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**Authors:** Tiow-Gan Ong, Yi-Chen Chan, Yuna Bai, Wen-Ching Chen, Hsing-Yin Chen, Chen-Yu Li, Ying-Yann Wu, Mei-Chun Tseng, Glenn P. A. Yap, Lili Zhao, and Hsuan-Yin Chen

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# Synergistic Catalysis by Brønsted Acid/Carbodicarbene Mimicking Frustrated Lewis Pair-Like Reactivity

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**Abstract:** Carbodicarbene (CDC), unique carbenic entities bearing two lone pairs of electrons are well-known for their strong Lewis basicity. We demonstrate herein, upon introducing a weak Brønsted acid benzyl alcohol (BnOH) as a co-modulator, CDC is remoulded into a Frustrated Lewis Pair (FLP)-like reactivity. DFT calculation and experimental evidence show BnOH loosely interacting with the binding pocket of CDC via H-bonding and π-π stacking. Four distinct reactions in nature were deployed to demonstrate the viability of proof-of-concept as synergistic FLP/Modulator (CDC/BnOH), demonstrating enhanced catalytic reactivity in cyclotrimerization of isocyanate, polymerization process for *L*-lactide (LA), methyl methacrylate (MMA) and dehydrosilylation of alcohols. Importantly, the catalytic reactivity of carbodicarbene is uniquely distinct from conventional NHC which relies on only single chemical feature of nucleophilicity. This finding also provides a new spin in diversifying FLP reactivity with co-modulator or co-catalyst.

## Introduction

Frustrated Lewis Pairs (FLPs), a unique concept first proposed in 1942,[1] have been adopted by Stephan[2] et al. in 2006 for their breakthrough studies in activating a small molecule like $H_2$. The ability of FLP to break up small molecules is attributed to its highly reactive chemical behavior caused by a long-range attractive force between Lewis acid and base components that are sterically prevented from forming classical Lewis acid–base adducts. Today, this conceptual stochiometric reactivity has expanded into metal-free catalytic processes with a plethora of FLP derivatives such as hydrogenation,[3] $CO_2$ reduction,[4] hydrosilylation,[5] borylation of heteroarenes,[6] amination of carbonyl compounds[7] and others.[8]

In considering many examples of FLP, we organize the FLP systems based on the number of bonds (*n*) in between the Lewis acid and base units. The most common FLP like phosphane/borane Lewis pair and its other variants can be classified as class **I** with an infinite number of bonding ($n = \infty$, see Chart 1) and are frequently coined as the intermolecular or non-bridging FLPs.[9] Steric substituents are generally introduced and precluded the association and formation of a classical Lewis acid–base adduct. Meanwhile, bridging FLPs (class **II-IV**) contain conformationally rigid backbone tethering both the Lewis acid and base units. They can generally be categorized according to the number of bonding in between the acid-base units that are $n \geq 3$[10], $n = 2$[11] and $n = 1$[12]. They were designed with the aim of addressing the unfavorable entropic term associated with a small molecule capture that is lacking in traditional class **I**.

Carbodicarbenes (CDCs) are classified into the family of carbones ($CL_2$) that feature a dicoordinated central carbon ($C^0$)


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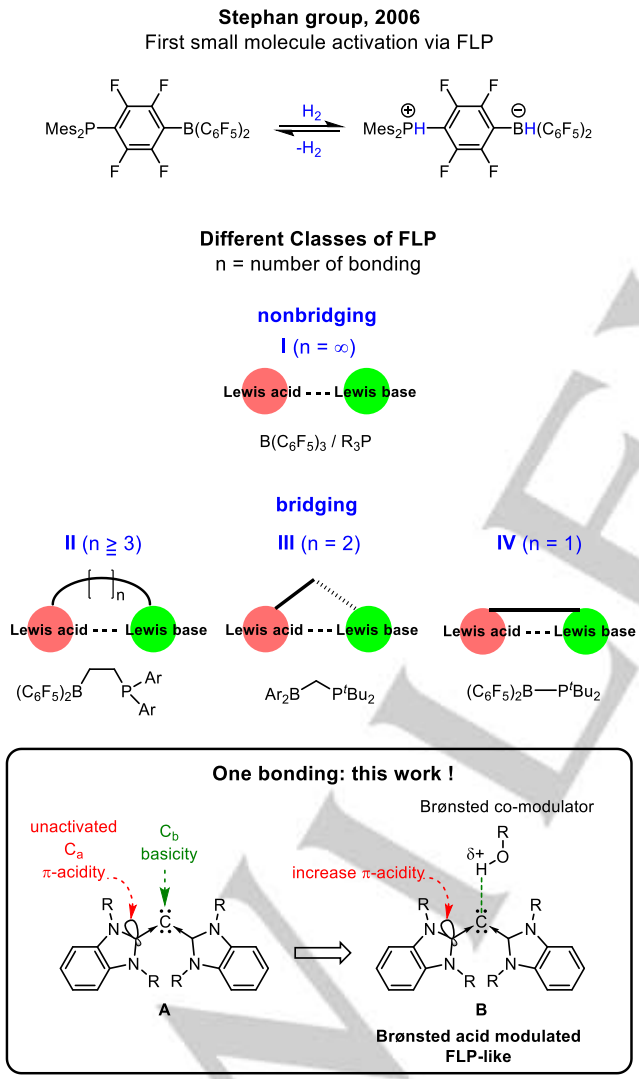
bearing two lone pairs of electrons with N-heterocyclic carbenes (NHCs) as flanking ligands (L).[13] Owing to the two lone-pairs on the central carbon, CDCs have been regarded as ligands with a strong σ-donation, allowing them to promote a myriad of metal-mediated catalysis[14] and serve as organic catalysts in $CO_2$ functionalization.[15] Apart from lone pairs residing at the central $C_b$ site (Chart 1), our group also recently uncovered that CDCs possess low-lying empty p-orbitals at the $C_a$ site after sequential activation of the electron-rich $C_b$ site, rendering CDCs capable of 1,2-addition reactions with a series of organic molecules.[16] Such chemical behavior bears certain degree of resemblance to those FLP of class **IV**,[17] but their reactivity might be less practical for catalysis, presumably due to quenching effect generated from the short distance with π-delocalization between $C_a$ (Lewis acid) and $C_b$ (Lewis base) sites.

**Chart 1.** Frustrated Lewis Pairs (FLPs) and Their Classifications.




To circumvent the impasse within CDCs, we sought an inspiration from Nature's enzyme/cofactor for which we introduced a specific assisting molecule so-called co-modulator that would mitigate or amplify the ambiphilic behavior within CDC through weak non-covalent interactions. In the course of investigation, we found Brønsted acid like alcohol is a suitable co-modulator, as it can lock-down on one of the lone pairs of CDCs, attuning a rather weak π-acidity locates at the $C_a$ site. Simultaneously, the second lone pair at $C_b$ is still available for nucleophilic reaction. It should be noted CDC/Brønsted acid can be considered as a Brønsted acid modulated synergistically FLP-like reactivity from CDC, which has a chemical uniqueness that is remarkably distinct from the traditional NHC as organic catalyst. In this work, we successfully applied carbodicarbene/benzyl alcohol (BnOH) to reactions of isocyanate cyclotrimerization, ring opening polymerization of *L*-lactide, methyl methacrylate polymerization and dehydrosilylation of alcohol. In addition, we also carried out mechanistic studies experimentally and computationally to delineate the synergistic nature of this new FLP-like behavior of CDC modulated by BnOH.

## Results and Discussion

**Identification of "co-modulator" molecule.** Prior to examining CDC for any catalytic application based on synergistic FLP model, one should identify a suitable co-modulator molecule. Ideally, such a molecule would feature a non-permanent non-bonding interaction with its hosting catalyst. In line with this thought, we selected a target molecule bearing a weakly acidic proton that would have a loose interaction with one of the electron lone-pairs of CDCs, thus enhancing the π-acidity at $C_a$. To find an appropriate candidate, we elected to perform NMR experiments on each ***C*$_1$-CDC** mixture with benzyl amine, BnOH and *t*-butanol. $^1$H NMR shows no interaction of ***C*$_1$-CDC** with benzyl amine and *t*-butanol (see Figure S3). For BnOH, we observed subtle NMR shift changes at the methylene signal (δ 4.32→5.06 ppm) and methine signal of ***C*$_1$-CDC** (δ 4.49→4.51 ppm). Importantly, the hydroxy peak of BnOH became broad centered around δ 9.50 ppm, explicitly shifted downfield from its origin sharp triplet at δ 1.70 ppm (Figure S3b).

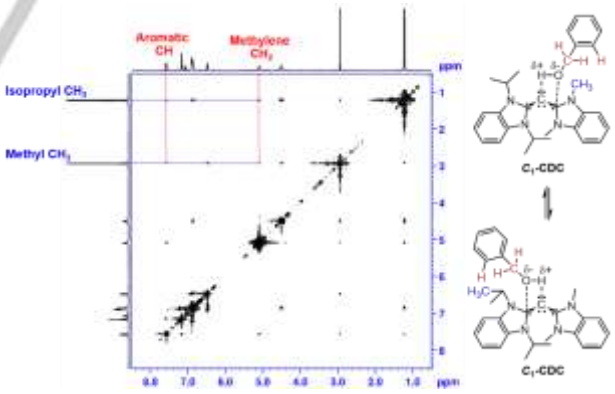



**Figure 1.** $^1$H-$^1$H NOESY NMR mixture of ***C*$_1$-CDC** and BnOH in 1:1 ratio.

To further verify such a non-covalent interaction, we carried out a NOESY experiment. Two concomitant peaks of BnOH were correlated with the two side arm peaks of ***C*$_1$-CDC** ($CH_3$ of isopropyl and $CH_3$ of methyl (Figure 1)), implying those protons were closely associated in space. Again, downfield shift in $^{13}$C NMR (Figure S4) with an average value of 4.9 ppm attributed to the flanking NHC fragment was consistent with the reduction of electron density at $C_a$ site. This is due to the non-bonding interaction of the hydrogen of BnOH with one of the lone-pairs of



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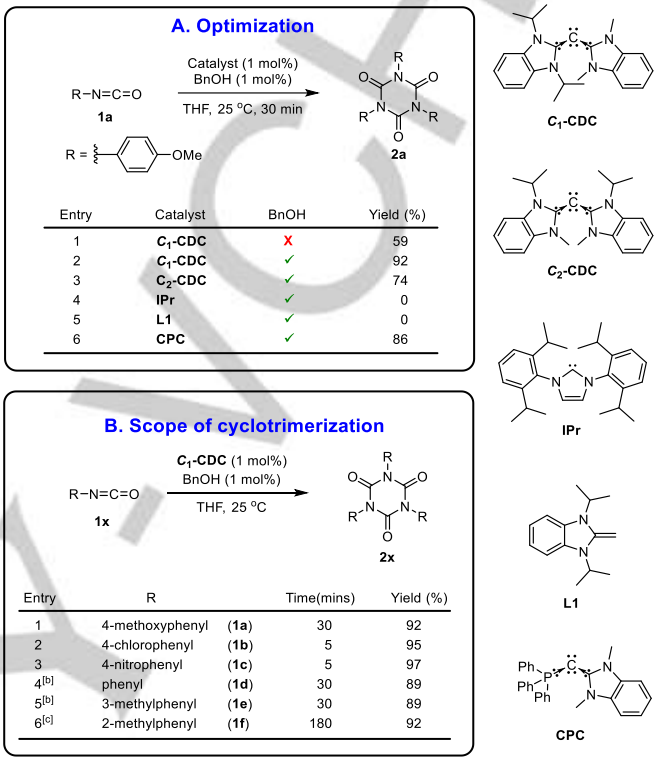
***C*$_1$-CDC**. Finally, we detected no protonated ***C*$_1$-CDC** species after prolonged exposure to BnOH in solution for 18 hours, indicating the chemical stability of ***C*$_1$-CDC** against any chemical or structural transformation by BnOH.

**Cyclotrimerization of isocyanate as model reaction.** Next, we selected cyclotrimerization of isocyanate as a simple model reaction to test the feasibility of concept using "***C*$_1$-CDC**/BnOH" in reaction. First, the cyclotrimerization of 1-methoxy-4-isocyanatobenzene **1a** was attempted against a series of carbodicarbenes at ambient temperature (Scheme 1A, entries 1-6). The cyclotrimerization of **1a** using 1.0 mol% $C_1$-symmetric carbodicarbene (***C*$_1$-CDC**) as a catalyst afforded the cyclic product **2a** in 59% yield within 30 mins in THF solution (entry 1). When the reaction was conducted with the addition of 1.0 mol% BnOH (entry 2), the catalytic activity of CDC increased dramatically to 92% yield under the same reaction time, hinting at the CDC mediated FLP-like reactivity promoted by BnOH. Subsequently, $C_2$-symmetric ***C*$_2$-CDC** was also examined and found to be an active catalyst with 74% yield (entry 3). Considering similarity in the electronic feature for both CDCs, we attributed the slightly lower reactivity to the higher steric demand of ***C*$_2$-CDC**. For comparison, typical NHC derivatives like **L1** and **IPr** (entries 4-5) were also evaluated under similar conditions, showing no sign of reactivity. The negative outcome of **L1** had also ruled out the possibility that the catalytic activity was generated by the decomposition of CDC. Notably, the presence of BnOH does not impose any beneficial effect on **IPr** catalytic activity (Figure S5), implying activity unique to the CDC-type framework.[18] Finally, a carbone flanked by triphenylphosphine (**CPC**, entry 6) also served as excellent catalyst for cyclotrimerization process with 86% yield.

Utilizing the optimized process from Scheme 1A which led to 92% yield, we expanded the scope of isocyanates in Scheme 1B. Chloro (**1b**) and nitro (**1c**) electron-withdrawing derivatives afforded nearly quantitative yield (>~95%) in only 5 mins (entries 2-3). Meanwhile, electron-neutral phenyl isocyanate **1d** furnished a good yield (89%) of cyclotrimeric product (entry 4). Electron-rich derivatives like 3-methyl (89%, **1e**) were also effective in this reaction (entry 5). **1f** possessing steric encumbrance at the *ortho* position required more than 3 h to achieve 92% yield (entry 6).[19]

**Mechanistic investigations and determination of the role of BnOH.** A series of experiments were conducted to gain more insight into the reaction mode of isocyanate based with CDC. Performing a reaction in the presence of BnOH or combination of $NBu_4OBn$ and protonated ***C*$_1$-CDC** showed no sign of reactivity, illustrating that $BnO^-$ or $H^+$ were not active species (Figure 2A). We managed to obtain a single crystal X-ray structure of **3c** derived from the stoichiometric reaction of ***C*$_1$-CDC** with **1c** in the absence of BnOH. A nucleophilic attack of ***C*$_1$-CDC** via $C_b$ site onto 4-nitrophenyl isocyanate generated an organic zwitterion bearing a cationic $sp^2$ type of C(3)-C(1)-C(12) (1.398 and 1.445 Å) and N(1) with anionic feature (Figure 2B). Upon closer investigation of **3c**, one would also find an unexpected close non-bonding interaction at N(1)---C(12) with 2.723 Å, which is shorter than the sum of *van der Waals* radii of C---N with ~3.25 Å.[20] Indeed, the short contact could be rationalized by a π-acidity feature which exists at the $C_a$ site of CDC, working synergistically with the nucleophilic site at $C_b$ to promote the catalytic cyclotrimerization. These experimental evidences also suggest that ***C*$_1$-CDC** manifests FLP-like character in isocyanate cyclotrimerization without $BnO^-$ or $H^+$, but also a further indication that BnOH may act as co-modulator in this reaction.

**Scheme 1.** Cyclotrimerization of Isocyanate **1**.[a]

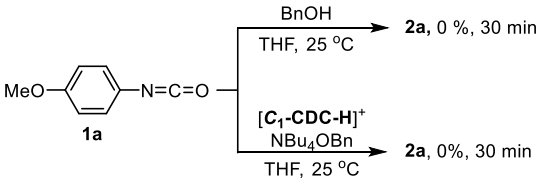



| Entry | Catalyst | BnOH | Yield (%) |
|---|---|---|---|
| 1 | ***C*$_1$-CDC** | X | 59 |
| 2 | ***C*$_1$-CDC** | ✓ | 92 |
| 3 | ***C*$_2$-CDC** | ✓ | 74 |
| 4 | **IPr** | ✓ | 0 |
| 5 | **L1** | ✓ | 0 |
| 6 | **CPC** | ✓ | 86 |

| Entry | R | | Time(mins) | Yield (%) |
|---|---|---|---|---|
| 1 | 4-methoxyphenyl | (**1a**) | 30 | 92 |
| 2 | 4-chlorophenyl | (**1b**) | 5 | 95 |
| 3 | 4-nitrophenyl | (**1c**) | 5 | 97 |
| 4[b] | phenyl | (**1d**) | 30 | 89 |
| 5[b] | 3-methylphenyl | (**1e**) | 30 | 89 |
| 6[c] | 2-methylphenyl | (**1f**) | 180 | 92 |

[a] Each reaction carried out in the mixture of 0.5 M isocyanate, 1.0 mol% ***C*$_1$-CDC** (or catalyst) and 1.0 mol% BnOH in 5 mL THF at 25 °C. All yields are isolated unless otherwise mentioned. [b] NMR yield with 1,3,5-trimethoxybenzene as Internal Standard. [c] 2.5 mL of THF was used to make a 1.0 M reaction mixture.

### A. Experiments for mechanism study




### B. Solid-state structure of 3c

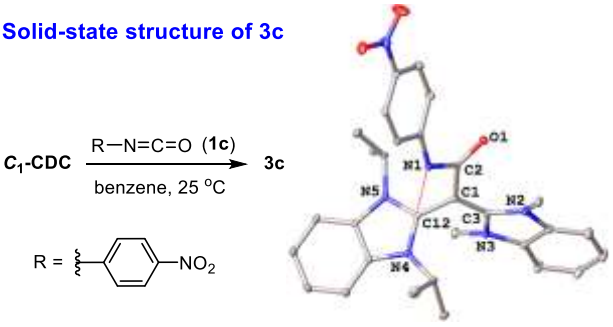





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**Figure 2.** (A). Experiments for mechanism study. (B) Solid-state structure of **3c** with thermal ellipsoids set at 30% probability. All hydrogen atoms and THF solvent molecules have been omitted for clarity. Selected bond lengths [Å], interatomic distances [Å] and bond angles [°]: C(1)-C(12) 1.445(3), C(1)-C(3) 1.398(3), C(1)-C(2) 1.482(3), C(2)-O(1) 1.248(3), C(2)-N(1) 1.362(3), C(12)-C(1)-C(3) 119.34(19), C(12)-C(1)-C(2) 117.33(17), C(3)-C(1)-C(2) 123.3(2), C(12)···N(1) 2.723(3).

Based on the structural evidence of **3c** and experimental outcomes, we next carried out DFT calculations to gain insight into the positive influence of BnOH upon the rate as well as mechanistic insight of this reaction. As detailed in Figure 3, the reaction initiates from the coupling step of **1d** and ***C*$_1$-CDC** via the transition state **TS1** with the assistance of BnOH, leading to the thermodynamically more stable zwitterionic complex **IM1**. This is in line with the experimentally observed molecule **3c**. Therein, the weak interactions between the electron rich N-center of simplified substrate **1d** and the electron-deficient π-acidity at the $C_a$ site of CDC, as indicated by the $^{OCN}N$---$C_a^{CDC}$ distance of 2.787 Å, provides a stabilizing effect to **TS1**. This means the CDC behaves as both a σ-donor at $C_b$-center and π-accepter at $C_a$ site, hence the appropriation of synergistic FLP-like behavior. In addition, the favorable $C_b$---H-O hydrogen bonding (1.928 Å) and π-π stacking interactions between the BnOH and CDC species (3.718 Å) also play important roles as witnessed in **TS1** and other reaction pathways. After overcoming a small barrier of 10.6 kcal/mol (i.e., **IM1→TS2**), the second equivalent **1d** will insert easily into **IM1** via the electron-rich N-anion site to generate **IM2** that is 4.5 kcal/mol lower than **IM1**. Similarly, the addition of the third and fourth equivalent of **1d** generates the zwitterionic complex **IM3** and **IM4** via the transition states **TS3** and **TS4**, respectively. Again, these two barriers related to C-N bond formation with 13.8 and 10.7 kcal/mol, respectively, were in the range of experimental realization under mild conditions. Note that, the second equivalent of BnOH can further reduce the C-N coupling barrier of **TS4** via weak interactions, which is detailed in Figure S45. After crossing a smaller barrier of 6.9 kcal/mol, the ring-closure step can be readily achieved via the six-membered-ring transition state **TS5** forming intermediate **IM5**. Subsequently, the final product **2d** can be easily released via a very small barrier of 1.0 kcal/mol (i.e., **IM5 →TS6**), to regenerate the intermediate **IM1** for the next catalytic cycle. The highest barrier along the reaction pathway, measured from the most stable intermediate **IM2**, is predicated to be 16.5 kcal/mol, which should be the rate-determining step (RDS) for the catalytic cycle. It should be emphasized that the favorable interactions between N-anion species and the electron-deficient π-acidity at the $C_a$ site of CDC, as well as the hydrogen bonds and π-π stacking interactions between the BnOH and CDC species, play important roles in stabilizing the geometry of the stationary points during catalysis. The whole reaction is exergonic by 38.6 kcal/mol, which can provide enough thermodynamic driving force for moving the reaction forward. On the other hand, we have also explored the reaction without addition of BnOH, which is less favorable in terms of both kinetics and thermodynamics (see Figure S46). This suggests the addition of BnOH can accelerate the reaction rate, which is in good agreement with the experimental observations.

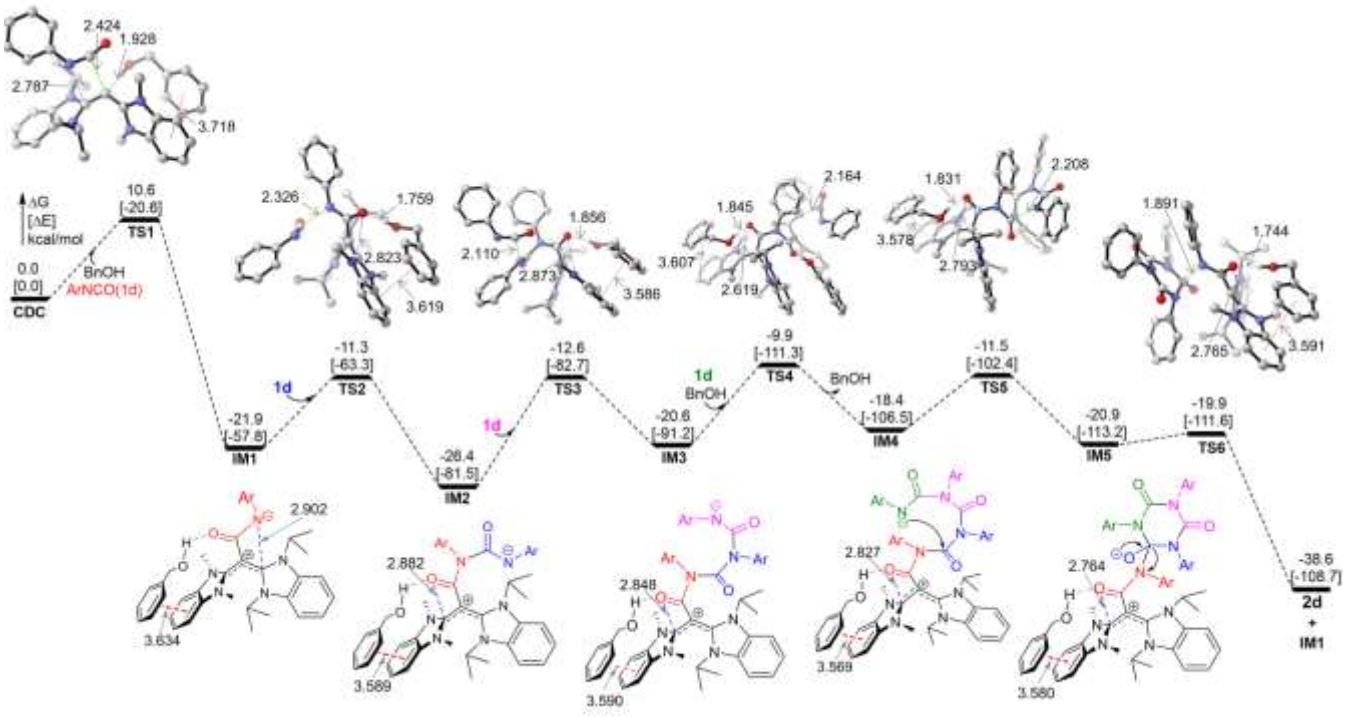


**Figure 3.** calculated energy profile at M06-2x+D3/6-311+G(d,p)(CPCM,solvent=toluene)//M06-2x+D3/6-31G(d)(CPCM, solvent=toluene) level for the addition of carbodicarbene ***C*$_1$-CDC** to phenyl isocyanate (**1d**) leading to product **2d**. Key interatomic distances are given in Ångstroms, while other geometries are given in Figure S44. Non-interacting hydrogen atoms have been omitted for clarity. (color code, C: gray, O: red, N: blue, H: white)



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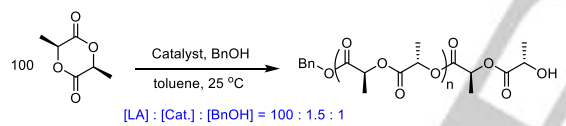
***L*-Lactide ring opening polymerization and methyl methacrylate polymerization based on CDC/BnOH.** Following the above mechanistic studies, we wondered if this synergistic CDC/BnOH could be further extended to other catalytic reactions. Several carbodicarbenes were tested for ring-opening polymerization (ROP) of *L*-lactide (LA) in the presence of BnOH in toluene at ambient temperature (Scheme 2A). ***C*$_1$-CDC** exhibited the best activity with almost 90% conversion within 1 min with a good dispersity (Đ) of 1.44 (entry 1). ***C*$_2$-CDC**, which possesses similar electronic features, but with a bulkier steric environment gave 87% conversion with a longer reaction time (65 mins) and slight increase in Đ of 1.53 (entry 2). **CPC** performed poorly with 57% conversion and higher Đ of 2.18 value (entry 3).

To better optimize the polymerization process, we also tested various conditions affecting the catalytic behavior of ***C*$_1$-CDC**/BnOH. First, we examined solvent scope and toluene appeared to be the ideal solvent (entries 1-3, Scheme 2B). No conversion occurred in THF, implying that coordinating solvents may compete with LA for CDC, hence reducing the catalytic activity drastically.[21] Whereas, $CH_2Cl_2$ posed a vulnerability to ***C*$_1$-CDC** catalyst, as it ceased to operate after 1 min with only 53% conversion (Đ = 1.10). The control experiment showed that the presence of BnOH is crucial to the efficiency and narrow molecular weight distribution (entries 2 vs 4); as it would take a longer time (27 mins) to reach 91% conversion accompanying with large Đ value (1.60) in the absence of BnOH. We also discovered that pre-mixing ***C*$_1$-CDC** and BnOH prior to the LA addition leads to narrower dispersity (Đ =1.26, entry 5), while maintaining the high activity of polymerization.

**Scheme 2.** CDC Mediated Polymerization Process.

**A. Ring Opening Polymerization of LA catalyzed by various CDC.**[a]

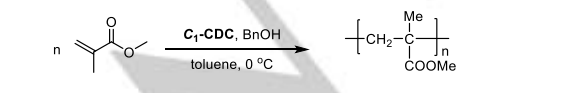



| Entry | Catalyst | Time (mins) | conv (%) | $Mn_{NMR}$[b] | $Mn_{GPC}$[c] | Đ[d] |
|---|---|---|---|---|---|---|
| 1 | ***C*$_1$-CDC** | 1 | 90 | 13000 | 13100 | 1.44 |
| 2 | ***C*$_2$-CDC** | 65 | 87 | 12800 | 11300 | 1.53 |
| 3 | **CPC** | 8 | 57 | 8400 | 8500 | 2.18 |

**B. Optimization of LA Polymerization based on *C*$_1$-CDC.**[a]

| Entry | [LA] : [Cat.] : [BnOH] | Solvent (mL) | Time (mins) | conv (%) | $Mn_{NMR}$[b] | $Mn_{GPC}$[c] | Đ[d] |
|---|---|---|---|---|---|---|---|
| 1 | 100 : 1.5 : 1 | THF (5) | 135 | 0 | n/a | n/a | n/a |
| 2 | 100 : 1.5 : 1 | toluene (5) | 1 | 90 | 13000 | 13100 | 1.44 |
| 3 | 100 : 1.5 : 1 | $CH_2Cl_2$ (5) | 1 | 53 | 2100 | 2200 | 1.10 |
| 4 | 100 : 1.5 : 0 | toluene (5) | 27 | 91 | n/a | 16000 | 1.60 |
| 5[e] | 100 : 1.5 : 1 | toluene (5) | 2 | 97 | 13600 | 13800 | 1.26 |
| 6[f] | 1200 : 1.5 : 30 | toluene (10) | -- | 90 | 3500 | 4800 | 1.38 |

**C. MMA Polymerization based on *C*$_1$-CDC.**[g]




| Entry | [MMA] : [Cat.] : [BnOH] | Time(mins) | conv (%) | $Mn_{GPC}$[c] | Đ[d] |
|---|---|---|---|---|---|
| 1 | 100 : 1 : 1 | 12 | 99 | 17500 | 1.79 |
| 2 | 200 : 1 : 1 | 9 | 99 | 27500 | 1.51 |
| 3 | 300 : 1 : 1 | 7 | 99 | 35600 | 1.47 |
| 4 | 400 : 1 : 1 | 6 | 99 | 46100 | 1.43 |
| 5 | 500 : 1 : 1 | 5 | 99 | 55100 | 1.36 |
| 6 | 600 : 1 : 1 | 7 | 98 | 71300 | 1.47 |
| 7 | 100 : 1 : 0 | 5 | 99 | 187300 | 3.50 |

[a] Mixture of LA & BnOH prepared prior to catalyst addition. [LA] = 0.5 M in 5 mL solution at 25 °C. [b] Determined by NMR. [c] Values by Gel Permeation Chromatography (GPC) × 0.58 of PLA. [d] Dispersity index by GPC. [e] ***C*$_1$-CDC** and BnOH were mixed for 5 mins prior to LA addition. [f] Initial with each addition [LA] : [Cat.] : [BnOH] = 200 : 1.5 : 30, [Cat.] = 3.25 mM, 10 mL. Final tally = 1200: 1.5: 30. [g] [Cat.] = 50 mM in 0.5 mL solution at 0 °C.

The tolerance of ***C*$_1$-CDC** towards monomer loading was also evaluated. The reaction was initiated with [LA]:[Cat]:[BnOH] = 200:1.5:30 to reach 90% conversion in 10 mins duration and the polymerization process could be carried out for nearly 10 successive additions of 100 equivalent of LA until the solution could not be further mechanically stirred, making the final tally of this experiment with a record of [LA]:[Cat]:[BnOH] of 1200:1.5:30 (entry 6). Interestingly, this strategy based on fragmentation additions could also be used to improve the dispersity of polymer (Đ=1.38). Several advantageous aspects of CDC are noteworthy. First, ***C*$_1$-CDC** possesses an immortality feature in polymerization process, as the excessive BnOH loading does not affect its catalytic activity (entry 6, also see Table S2).[22] Generally, most organometallic catalyst mediated PLA process are not tolerant to protic reagents like alcohol.[23] Second, ***C*$_1$-CDC** took a much shorter time to accomplish the catalytic ROP of LA than its counterparts (classical NHCs).[24] Third, the good controllability of ***C*$_1$-CDC** in the PLA polymerization process was reflected in the linear relationship plot of $Mn_{GPC}$ and [LA]/[BnOH] with acceptable Đ values (see Figure S2).

Tacticity of the resulting PLAs was investigated, and epimerization occurred in the absence of BnOH (entry 4, Pm = 0.66, Figure S7). It implied the strong basicity of ***C*$_1$-CDC** and deprotonation of *L*-LA took place, causing the loss of optical purity of the monomer and therefore affecting tacticity of the corresponding polymer. Similar situation was also observed in other highly basic catalysts like NHCs.[25] However, PLA with high isotacticity was obtained in the presence of sufficient BnOH (entry 6, see Figure S8); indicating the modulating effect by BnOH on the basicity of ***C*$_1$-CDC**. Additionally, we performed a small scale reaction with [LA]:[***C*$_1$-CDC**] of 10:1.5 for MALDI-TOF MS analysis in order to understand the nature of ROP process. The mass analysis showed peaks corresponding to fragment ***C*$_1$-CDC** + 2LA as well as *n*LA monomer repeating units (see Figure S9). This indicated that ***C*$_1$-CDC** initiated the polymerization and later stage transesterification (back-biting) on the propagating species occurred to give cyclic PLAs. However, only linear PLAs with benzyl alkoxide (BnO) end-chain group was observed for entry 6 when high ratio of BnOH presented (also see Figure S10). Again, adequate amount of BnOH as co-modulator is critical in minimizing transesterification side reaction.

The CDC/BnOH mediated-reaction could also be applied to polymerization of methyl methacrylate; a different reaction pathway from PLA polymerization (Scheme 2C). Initially, we performed the reaction in 0.5 mL toluene with 100:1:1 of [MMA]:[***C*$_1$-CDC**]:[BnOH] to generate polymeric product with *Mn* of 17500 and Đ of 1.79 in a short time (12 mins, entry 1). The narrow Đ of 1.36 and high molecular weight of 55100 could be achieved by incrementally increasing the amount of MMA (entries 2-6) without sacrificing the rate of the reaction. On the contrary, [MMA]:[***C*$_1$-CDC**] with 100:1 without BnOH additive gave a relatively large $M_n$ (~180,000) with broad Đ value of 3.50 (entry 7). This outcome indicated the BnOH had played a co-modulating role by moderating the rate of polymerization for better dispersity.

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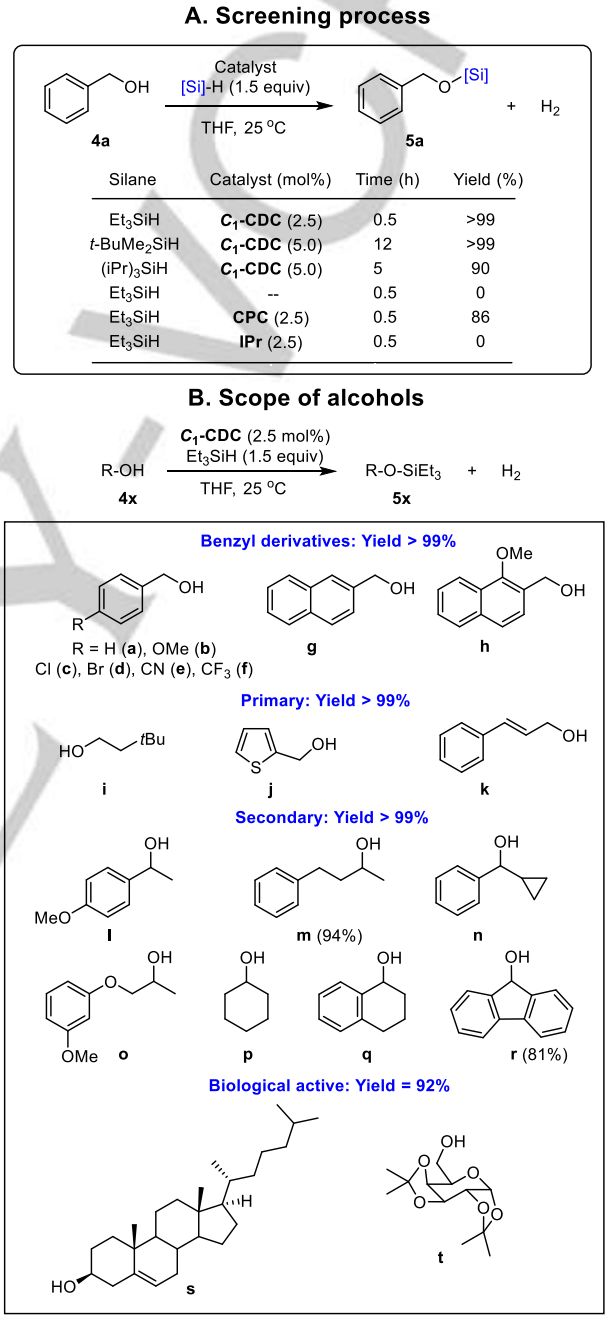
To better understand the nature of the polymerization, MALDI-TOF mass analysis was carried out to examine the small-scale reaction. The feed of monomer/catalyst/BnOH in 10:1:1 (Figure S12) showed mass series of oligomers with analogous pattern having signal interval that coincide with MMA repeating unit (MW = 100) and incorporation of one ***C*$_1$-CDC** (MW = 360), implying that CDC is responsible for the initiation of the chain addition in polymerization. Mass analysis also illustrated some of the pendant group (COOMe) dangled on oligomers had been converted to COOBn, which was attributed to the CDC-promoted transesterification in presence of BnOH. In lower molecular mass analysis, the feed of monomer/catalyst/BnOH in 2:1:1 (Figure S13) again consistently showed that the CDC unit was incorporated into a series of oligomers with m/*z* = 561, 661, 761 and 861. However, the feed of 2:1:0; in the absence of BnOH revealed only major peak corresponded to m/*z* of 561 (Figure S14), hinting the propagation rate is relatively greater than initiation rate for which we would not be able to detect the other low mass oligomers. Hence, BnOH does affect the nucleophilicity of CDC and its presence is necessary to slow down the propagation rate of polymerization and thus for improved dispersity of the resulting polymer. Finally, it is noteworthy to mention that the catalytic polymerization of MMA by ***C*$_1$-CDC** is distinctly unique. No additional strong Lewis acid like $Al(C_5F_6)_3$ is required, that is usually present in NHC-promoted PMMA polymerization.[26] Moreover, no NHC were found to polymerize MMA in toluene and yet the catalytic property of NHC is highly dependent on its structures.[27]

**Extension of the reaction model: Dehydrosilylation of alcohols.** BnOH has been shown to serve as an effective co-modulator for CDC to promote the FLP-like reactivity in cyclotrimerization of isocyanate, PLA and MMA polymerizations. We sought to further exploit the BnOH---CDC interaction for chemical transformations in the presence of a suitable substrate. Yet, *in situ* formation of H[***C*$_1$-CDC**]$^+$ generated from the reaction with BnOH should not be the active species responsible for these catalytic reactions. Dehydrosilylation of alcohols, important methodology in organic synthesis appeared to be a perfect reaction model to rule out this possibility and **4a** was selected as the test candidate along with several hydrosilanes (Scheme 3). The reaction proceeds smoothly in THF solution with 2.5 mol% of ***C*$_1$-CDC** catalyst at ambient temperature to furnish desired benzyl silyl ether, **5a** in quantitative yield using $Et_3SiH$. More sterically bulky and robust hydrosilanes like (*t*-Bu)$Me_2SiH$ and (*i*-Pr)$_3SiH$ posed no problem in this catalytic reaction with excellent yields; albeit under longer reaction times. It is noteworthy to mention that no catalytic activity was observed for ***C*$_1$-CDC** if both BnOH and $Et_3SiH$ were not added together, indicative of a synergistic interaction among these substrates with CDC.

Next, we also examined the scope of alcohols. A variety of electron-deficient and rich benzyl alcohols (**4a-f**) and naphthyl alcohols (**4g-h**) were amenable to the CDC-catalyzed reaction (Scheme 3B). Other primary alcohols, containing functionality of alkyl (**4i**), heteroaryl (**4j**) and allylic (**4k**) underwent dehydrosilylation smoothly. We were pleased to find that a series of secondary alcohols (**4l-r**) reacted well with the desired silyl ethers without any side products. Finally, this catalytic reaction could also be applied to biologically active compounds like cholesterol (**4s**) and sugar derivative (**4t**) with excellent yields. Since there is no obvious loose interaction between ***C*$_1$-CDC** and tertiary alcohols (eg. *t*-butanol, Figure S3c and 2-phenyl-2-propanol, Figure S6); probably due to steric interference; no silylated products were obtained. These findings further validate the synergistic model of CDC/BnOH through non-bonding interactions.

**Scheme 3.** CDC-mediated Dehydrosilylation of Alcohols.[28]




## Conclusion

In summary, our findings bring to light a FLP-like feature in carbodicarbene attuned by a co-modulator BnOH to direct isocyanate cyclotrimerization. Moreover, this proof-of-concept could be expanded to other different catalytic reactions such as



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ring opening polymerization of *L*-lactide, methyl methacrylate polymerization and dehydrosilylation of alcohols. DFT calculation and NMR analysis indicated that π-π stacking and weak Brønsted acid/Lewis base pair interactions between the BnOH and CDC played a major role to generate this subtle synergistic FLP behavior in catalysis. Undeniably, several aspects of this work should have broad future impacts on (i) carbone-like organic catalysts based on Frustrated Lewis Pairs (ii) enriching and diversifying the reactivity of FLP reactions by adding different "co-modulator" molecules bearing variable functionalities and (iii) catalytic reactivities of carbone is uniquely distinct from conventional NHC, as carbone can access its second lone-pair and π-acceptability, which are lack in NHC. Ongoing application of this FLP reactive behavior of ***C*$_1$-CDC** with the assistance of co-modulator is currently one of the focus of our group.

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In the present of co-modulator alcohol, the putative strong σ donor, CDC is reshaped into Frustrated Lewis Pair-like reactivity. The unique synergistic FLP behavior of CDC; unachievable by its counterpart NHCs, shown to have beneficial and complementary effects on isocyanate cyclotrimerization, LA polymerization, MMA polymerization and dehydrosilylation of alcohols.

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