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Reductive Elimination at Carbon under Steric Control

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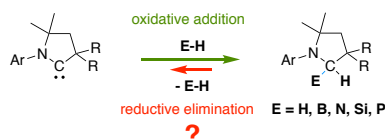
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Supporting Information Placeholder

ABSTRACT: *It has been previously demonstrated that stable singlet electrophilic carbenes can behave as metal surrogates in the activation of strong E-H bonds (E = H, B, N, Si, P), but it was believed that these activations only proceed through an irreversible activation barrier. Herein we show that, as is the case with transition metals, the steric environment can be used to promote reductive elimination at carbon centers.*

The ability of transition metals to switch reversibly between oxidation states is the foundation of transition metal catalysis.¹ In marked contrast, oxidative addition and reductive elimination at carbon are traditionally seen as being irreversible and challenging, respectively.² In recent years, our group and others have shown that thanks to the presence of a lone pair and a vacant orbital, singlet electrophilic carbenes resemble, to some extent, transition metals.³ It has been shown that cyclic(alkyl)(amino)carbenes (CAACs)⁴ can undergo the oxidative addition of strong E-H bonds (E = H, B, N, Si, P) (Scheme 1).⁵ More recently, Bielawski⁶ and César⁷ showed that this transition metal-like reactivity can be extended to other very electrophilic carbenes such as N,N'-diamidocarbenes (DACs)⁸ and anionic N-heterocyclic carbenes featuring a malonate backbone (*malo*NHCs).



Scheme 1. Known E-H bond (E = H, B, N, Si, P) oxidative addition at CAACs, and the proposed reverse reaction.

Thus, although examples of oxidative addition at carbon are becoming more common, there are far fewer reports describing the reverse reaction. In 2015, Bielawski *et al.* reported the preparation of a photoswitchable *N*-

heterocyclic carbene ligand capable of promoting reversible activation of ammonia under photolysis.⁹ More recently Radius *et al.*^{10,11} showed that CAACs could insert into the B-C(sp²) bond of a range of organoborates, and noted that the reverse reaction could be triggered upon heating. The difficulty of the reductive elimination step may be one of the most significant challenges toward the development of main-group catalyzed coupling processes.

It is well-accepted that, at transition metals, reductive elimination is heavily influenced by the steric environment around the metal center.^{1,12,13,14} We therefore speculated whether the latter conclusion could be extended to non-metals? Here we show that indeed the steric environment is also a key parameter in promoting the reductive elimination at a carbon center.

We first computationally¹⁵ assessed the thermodynamics of the reductive elimination of Ph₂NH and Ph₂PH from CAACs featuring different steric environments. While with the smallest^{Me}CAAC **1**¹⁶ we found these processes to be endergonic by 16.6 and 24.7 kcal/mol, with the more sterically demanding^{Menth}CAAC **2**,¹⁶ the reductive eliminations are endergonic by only 6.1 and 12.8 kcal/mol, respectively (Figure 1).

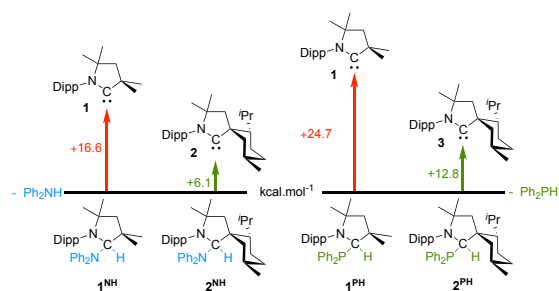
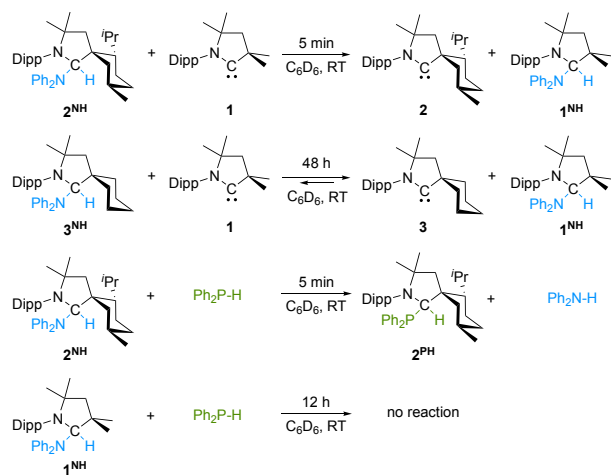


Figure 1. Impact of sterics on the calculated free energies of reductive elimination of Ph₂NH and Ph₂PH from CAAC(NPh₂)(H) **1**^{NH} and **2**^{NH}, and CAAC(PPh₂)(H) adducts **1**^{PH} and **2**^{PH}.

To probe experimentally the effects of sterics, we first reacted at room temperature the diphenylamine adduct 2^{NH} of the sterically hindered $^{\text{Menth}}$ CAAC **2** with the small free $^{\text{Me}}$ CAAC **1** and observed the rapid formation of the free $^{\text{Menth}}$ CAAC **2** along with $^{\text{Me}}$ CAAC(NPh₂)(H) **1^{NH}** (Scheme 2).¹⁷ In contrast using the cyclohexyl CAAC, we observed an equilibrium (**3^{NH}**/**3**: 40/60; $K = 2.25$). Less ambiguously, diphenylamine can be displaced from 2^{NH} by Ph₂PH, affording 2^{PH} , but not from **1^{NH}**.

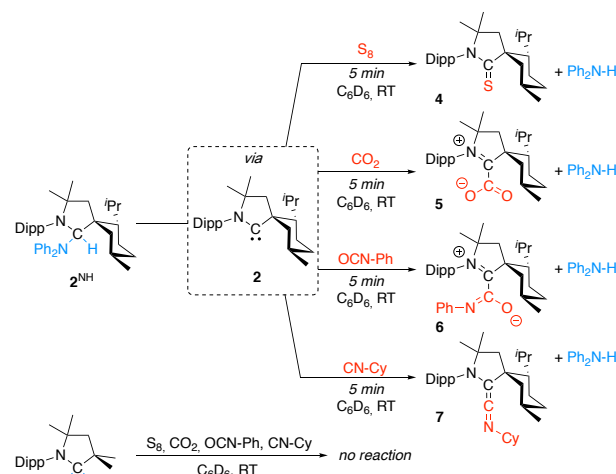


Scheme 2. Influence of sterics on the exchange reactions.

To gain insight into the mechanisms of these exchange reactions, free energy profiles were computed for the reductive elimination of Ph₂NH from 2^{NH} and the subsequent reaction of **2** with Ph₂PH to form 2^{PH} (profile in black, Figure 2). Starting from 2^{NH} , formal reductive elimination proceeds in two steps: (i) C–N heterolysis to give a contact ion-pair, **[2-H][NPh₂]**; (ii) proton transfer to form an H-bonded adduct **2·HNPh₂**. Exchange with Ph₂PH then gives adduct **2·HPPH₂** from which the complementary two-step P–H activation leads to 2^{PH} at -12.8 kcal/mol, making the overall exchange reaction exergonic by 6.7 kcal/mol. N–H reductive elimination from 2^{NH} has an overall barrier of 21.0 kcal/mol via **2-TS1^{NH}**,

which is significantly lower than the equivalent P–H reductive elimination from 2^{PH} ($\Delta G^\ddagger = 27.3$ kcal/mol). In the latter, the rate-limiting step is the proton transfer via **2-TSII^{PH}** whereas formation of ion-pair **[2-H][PPh₂]** is more kinetically accessible with a barrier of 22.9 kcal/mol relative to 2^{PH} . For **1^{NH}** (Figure 2, orange) the free energy barrier for N–H reductive elimination is 25.4 kcal/mol. This is significantly higher than for 2^{NH} and so is consistent with the lack of exchange seen at room temperature with **1^{NH}**.

As the calculations showed N–H reductive elimination from 2^{NH} to be endergonic, but kinetically accessible, we set out to trap the putative carbene intermediate, **2**, that should be formed. Elemental sulfur,¹⁸ carbon dioxide,¹⁹ phenyl isocyanate,²⁰ and cyclohexyl-isocyanide²¹ are all known to react with free carbenes (Scheme 3). In each case we were able to confirm the formation of free diphenylamine along with the corresponding adducts **4-7**. Note that the same reactions do not occur with the less encumbered $^{\text{Me}}$ CAAC(NPh₂)(H) adduct **1^{NH}**.



Scheme 3. Reductive elimination of Ph₂NH occurs from the sterically demanding 2^{NH} , but not from **1^{NH}**.

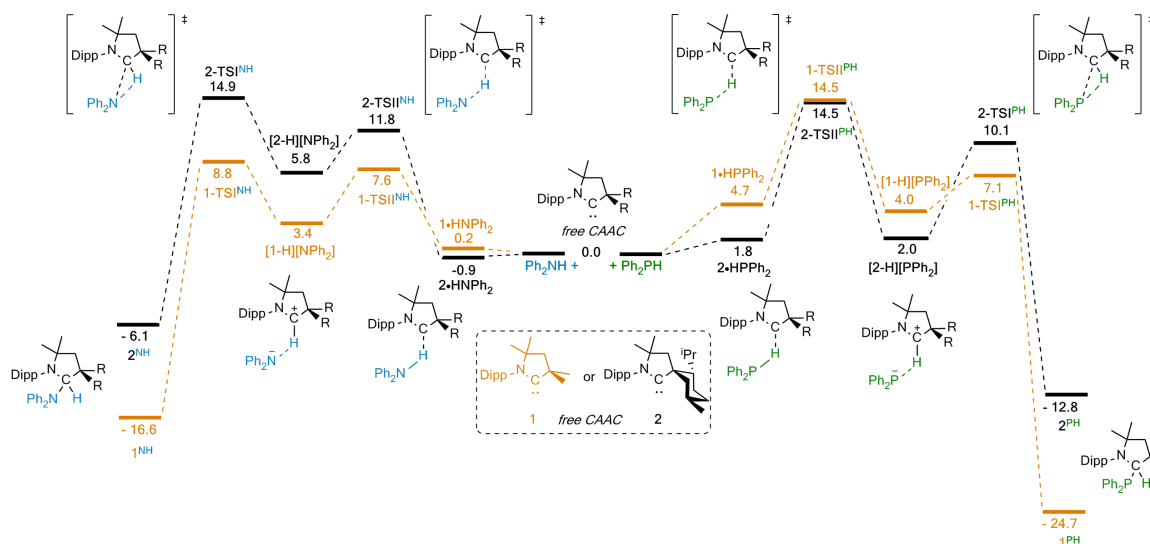
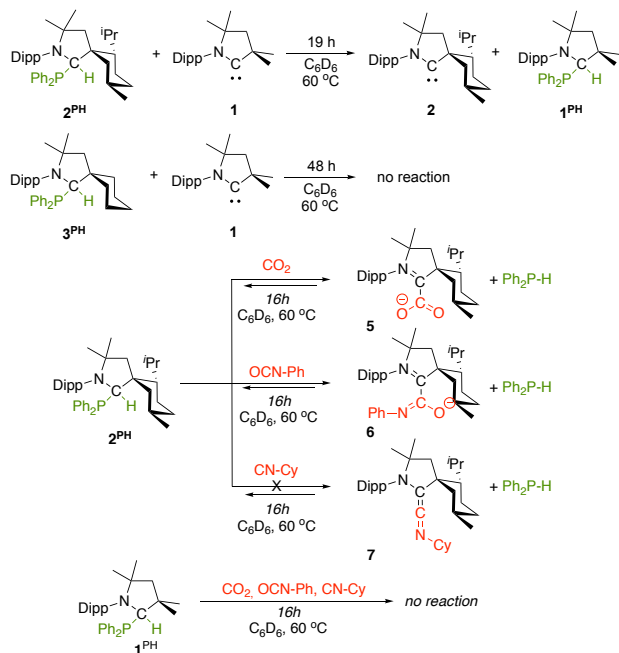


Figure 2. Computed free energy profiles for the reactions of Ph₂E–H with $^{\text{Me}}$ CAAC **1** and $^{\text{Menth}}$ CAAC **2** highlighting the influence of sterics. (E = N, P; kcal/mol, M062X-D3(FHF)/def2-TZVP//TPSS(THF)DZP level).

To evaluate the generality of the reductive elimination process at a carbon center, we extended our study to the diphenylphosphine CAAC adducts (Scheme 4). No reaction was observed at room temperature in benzene between the bulky ^{Menth}CAAC(PPh₂)(H) (**2^{PH}**) and the small ^{Me}CAAC **1**. However, upon heating the mixture at 60 °C, we observed the slow formation of free ^{Menth}CAAC **2** along with ^{Me}CAAC(PPh₂)(H) (**1^{PH}**). In contrast, no reaction occurred between the less sterically encumbered **3^{PH}** and **1**. Heating **2^{PH}** at 60 °C in the presence of carbon dioxide and phenyl isocyanate led to an equilibrium between **2^{PH}** and the corresponding adducts **5** and **6**, respectively. Not surprisingly, the same equilibria were observed when diphenylphosphine was added to pure **5** and **6**. When cyclohexyl isocyanide was used as a carbene trapping agent, no reaction occurred even at 60 °C, whereas addition of free Ph₂PH to adduct **7** (prepared independently) led to the clean formation of **2^{PH}**. Importantly, attempts to trap the free small carbene **1** from ^{Me}CAAC(PPh₂)(H) **1^{PH}** failed.

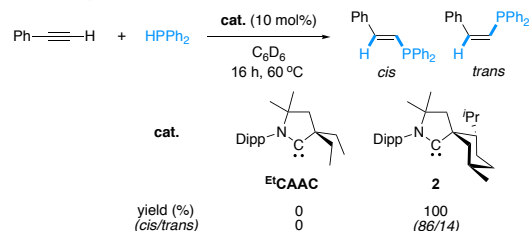


Scheme 4. Evidence for phosphine reductive elimination from the bulky adduct **2^{PH}**

Having shown the influence of the sterics on the reductive elimination process, we wondered if we could show its implications in catalysis. Recently, some of us²² reported that *N*-alkyl substituted *N*-heterocyclic carbenes NHCs can promote the anti-Markovnikov hydrophosphination of terminal alkynes,²³ whereas ^{Et}CAAC fails to catalyze this reaction. Capitalizing on our findings, we found that the bulkier ^{Menth}CAAC **2** (10 mol%) allows for the anti-Markovnikov hydrophosphination of phenyl acetylene with diphenylphosphine in full conversion after 16 h at 60 °C (Scheme 5).

In conclusion, we have provided experimental and computational evidence for the reductive elimination of amines and phosphines from a carbon center. Just as for

transition metals, these processes are favored by sterically demanding environments. We expect these results to inspire and act as guiding principles towards the development of novel main-group catalyzed coupling reactions based on conventional oxidative addition/reductive elimination processes.



Scheme 5. Influence of the sterics on the carbene catalyzed hydrophosphination of terminal alkynes.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/.

Experimental procedures, characterizations, and NMR spectra of all new compounds (PDF)

X-ray crystallographic data for **1^{PH}**, **1^{NH}**, **2^{PH}**, **2^{NH}**, **4**, **5**, **6**, and **7** (ZIP).

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