

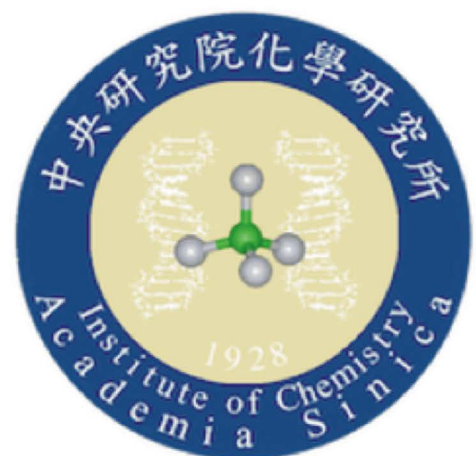


# 2020「中技社科技獎學金」

2020 CTCI Foundation Science and Technology Scholarship

## 境外生生活助學金

Living Grant for International Graduate Students



### Carbodicarbenes: Unexpected $\pi$ -Accepting Ability during Reactivity with Small Molecules

Yi-Chen Chan<sup>a,b,c</sup>, Wen-Ching Chen<sup>a</sup> and Tiow-Gan Ong<sup>a,b,\*</sup>

<sup>a</sup>Institute of Chemistry, Academia Sinica, No. 128, Sec. 2, Academia Road, Nangang, Taipei 11529, Taiwan, R.O.C.

<sup>b</sup>Department of Applied Chemistry, National Chiao Tung University, No. 1001, Ta Hsueh Road, Hsinchu 300, Taiwan, R.O.C.

<sup>c</sup>Sustainable Chemical Science and Technology, Taiwan International Graduate Program, Academia Sinica and National Chiao Tung University, Taiwan, R.O.C.

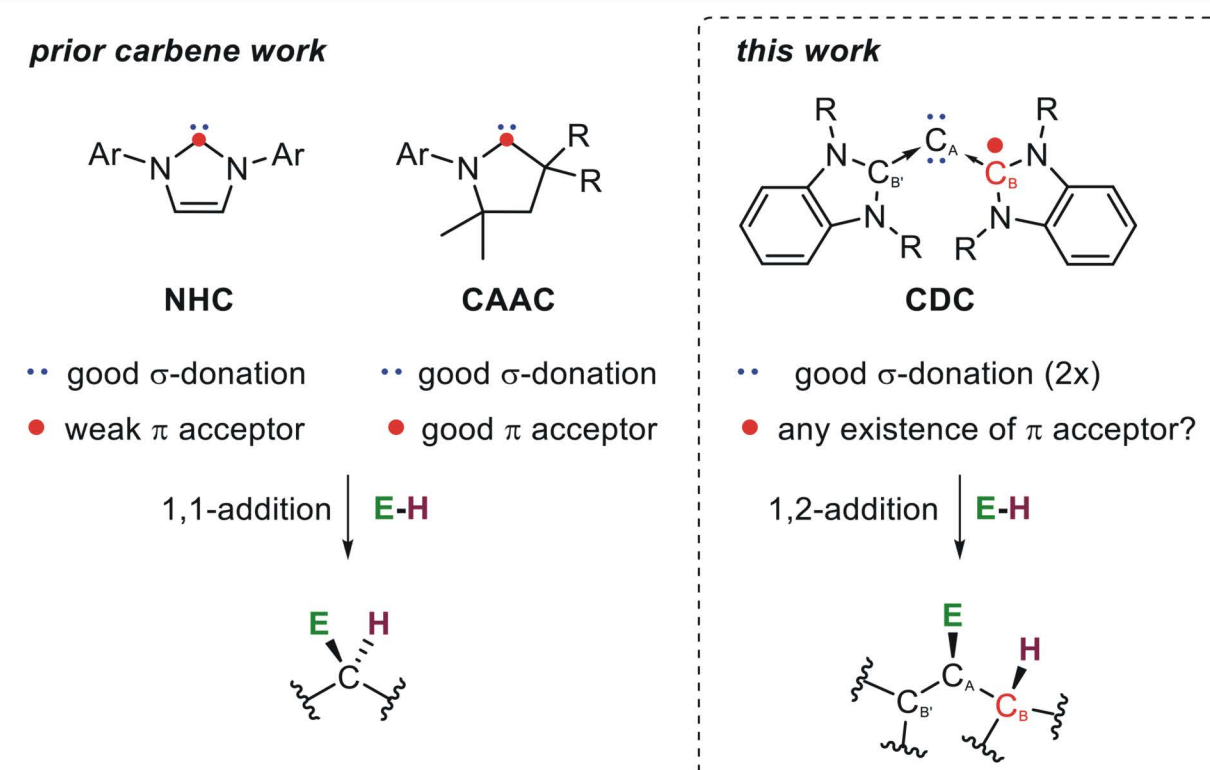
E-mail: [tgong@gate.sinica.edu.tw](mailto:tgong@gate.sinica.edu.tw)



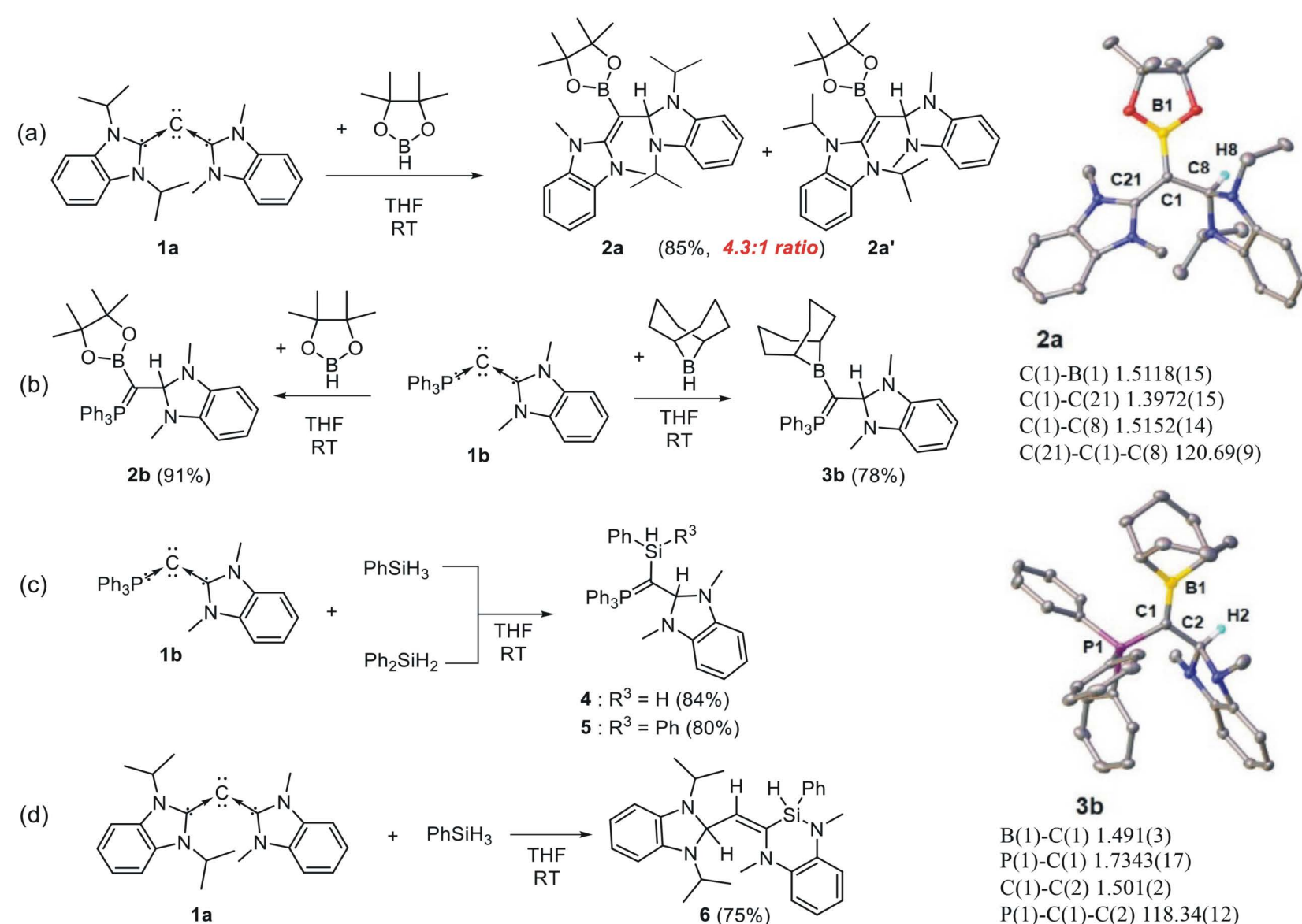
#### Abstract

Carbodicarbenes (CDCs), a unique carbenic entities bearing two lone pairs of electrons on the central carbon (0) atom, are indisputably strong  $\sigma$ -donating surrogates. Yet, CDCs have dissimilar electronic features and concomitant reactivities than their well-established counterparts N-heterocyclic carbenes (NHCs) and cyclic (alkyl) (amino) carbenes (CAACs). Herein, the observed 1,2-addition of E-H bonds (E= B, C, Si) across the carbene central atom and the flanking NHC fragment, supported by the X-ray crystallography studies of a model Pd complex; clearly illustrated the hidden low-lying empty p-orbital embedded in the CDC framework. The ambiphilic nature has rendered CDCs with reactivity more commonly observed for frustrated Lewis pairs (FLPs) rather than the closely related NHCs and CAACs.

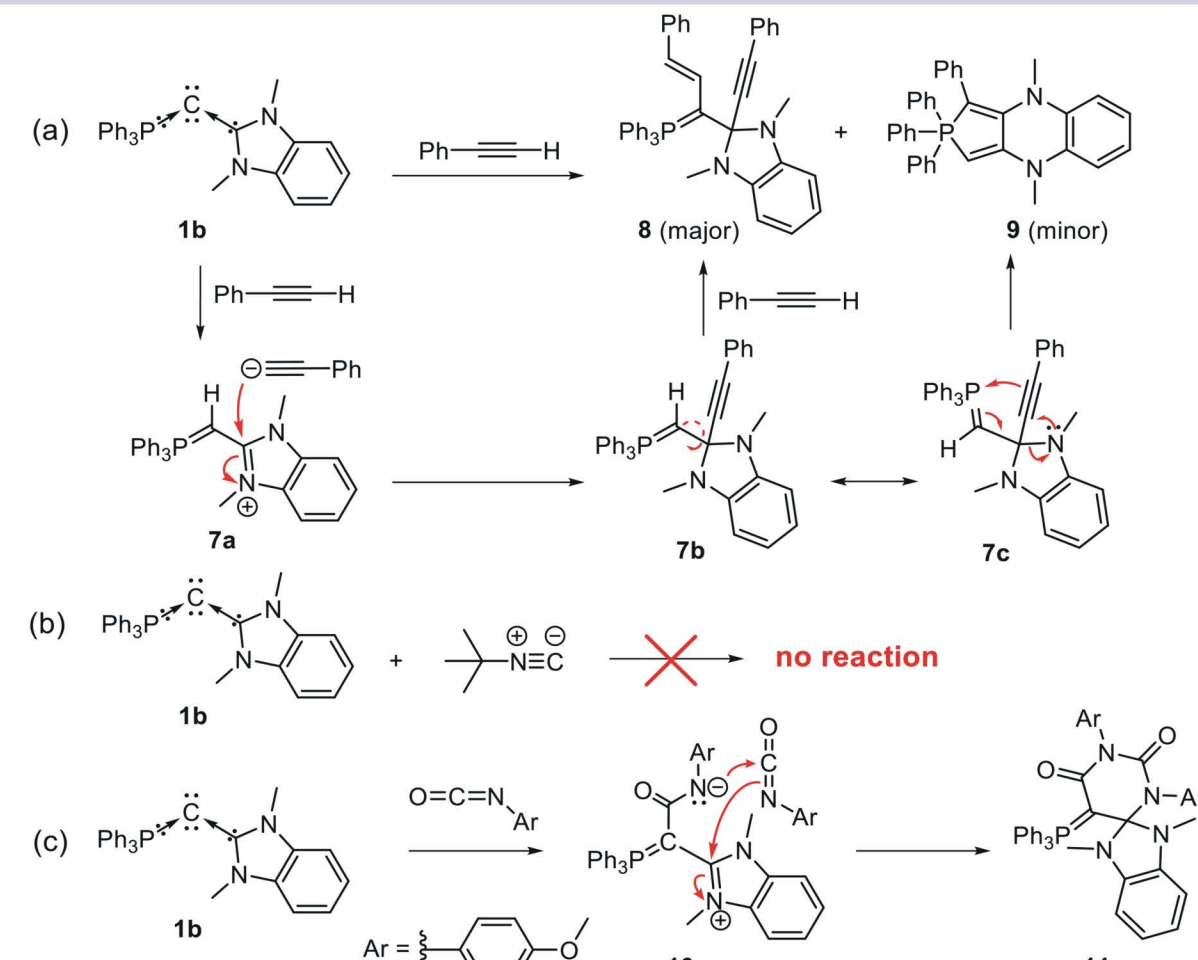
#### Properties of common NHCs, CAACs, and CDCs



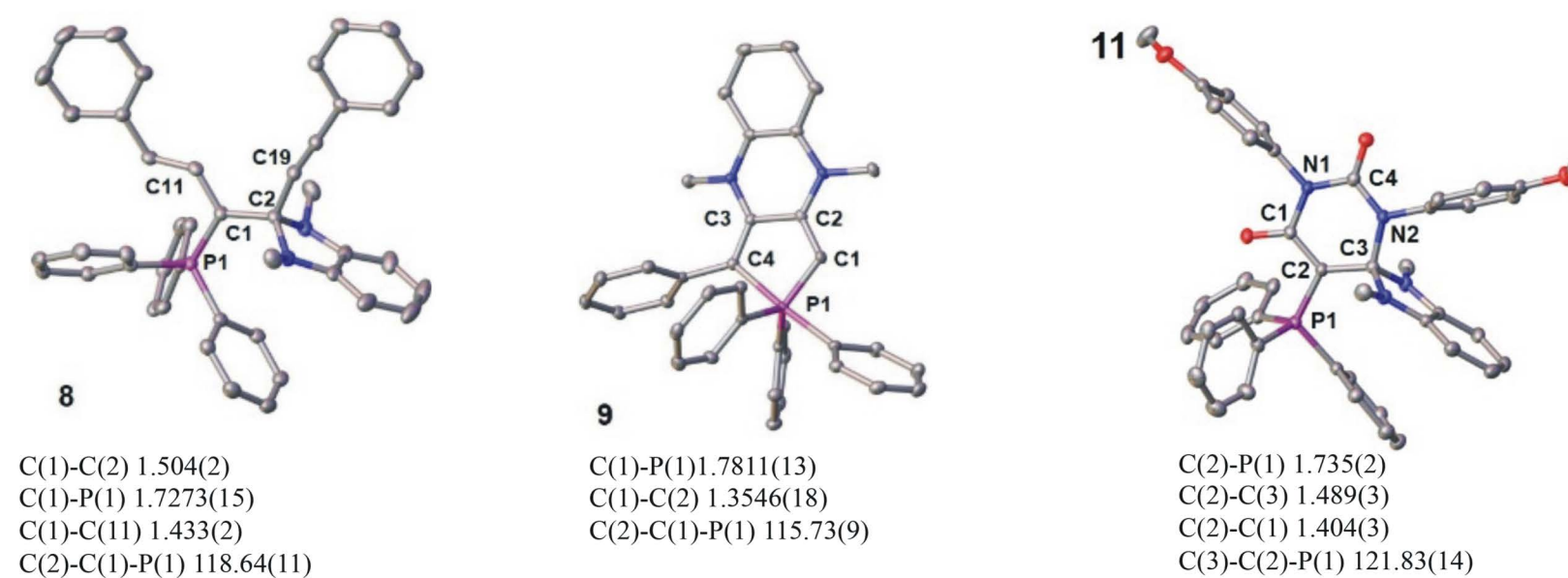
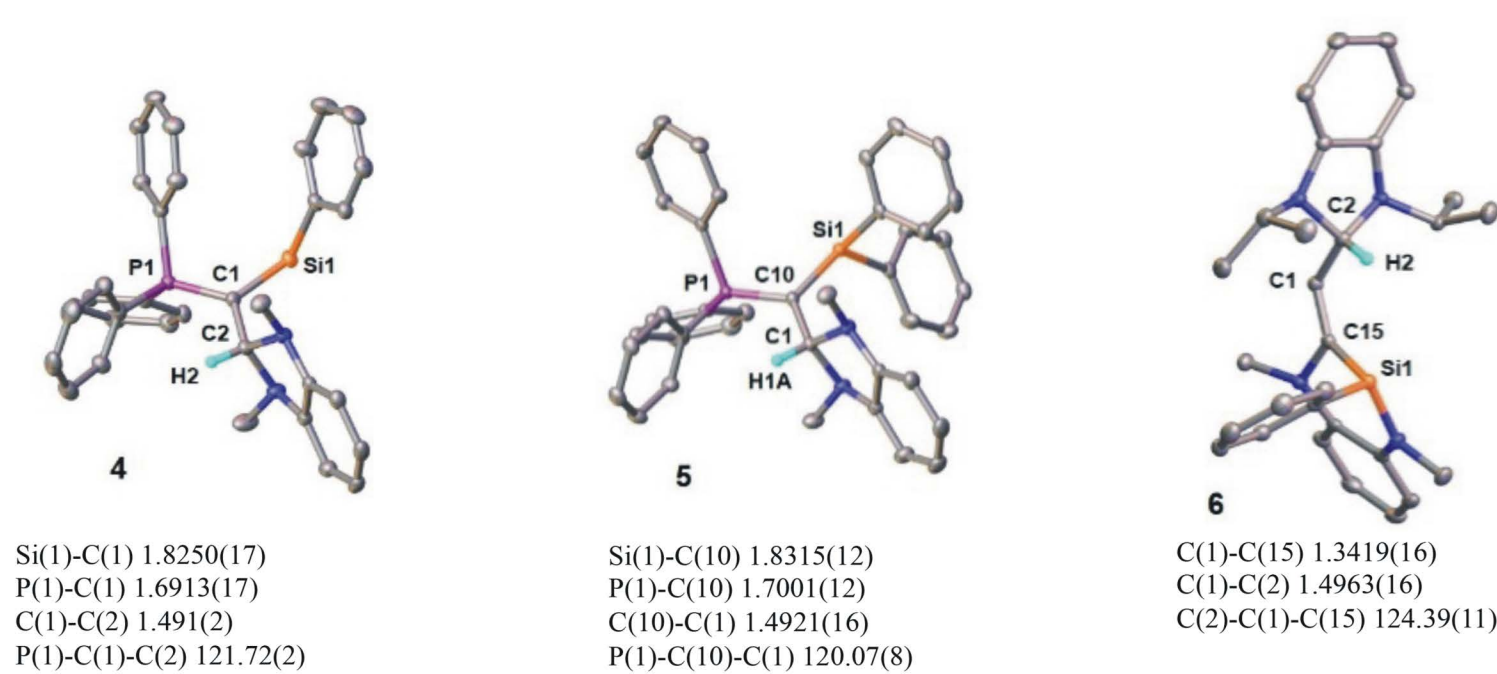
#### Reactions of carbene with Borane and Silane Substrates



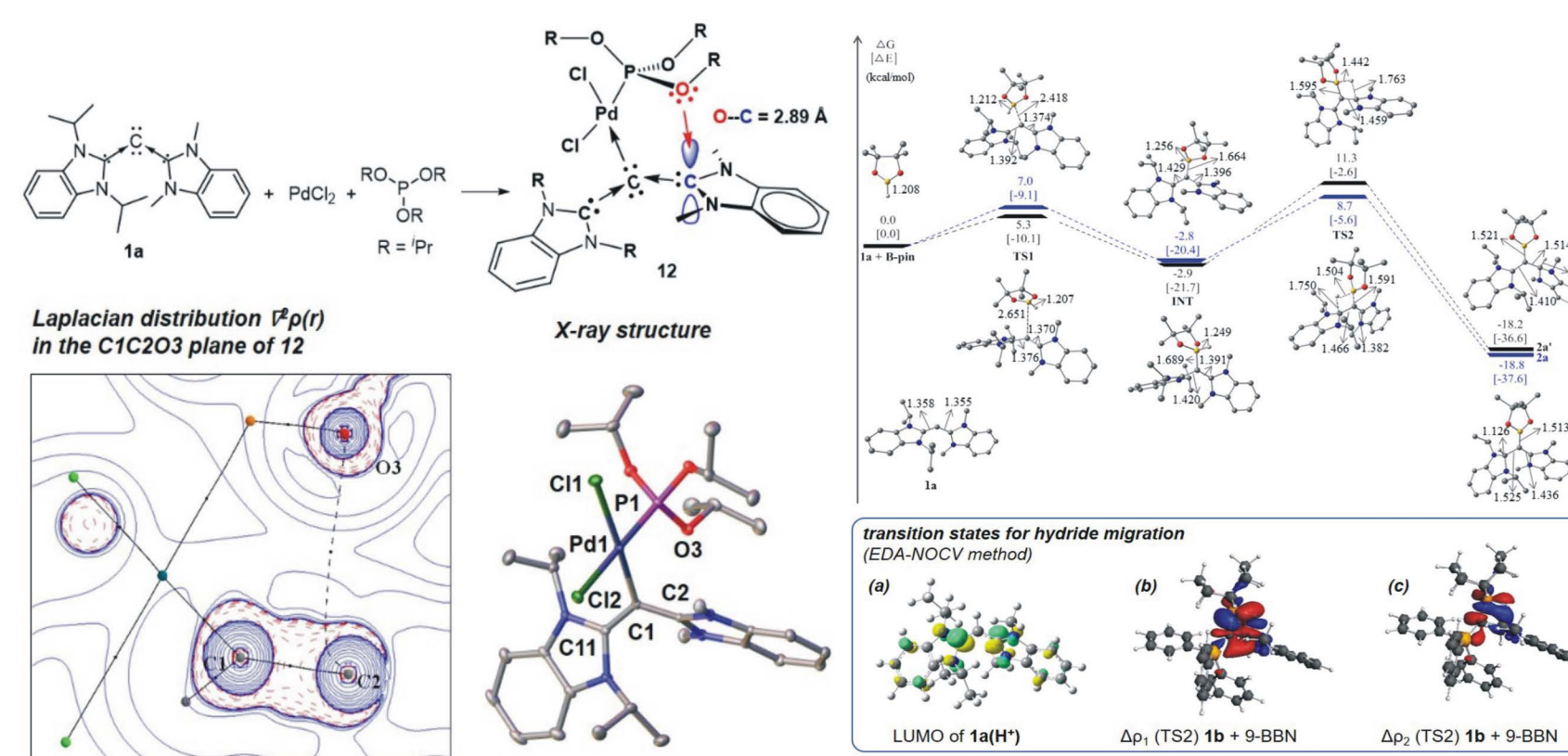
#### Highlighting Amphiphilic-like Reactivity



#### X-ray structures



#### Laplacian distribution $\nabla^2\rho(r)$ (left) and Calculated energy profile (right)



#### Calculated Reaction Energies

Table 1. Calculated Reaction Energies,  $\Delta G$  ( $\Delta E$ ),<sup>a</sup> at BP86(D3)/def2-SVP

No.	reaction	educt	TS1	INT	TS2	ATST2 <sup>b</sup>	product	Byproduct
1	1a + B-pin → 2a	0.0	7.0 (-9.1)	-2.8 (-20.4)	8.7 (-5.6)	11.5 (14.8)	-18.8 (-37.6)	-16.0 (-17.2)
1'	1a + B-pin → 2a'	0.0	5.3 (-10.1)	-2.9 (-21.7)	11.3 (-2.6)	14.2 (19.1)	-18.2 (-36.6)	-15.3 (-14.9)
2	1b + B-pin → 2b	0.0	2.4 (-12.1)	-5.8 (-24.3)	8.0 (-5.8)	13.8 (18.5)	-30.0 (-46.9)	-24.2 (-22.6)
3	1a + 9-BBN → 3a	0.0	5.8 (-8.5)	-7.2 (-27.4)	-2.5 (-20.8)	4.7 (6.6)	-24.0 (-44.6)	-16.8 (-17.2)
3'	1a + 9-BBN → 3a'	0.0	4.5 (-9.5)	-14.3 (-36.1)	-3.5 (-21.5)	10.8 (14.6)	-22.3 (-42.4)	-8.0 (-6.3)
4	1b + 9-BBN → 3b	0.0	2.9 (-12.1)	-18.2 (-37.3)	-7.4 (-22.6)	10.8 (14.7)	-39.2 (-58.6)	-21.0 (-21.3)

<sup>a</sup>Energies in kcal/mol. <sup>b</sup>Activation barrier for the second step  $\Delta TS2 = INT - TS2$ . <sup>c</sup>Reaction energy of the second step  $\Delta product = INT - product$ .

#### Conclusion

In summary, we have demonstrated a new reaction path for carbodicarbenes. The observed 1,2 addition of E-H bonds (E = B, C, Si) across the carbene central carbon (C<sub>A</sub>) and that of the flanking NHC fragment (C<sub>B</sub>) suggests ambiphilic-type activity. Unforeseen  $\pi$ -acidity is critical for facilitating the 1,2-addition of E-H to carbones. Further elaboration of this nonclassical 1,2 reactive behavior is compelling for the development of novel organocatalytic reaction pathways and frames the focus of ongoing studies in our group.

#### References

- Chen, W.-C.; Shen, J.-S.; Jurca, T.; Peng, C.-J.; Lin, Y.-H.; Wang, Y.-P.; Shih, W.-C.; Yap, G. P. A.; Ong, T.-G. *Angew. Chem., Int. Ed.* **2015**, *54*, 15207-15212.
- Chen, W.-C.; Shih, W.-C.; Jurca, T.; Zhao, L.; Andradá, D. M.; Peng, C.-J.; Chang, C.-C.; Liu, S.-K.; Wang, Y.-P.; Wen, Y.-S.; Yap, G. P. A.; Hsu, C.-P.; Frenking, G.; Ong, T.-G. *J. Am. Chem. Soc.* **2017**, *139*, 12830-12836.



財團法人中技社  
CTCI FOUNDATION