Carbene Ligands

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Expanding the Ligand Framework Diversity of Carbodicarbenes and Direct Detection of Boron Activation in the Methylation of Amines with CO_2

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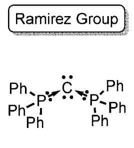
Abstract: *A simple and convergent synthetic strategy used to increase the diversity of the carbodicarbene ligand framework through incorporation of unsymmetrical pendant groups is reported. Structural analysis and spectroscopic studies of ligands and their Rh complexes are reported. Reactivity studies reveal carbodicarbenes as competent organocatalysts for amine methylation using CO_2 as a synthon. A unique B−H-activated boron–carbodicarbene complex was isolated as a reaction intermediate, providing mechanistic insight into the CO_2 functionalization process.*



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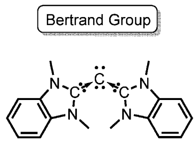

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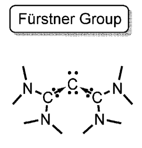

C

The first example of a ligand-stabilized, lone-pair-containing carbon derivative in the zero oxidation state, CL_2,[1] was reported by Ramirez and co-workers with the isolation of carbodiphosphoranes **A**.[2] However, the unique chemical nature of **A** was not fully realized at that time, as organic chemistry was strictly based on the doctrine of four valence electrons in the bonding of carbon. However, this paradigm began to shift with the landmark theoretical report of a species coined as a "carbodicarbene" composed of a divalent carbon(0) center with two N-heterocyclic carbene (NHC) ligands, NHC→C(0)←NHC, from Frenking and co-workers.[3] They postulated that the central carbon atom would possess two lone pairs of electrons and would reside within a nonlinear C−C−C moiety. Less than a year later, Bertrand et al. and Fürstner and co-workers took up the conceptual challenge and successfully synthesized the corresponding carbodicarbenes **B**[4] and **C**,[5] respectively.

Carbodicarbenes (CDCs) or bent allenes have been proven to be stronger donor ligands for both main group elements and transition metals in catalytic applications.[6] For example, Stephan et al. reported that ruthenium complexes bearing cyclic bent allene ligands are highly active and functional-group-tolerant catalysts for the hydrogenation of inert olefins.[6a] Both our group and Meek and co-workers have reported the first examples of CDC-based pincer ligand scaffolds, which were successfully utilized for a range of catalytic transformations, such as C−C cross-coupling,[6b] intermolecular hydroamination,[6c] and hydro-heteroarylation.[6d] Moreover, aided by the strong σ basicity and peculiar bonding topology embedded in the CDC framework, our group has successfully isolated the elusive dicationic borane species,[7] which is, to date, unattainable through the use of other common σ-donating ligands. As a consequence, this family of captodative carbogenic compounds has a promising future as a complementary surrogate to the well-established NHC[8] and cyclic(alkyl)(amino)carbene (CAAC)[9] ligands, with the possibility of accessing new modes of chemical reactivity. Regrettably however, interest in these CDC frameworks has remained low, largely as a result of the lack of diverse architectural scaffolds for possible organometallic chemistry and catalysis applications.[10,11]

Unquestionably, the development of synthetic strategies for increasing the structural diversity of CDCs would not only dramatically expand the utility of the ligand, but would also facilitate the discovery of new and unconventional reaction pathways. Our group has previously successfully prepared several CDC scaffolds.[6b,11] However, as structural diversity has mostly been introduced by varying the substituents around the nitrogen centers (Scheme 1a), the overall scope of this ligand topology has remained relatively narrow.[6b,11,12] To broaden the scope of the CDC ligand framework with a view to accessing new reaction pathways, we sought to assemble CDCs bearing unsymmetrical units.

Based on retrosynthetic analysis, we postulated that a modular S_N2-type reaction between a nucleophile and an electrophile (Scheme 1b), akin to that initially reported by Kuhn and co-workers for the synthesis of bis(1,3,4,5-tetramethyl-2-imidazolyl)methylium iodide,[13] would be suitable

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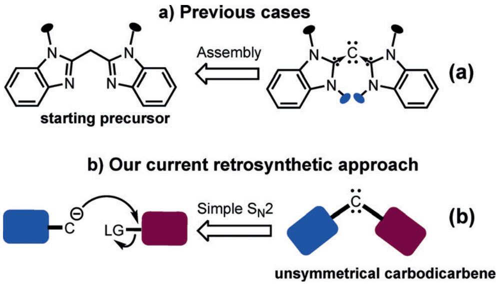
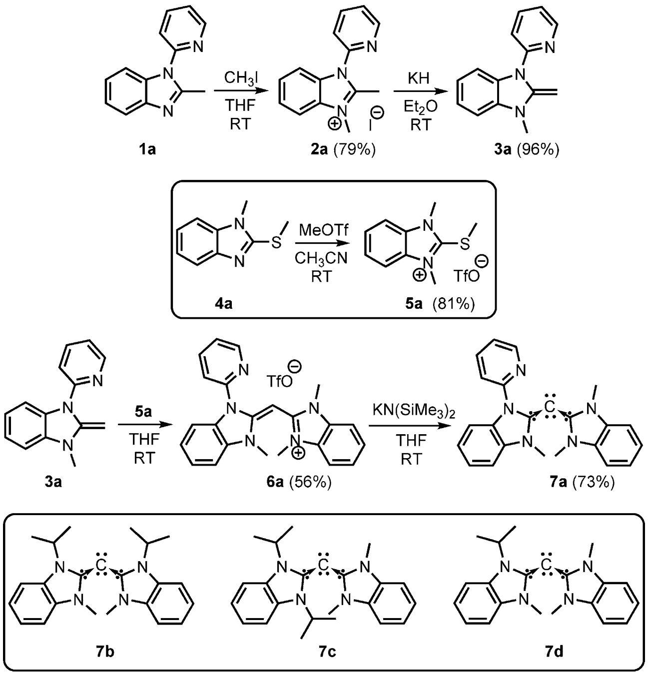


Scheme 1. Synthetic strategies for carbodicarbenes (CDCs).

for constructing an array of unsymmetrical CDCs. As N-heterocyclic olefin (NHO) adducts possess a strong nucleophilicity and can be easily synthetically modified, they are ideal nucleophiles for this synthetic approach.[14] Herein, we describe the development of a simple, modular synthetic procedure for the preparation of unsymmetrical CDCs bearing different ligands. Furthermore, we were able to employ CDCs to perform reductive N-methylation of amines with CO_2 in the presence of borane. Additionally, the isolation of a carbodicarbene-activated borane provides key information to determine the mechanism of the CO_2 sequestration process by carbenoid-based organocatalysts, an area of intense recent interest (see below).

To our knowledge, there are currently no examples of unsymmetrically substituted CDCs and thus we set out to synthesize ligands with this challenging topology. The NHO molecule ene-1,1-diamine **3a** was chosen as our target nucleophilic fragment. The multi-step synthetic approach began with the copper-promoted C−N cross-coupling reaction of commercially available 2-methylbenzoimidazole and *o*-bromopyridine in the presence of tetrabutylammonium fluoride (TBAF) and 2-aminopyrimidine-4,6-diol to afford **1a**.[15] Subsequent methylation of **1a** with iodomethane furnished imidazolium **2a** which was deprotonated by potassium hydride to afford the desired product **3a** in nearly quantitative yield (96%; Scheme 2). The complementary electrophilic fragment **5a**, containing a thioether moiety, was synthesized by a one-step reaction of 1-methyl-2-(methylthio)benzoimidazole (**4a**)[16] with MeOTf in acetonitrile. With compounds **3a** and **5a** in hand, we set out to attempt the fusion of these two distinct fragments to form the unsymmetrical carbodicarbene **7a**. Reaction of **3a** with **5a** in THF solution furnished cationic salt **6a** in 56% yield by recrystallization, whose structure was confirmed by single-crystal X-ray diffraction and other conventional spectroscopic methods.[17] Deprotonation of **6a** with the base $KN(SiMe_3)_2$ afforded the air-sensitive, free, unsymmetrical carbodicarbene **7a** in 73% yield (Scheme 2). Although we were unable to obtain single crystals of **7a** suitable for X-ray diffraction, NMR analysis was able to definitively confirm its formation; disappearance of the signature resonance signal for the methine CH of **6a** at $\delta = 5.04$ ppm confirmed the formation of free carbodicarbene **7a**. Utilizing this synthetic method, we were able to access C_2-symmetric CDC **7b**, as well as the other unsymmetrically substituted CDCs **7c** and **7d** (Scheme 2).



Scheme 2. Synthesis of carbodicarbene **7a** and related carbodicarbenes **7b–d**.

Encouraged by our success in constructing CDCs **7a–d**, we were curious if our facile S_N2 strategy could be applied towards the synthesis of more sterically challenging analogues, the success of which would represent significant growth in the scope of CDC ligand topology. With this in mind, we sought to transform the commonly used NHC 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr; **2e**), to the corresponding methylene imidazole **3e** using a two-step sequential olefination process with CH_3I, followed by treatment with $NaN(SiMe_3)_2$ (Scheme 3a). The resulting compound **3e** was then reacted with **5a**, resulting in the formation of cationic **6e**, which was subsequently converted into the target CDC **7e** by deprotonation. We were also able to construct phosphine-stabilized carbone **7f** using a similar method (Scheme 3b), further reinforcing the general utility of our approach. Interestingly, the ^{13}C NMR spectrum of **7f** showed a signal attributable to a carbenic carbon at $\delta = 64.4$ ppm, which was more upfield than the corresponding signal in the spectra of compounds **7a–e** ($\delta \approx 110$ ppm). It is noteworthy to mention that the isolation of non-benzannelated carbones like **7e** and **7f** further reinforces the theoretical prediction by Frenking and co-workers about the stability of such species in the condensed state.[3c]

The molecular structures of **7c** and **7e** were confirmed by single-crystal X-ray diffraction studies (Figure 1a,b). Structure **7c** featured a bent C11−C1−C2 moiety with C−C bond lengths of 1.3455(16) and 1.3401(16) Å and a bond angle of 137.55(12)°, which were comparable to previously reported examples.[4,11] In contrast to **7c**, the C2−C1−C29 moiety in **7e** featured unequal electronic interactions resulting in C−C bond lengths of 1.318(3) and 1.344(3) Å, respectively. The shorter C1−C29 bond in **7e**, close to the benzimidazole fragment, was more planar (torsional angle ≈ 169°) than the

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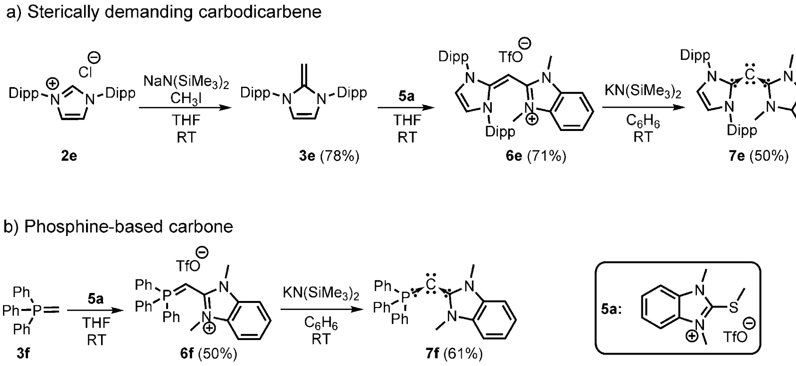

Scheme 3. Synthesis of carbodicarbenes a) **7e** and b) **7f**. Dipp = 2,6-diisopropylphenyl.

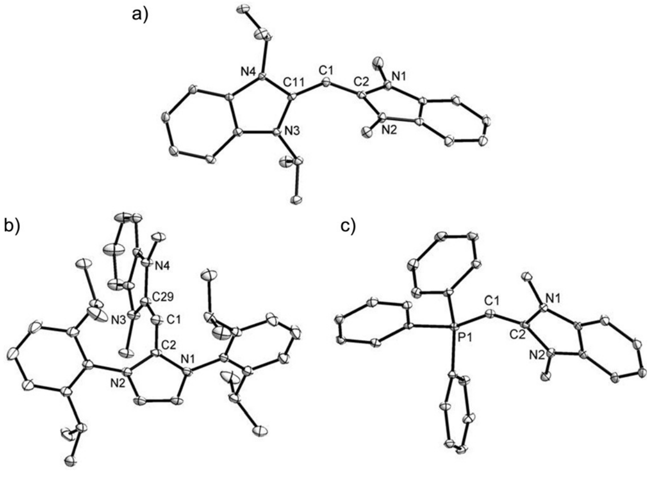

Figure 1. Solid-state structures of a) **7c**, b) **7e**, and c) **7f** with thermal ellipsoids set at 30% probability.[29] Hydrogen atoms have been omitted for clarity.

imidazole fragment (IPr), signifying a more effective π conjugation along the C1–C29 bond with the aromatic ring. Consequently, the shift towards greater sp^2 character for the C1–C29 bond would decrease the electronic repulsion, in turn rendering the C-C-C bond angle more linear. It was thus unsurprising that the allenic C-C-C angle of **7e** (146.11(19)°) was larger than that of **7c** (137.55(12)°). The molecular structure of **7f** stabilized by PPh$_3$ was also confirmed by single-crystal X-ray diffraction (Figure 1c). The P1–C1 bond length (1.6435(12) Å) in **7f** was shorter than typical P–C single bonds (1.8 Å), indicating a partial double-bond character. This was comparable with a recent carbodiphosphorane structure reported by Alcarazo, Fürstner, and co-workers (P–C bond length ≈ 1.6398–1.6416 Å).[18] However, the P-C-C bond angle (133.25(10)°) was smaller than the P-C-C bond angle for **7f** (143.04(10)°).

The comparison of solid-state structures of transition metal centers supported by CDCs can shed light on various aspects of ligand structure and bonding behavior. We chose to investigate the coordination of CDCs **7a** and **7e** to rhodium centers. Carbodicarbene **7a** in benzene was allowed to react with [{Rh(CO)$_2$Cl}$_2$] at ambient temperature affording complex **8a** in good yield (71%).[17] Similar conditions were employed with **7e** to furnish complex **8e**. Single-crystal X-ray diffraction studies revealed the structures of both **8a** and **8e** (Figure 2). Both species featured the bent allenic moieties coordinated in a η^1 monodentate fashion to a rhodium center with the complex having an overall square-planar configuration. The Rh–CDC bond lengths of molecules **8a** and **8e** (2.117(2) and 2.116(2) Å, respectively) were longer than those previously reported for molecules from both our group (2.109(2) Å)[11] and that of Bertrand et al. (2.089(7) Å),[4] highlighting the sterically encumbering environment within this CDC framework. The strongly electron-donating CDC moiety for both **8a** and **8e** exerted a *trans* influence on the Rh–C bond of the opposite carbonyl ligand, with a Rh–CO bond length approximately 0.040 Å longer compared to the Rh–CO bond of the *cis* carbonyl ligand (1.840(4) Å) detected in **8a**. As a result of the strong push–push effect caused by the IPr moiety on the carbon center, the electron-donating capability of carbodicarbene **7e** was enhanced compared to its pyridinyl counterpart **7a**. This was confirmed by means of IR spectroscopy, with the IR stretching modes of the CO groups of **8e** (2045, 1964 cm^{-1}) occurring at lower wavenumbers than those of **8a** (2054, 1977 cm^{-1}).

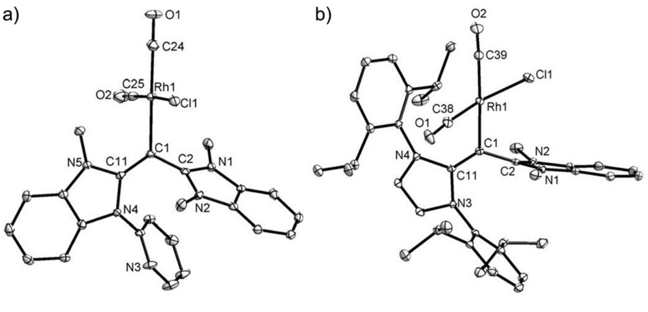

Figure 2. Solid-state structures of a) **8a** and b) **8e** with thermal ellipsoids set at 30% probability.[29] Solvent molecules and hydrogen atoms have been omitted for clarity.

As a result of fluctuating costs and the finite resources of petroleum-based carbon feedstocks as well as the implications of CO$_2$ in climate change, the production of organic chemicals using carbon dioxide as a C1 source has become an area of intense research.[19,20] As a consequence, many systems demonstrating the recycling of CO$_2$ have been reported; for example the generation of methanol by hydroboration,[21] carboxylation by C–C bond formation,[22] formylation through C–N bond formation,[23] and synthesis of cyclic carbonate products.[24] Recently, an elegant procedure for the CO$_2$-based methylation of N–H moieties mediated by ruthenium catalysts has been developed.[25] Shortly thereafter, this proof of principle was successfully adapted for more benign organocatalysts, namely NHC- and proazaphosphatrane-promoted reductive functionalization of CO$_2$ for meth-

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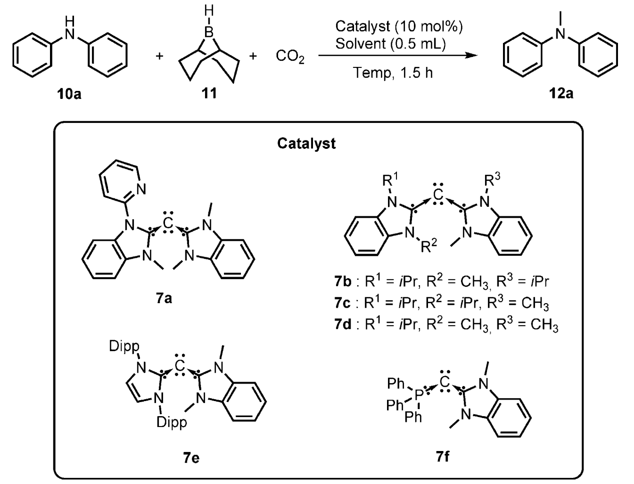
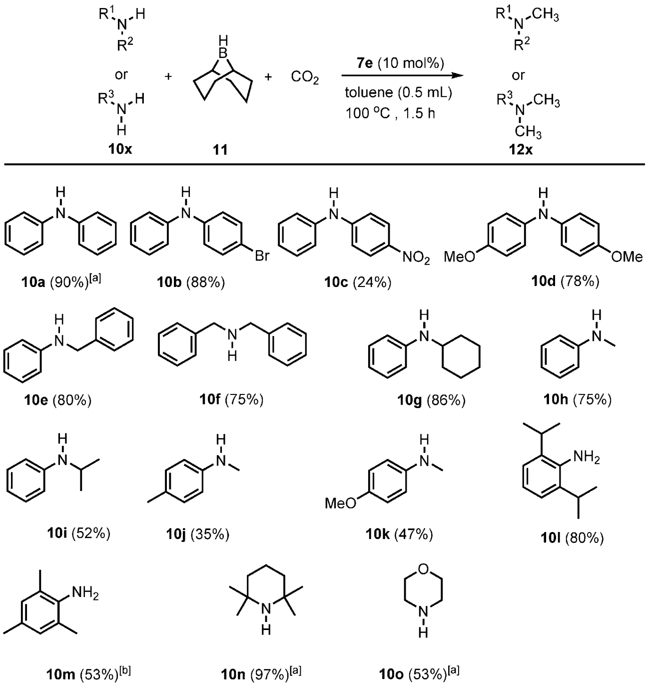
ylation of amines.[26] We have thus explored the analogous utility of CDCs as organocatalysts for the methylation of amines with CO_2 as substrate. The initial optimization study was performed in THF solution with diphenylamine (**10a**) and 9-borabicyclo[3.3.1]nonane (9-BBN; **11**) under 1 atmosphere of CO_2 using 10 mol% CDC catalyst. It was found that catalysts **7b** and **7e** (at a reaction temperature of 80°C) effectively mediated the reaction to afford *N*-methyldiphenylamine **12a** in excellent yields of 84–86% (Table 1; entry 4 and 8). Thus both CDCs were selected as benchmark catalysts for subsequent exploration. Further optimization revealed that the activity of these catalysts could be improved further to obtain the desired products in yields of circa 90% by changing the solvent to toluene and increasing the reaction temperature to 100°C (entry 9,10).

Table 1: Optimization process for the methylation of amine using CO_2.



Entry	Catalyst	Solvent	Temp [°C]	Yield [%][a]
1	**7b**	THF	90	67[b]
2	**7b**	THF	50	13[b]
3	**7b**	THF	90	83
4	**7b**	THF	80	86
5	**7a**	THF	80	80
6	**7c**	THF	80	80
7	**7d**	THF	80	25
8	**7e**	THF	80	84
9	**7b**	toluene	100	89
10	**7e**	toluene	100	90
11	**7f**	toluene	100	86

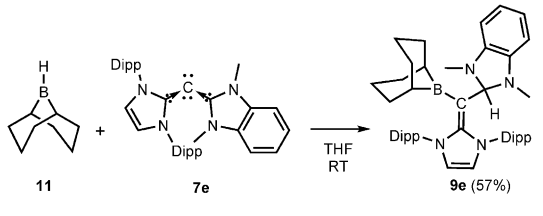
Reaction conditions: amine (1 mmol), 9-BBN (4 equiv), solvent (0.5 mL), catalyst (10 mol%), CO_2 (1 atm), 1.5 h. [a] Yield determined by GC. [b] 5 mol% of **7b**.



Scheme 4. Methylation of various amines using CO_2. Standard conditions: amine (1 mmol), 9-BBN (4 equiv), toluene (0.5 mL), **7e** (10 mol%), CO_2 (1 atm), 100°C, 1.5 h. Yields are of the isolated product. [a] Yield determined by GC. [b] In the presence of 9-BBN (4.5 equiv).

With the optimized reaction conditions in hand, the scope of the CDC-catalyzed amine methylation reaction with CO_2 as carbon source was expanded, using in particular **7e** as the catalyst (Scheme 4). Excellent yields (circa 90%) were obtained for diphenylamine (**10a**) and bromo-substituted diphenylamine **10b**. A lower yield was obtained using nitro-substituted derivative **10c**, whereas the yield with the diphenylamine derivative containing electron-donating methoxy groups **10d** was moderate (78%). Using *N*-benzylaniline (**10e**), *N*-cyclohexylaniline (**10g**), dibenzylamine (**10f**), or *N*-methylaniline (**10h**) as the reagent generally led to good yields of product. Even the sterically encumbered *N*-isopropylaniline (**10i**) resulted in a yield of 52% for the isolated product, highlighting reasonable tolerance for steric bulk within this system. *N*-methylaniline bearing an electron-donating group, such as methyl (**10j**) or methoxy (**10k**), resulted in lower yields. The CDC-promoted double methylation was also readily extended to primary amines with sterically demanding substituents, such as **10l** and **10m**, to furnish dimethylated products. Finally, cyclic alkylamines, such as piperidine (**10n**) and morpholine (**10o**), were also readily methylated, with **10n** furnishing near quantitative yields (97%).

To obtain a better understanding of the reaction mechanism, we performed a series of experiments. First, an equimolar mixture of **7e** and 9-BBN (**11**) was allowed to react to afford adduct **9e** [Eq. (1)]. The solid-state structure of **9e** was confirmed by single-crystal X-ray diffraction studies (Figure 3). The structure was composed of a trivalent boron complex bearing a CDC ligand with a planar geometry (sum of angles = 360°). Surprisingly, the original hydride (H29) on



(1)

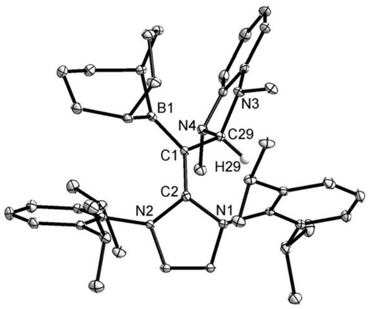
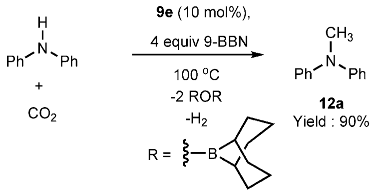


Figure 3. Solid state-structure of **9e** with thermal ellipsoids set at 30% probability.[29] Hydrogen atoms, with the exception of the C(29)H, have been omitted for clarity.

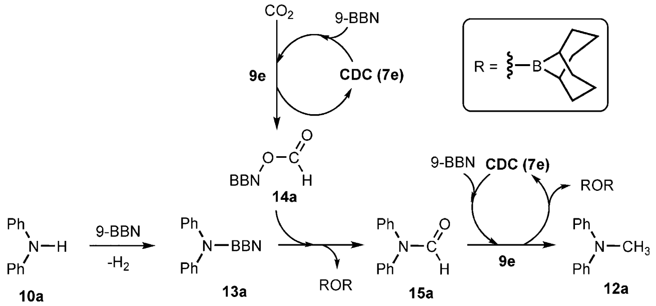
the boron center of 9-BBN has migrated to the C29 position of the CDC. In the ^{1}H NMR spectrum of **9e**, a typical singlet resonance signal for a tertiary C-H moiety at $\delta = 5.26$ ppm further confirmed the presence of the hydrogen atom at the C29 position. Performing a similar methylation reaction of amine **10a** with CO_2 using **9e** as catalyst generated product **12a** in yield of 90% [Eq. (2)].



(2)

To our knowledge, compound **9e** is the first isolated reaction intermediate for the reduction of CO_2 to methylamines in the presence of borane. Moreover, it shows a unique borane activation mode, whereby the C29 atom of the benzoimidazolylidene ligand unit appears to work synergistically with the carbon center (C1) as a facile hydrogen-transfer site. This is in contrast to the activation of the B–H fragment by other carbenoid species which typically involve oxidative addition at a single carbenic site.[27] Additionally, this result stands in contrast to other proposed types of activation modes for the analogous silane activation for CO_2 reductive functionalization, as predicted by DFT studies.[28] With the above findings, we believe that we have further validated the reaction pathway previously proposed by Cantat and co-workers[26a] as illustrated in Scheme 5.

In summary, a straightforward synthetic method for unsymmetrical carbodicarbenes has been reported. Employing this method, we have prepared what is, to our knowledge, the first example of such a species. These results are an important development in the diversification of this promising ligand framework. Unsymmetrical CDCs were successfully ligated to Rh centers, and analysis revealed that the resulting coordinated CDCs featured strong electron-donating characteristics. Finally, CDCs were shown to be competent catalysts for the reductive N-methylation of amines with CO_2 in the presence of borane; the first example of CDCs as organocatalysts. Additionally, through X-ray crystallographic studies, we have identified a unique B–H-activated species which we believe to be a key intermediate in the reaction process. This has important implications for the mechanistic understanding of the reaction as promoted not only by CDCs, but also by analogous NHCs, an area of intense recent interest.



Scheme 5. Proposed mechanism for the catalytic methylation of **10a** with CO_2 and 9-BBN.

The potential utility of CDCs as catalysts in the synthesis of valuable platform chemicals from renewable carbon feedstocks, or as ligands for the isolation of transition metal, or main group based coordination complexes, further underlines the importance of expanding the diversity of this framework. Further expansion of both ligand structure and reactivity, as well as a detailed mechanistic investigation of the CDC-mediated reductive N-methylation of amines with CO_2, is currently under investigation.

Acknowledgements

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Keywords: carbene ligands · carbodicarbenes · CO_2 activation · ligand design · organocatalysis

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[1] The use of arrows provides only one possible bonding description for the compounds discussed herein. Alternative structures are provided in the Supporting Information. For a thorough discussion, please see: a) D. Himmel, I. Krossing, A. Schnepf, *Angew. Chem. Int. Ed.* **2014**, *53*, 370; *Angew. Chem.* **2014**, *126*, 378; b) G. Frenking, *Angew. Chem. Int. Ed.* **2014**, *53*, 6040; *Angew. Chem.* **2014**, *126*, 6152.

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