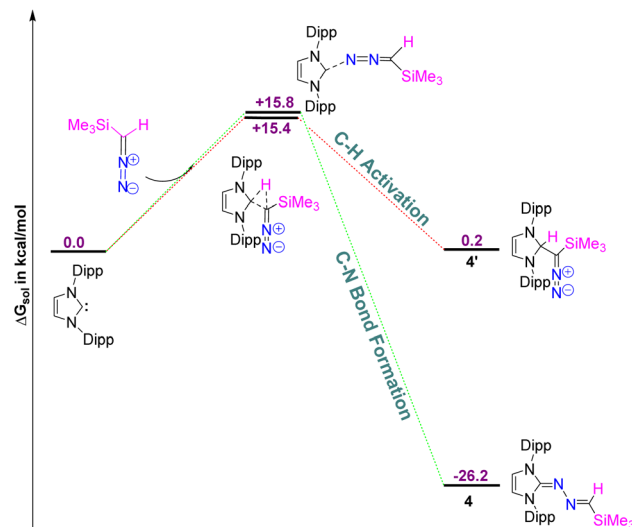


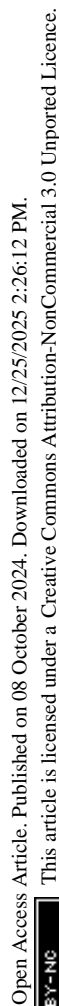
Fig. 6 The free energy profile for the formation of **4** and **4'**. The energy values are in kcal mol^{-1} . Level of theory: PBE0-D3/def2TZVP//PBE-D3/def2TZVP with solvent toluene ($\epsilon = 2.38$).

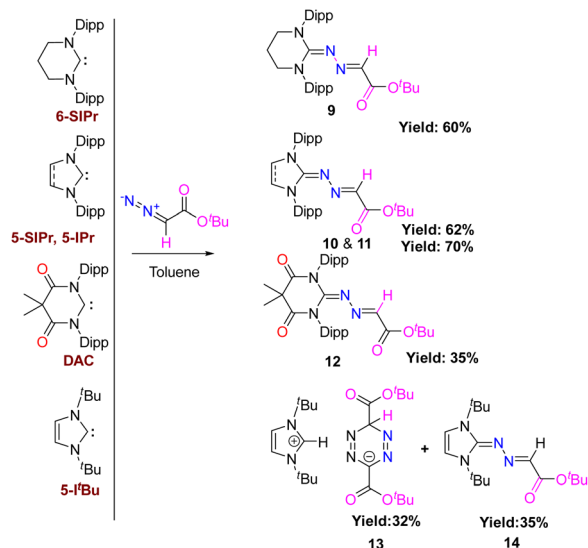
to 6-SIPr, the formation of **4** is favored over the alternative C–H activation product, **4'**, with a free energy (ΔG_{sol}) of $-26.2 \text{ kcal mol}^{-1}$ and a free energy barrier ($\Delta G_{\text{sol}}^\ddagger$) of $+15.8 \text{ kcal mol}^{-1}$, making it the thermodynamically controlled product (Fig. 6).

To gain insight into the composition of the reaction mixture, we performed the reaction at a low temperature for 1.5 hours to trap the kinetically controlled product. However, the ^1H NMR spectrum primarily displayed resonances corresponding to the starting material, with a slight formation of compound **4**. Furthermore, we monitored the reaction progress by recording ^1H NMR spectra at various time intervals, which confirmed the formation of a single product (ESI, Fig. MS1–MS3).†

Case IV: reaction with 5-I'Bu

Differing reactivities of $\text{Me}_3\text{SiCHN}_2$ with different nucleophilic carbenes prompted us to perform the reaction with the more basic I'Bu.²⁵ The reactivity of 5-I'Bu towards $\text{Me}_3\text{SiCHN}_2$ was not selective and resulted in the formation of a mixture of products, **6** and **7** (Scheme 5), which were confirmed by single crystal XRD studies (Fig. 7 and 8). The most interesting feature of **6** is the triazole ring formation from diazoalkane. The ^1H NMR of **6** shows three distinct peaks at 1.48, 7.37, and 8.27 ppm corresponding to methyl protons of I'Bu group, carbene backbone, and triazole ring protons, respectively. While the generation of **6** is quite unprecedented, and can be considered as a new type of N-heterocyclic olefin, the formation of **7** was anticipated from the aforementioned reactions with other NHCs. The separation of compounds **6** and **7** is simple. Compound **6** gets precipitated in hexane or toluene, while the filtrate contains a mixture of both **6** and **7**. Hence, we could not determine the yield of **7** as well as its complete spectroscopic characterization was not possible. The solid-state structure of **6** reveals that the C–C bond length between the triazole and imidazole ring is significantly longer than a C=C bond with a bond distance of $1.4651(15) \text{ Å}$. The tau value for **6** is 0.6 (Tables S1 and S2†). The increased



Scheme 8 Reaction of different carbenes with $\text{COO}^t\text{BuCHN}_2$.

formation of the same kind of products (9–12 and 14) except 5- t Bu as shown in Scheme 8. Their molecular structures are shown in Fig. 10.

The reaction of 5- t Bu with diazoester also resulted in the formation of the corresponding imidazolium salt with tetrazenide counter anion (13)²⁷ alongside 14. Even though X-ray diffraction of a single crystal provided clear proof into the connectivity of compound 12 (see Fig. S61, ESI†), we abstain from discussing bonding parameters due to the poor quality of the data. The DFT calculations for the reactions of various NHCs with diazoester are presented in Fig. 11. The energy profile diagram clearly indicates that for diazoester, all products (9–11 and 14) are formed through thermodynamically controlled pathways. This is evidenced by the higher free energy barriers for all direct C–N bond formation reactions compared to their competing C–H bond activation pathways.

Finally, in order to understand the formation of the new imidazolium salt with a tetrazenide counterion (13) from the reaction of a diazoester with 5- t Bu, comprehensive DFT calculations were performed (Fig. 11). As with other NHCs, 5- t Bu reacts with the diazoester in two possible ways, leading to either compound 14, *via* direct C–N bond formation, or compound 14', through C–H bond activation. The free energy difference between these pathways is 5.3 kcal mol^{−1}, with the C–N bond formation requiring 11.4 kcal mol^{−1}, and C–H activation requiring 6.1 kcal mol^{−1}. This suggests that both pathways are kinetically accessible. Despite the kinetic feasibility of both routes, compound 14 is thermodynamically more stable than compound 14' by 18.9 kcal mol^{−1} (see Fig. 12).

Moreover, the formation of compound 13 involves the reaction of an additional diazoester unit with either compound 14 or 14', so both pathways were explored as depicted in Fig. 12 below. The DFT calculations revealed that the reaction of diazoester with compound 14 leads to a six-membered cyclized product, **Int1'**, which is endergonic, requiring 55.4 kcal mol^{−1} of free energy. The free energy barrier ($\text{TS}_{\text{Int13'}}$) for this [3 + 3]

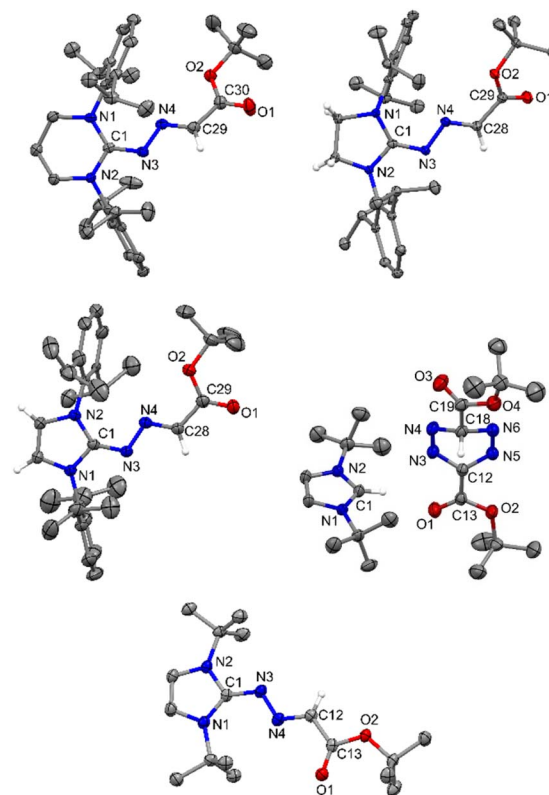


Fig. 10 The molecular structures of 9, 10, 11, 13, and 14 with anisotropic displacement parameters are depicted at the 50% probability level and 13 at the 30% probability level. Hydrogen atoms are not shown for clarity. Selected distances (Å) and angles (deg) 9: N3–C1 1.327(2), N3–N4 1.366(2), N4–C29 1.287(3), C29–C30 1.462(3), O1–C30 1.216(3), O2–C30 1.333(2), N2–C1–N1 117.53(17), C1–N3–N4 116.22(15), C29–N4–N3 111.92(16), O1–C30–O2 124.66(19), O1–C30–C29 120.08(19). 10: N3–C1 1.313(2), N3–N4 1.3745(18), N4–C28 1.283(2), C28–C29 1.474(2), O1–C29 1.213(2), O2–C29 1.3402(19), C1–N1–C2 109.54(13), C1–N3–N4 111.97(13), C28–N4–N3 113.59(14), N4–C28–C29 121.63(15), O1–C29–C28 120.95(15), O2–C29–C28 113.27(14). 11: (Vibrational atoms are omitted for clarity): N3–C1 1.328(2), N3–N4 1.365(2), N4–C28 1.288(2), C28–C29 1.461(3), O1–C29 1.216(2), O2–C29 1.336(2), C1–N1–C2 109.99(14), C1–N3–N4 112.05(15), C28–N4–N3 113.42(15), N4–C28–C29 122.29(17), O1–C29–C28 121.50(18), O2–C29–C28 114.02(16). 13: (Vibrational atoms are omitted for clarity): N1–C1 1.326(3), N2–C1 1.328(3), N3–N4 1.289(3), N5–N6 1.287(3), N3–C12 1.366(3), N5–C12 1.369(3), C12–C13 1.460(3), C18–C19 1.507(4), N1–C1–N2 109.8(2), N4–C18–N6 109.4(2), N3–C12–N5 117.7(2), N6–N5–C12 117.2(2), N4–N3–C12 117.2(2), N3–N4–C18 110.55(19), N5–N6–C18 110.31(19). 14: C1–N3 1.342(2), N3–N4 1.342(2), N4–C12 1.292(3), C12–C13 1.462(3), O1–C13 1.216(2), O2–C13 1.355(2), N1–C1–N2 106.78(16), C1–N3–N4 114.86(17), N3–N4–C12 114.94(17), O1–C12–C13 126.27(19), O2–C12–C13 109.21(17).

cyclization is 67.4 kcal mol^{−1}, which is too high to occur at room temperature. This suggests that this pathway is unlikely.

In contrast, when the diazoester reacts with compound 14', it forms the exergonic intermediate **Int13** (Fig. 12), passing through the transition state TS_{Int13} with a barrier of 16.9 kcal mol^{−1}, which is 29.6 kcal mol^{−1} lower than the corresponding barrier ($\text{TS}_{\text{Int13'}}$) for compound 14. Finally, **Int13** undergoes a six-membered cyclization to yield the final product, compound 13,



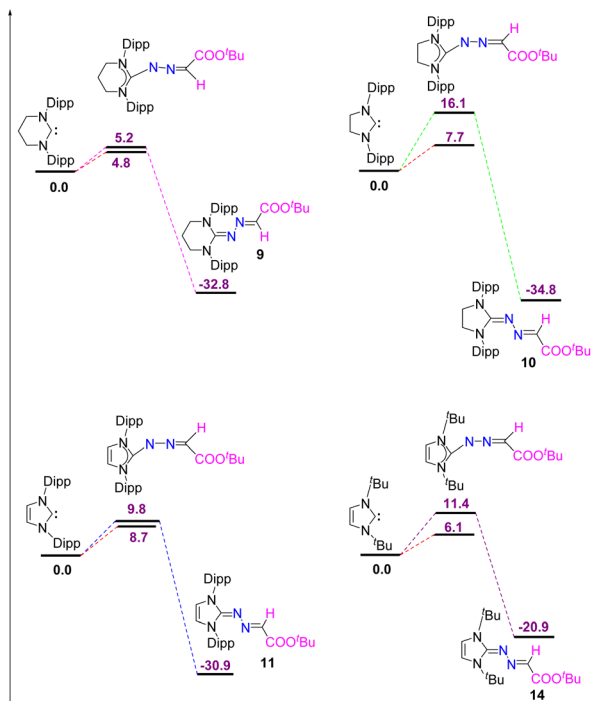


Fig. 11 The free energy profiles for the reaction of diazoester with different NHCs have been shown here. All values are in kcal mol⁻¹. Level of theory: PBE0-D3/def2TZVP//PBE-D3/def2TZVP with solvent toluene.

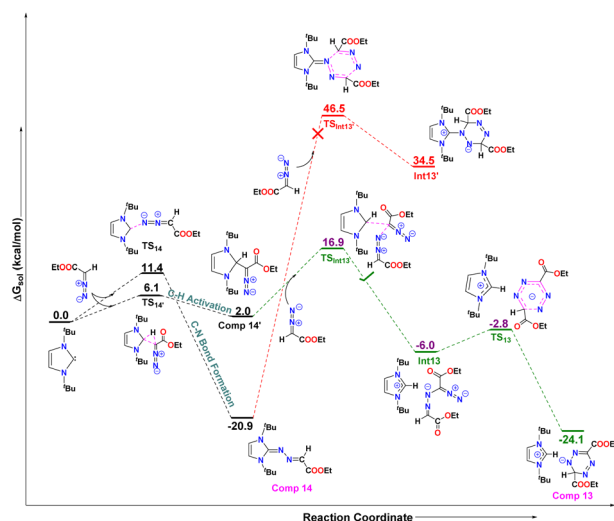


Fig. 12 The free energy profiles for the formation of compound 13 and compound 14 have been shown here. All values are in kcal mol⁻¹. Level of theory: PBE0-D3/def2TZVP//PBE-D3/def2TZVP with solvent toluene.

releasing 18.1 kcal mol⁻¹ of free energy. The activation energy for this step is only 3.2 kcal mol⁻¹, making it highly feasible.

Conclusions

From this comparative study, it can be concluded that the reactivity of one particular NHC is not representative for the

whole range of stable carbenes that are available. 5-IPr, 6-SIPr, and diamido carbene afforded N-heterocyclic methylene hydrazine derivatives upon reaction with Me₃SiCHN₂. 5-IPr and 5-I^tBu led to the formation of N-heterocyclic methylene hydrazines with terminal CH₂ formed *via* dehydrohalogenation of 5a using base or reacting 5-IPr and 5-I^tBu with Me₃SiCHN₂ in presence of stoichiometric amount of water. However, 5-SIPr activates the C–H bond of Me₃SiCHN₂. Another surprising results were obtained from the reaction 5-I^tBu, which undergoes triazole ring formation with an exocyclic C=C double bond. The same set of reactions were performed with COO^tBuCHN₂ instead of Me₃SiCHN₂, and in every case azine derivatives were obtained. These results should encourage the organometallic community to broaden the range of carbenes they use for small molecule activation or as ligands for transition metals.

Data availability

The data supporting this article have been included as part of the ESI.† CCDC 2347293 (1), 2347305 (3), 2363380 (4), 2347306 (5), 2347322 (5a), 2347308 (6), 2347310 (7), 2368081 (7a), 2347311 (8), 2347313 (9), 2347315 (10), 2347321 (11), 2375811 (13) and 2363384 (14) contain the supplementary crystallographic data for this paper.

Author contributions

K. B. and S. S. S. conceived the idea. K. B. has carried out the synthesis and characterization of the compounds. H. S. and K. V. executed the theoretical calculations. K. B. and R. G. G. performed the single-crystal X-ray structures of the molecules.

Conflicts of interest

There are no conflicts to declare.

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