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# The Emergence of Zerovalent Carbon Compounds from Structural Curiosities to Organocatalysts

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## Comments

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## Perspective

# The emergence of zerovalent carbon compounds from structural curiosities to organocatalysts

Allegra L. Liberman-Martin<sup>1,2,\*</sup>

## SUMMARY

Low-valent main group compounds have reactivity patterns and properties reminiscent of transition metals. While divalent carbon compounds such as carbenes are widely studied ligands and organocatalysts, zerovalent carbon species have received considerably less attention. This perspective highlights the properties and reactivity of zerovalent carbon compounds, focusing on their first applications as organocatalysts for small molecule reduction and polymerization reactions.

## INTRODUCTION

Most organic compounds feature tetravalent carbon atoms, in which all four of carbon's valence electrons are used to form covalent bonds. Other bonding motifs, including low-valent carbon species, are of significant synthetic and theoretical interest because low-valent main group compounds can mimic the reactions of transition metal complexes.<sup>1,2</sup> Within the realm of low-valent carbon compounds, carbenes differ significantly from zerovalent species (termed carbones).<sup>3</sup> A singlet carbene is divalent, featuring a carbon with one lone pair of electrons and two covalent bonds to neighboring substituents.<sup>4</sup> Instead, carbones contain a central carbon with two lone pairs of electrons flanked by two donor groups, making them zerovalent (Figure 1). Carbenes have been extensively studied, with *N*-heterocyclic carbenes (NHCs) emerging as a prominent class of ligands and organocatalysts.<sup>5–7</sup> In contrast, the chemistry of zerovalent carbon compounds is less comprehensively developed.

There have been animated discussions in the literature surrounding the structural depictions used to portray zerovalent carbon species (Figure 1).<sup>8–12</sup> The earliest bonding models tended to show allene-like structures for carbodiphosphoranes ( $R_3P=C=PR_3$ ).<sup>13,14</sup> Suggestions that carbodiphosphoranes could feature a zerovalent carbon atom were proposed as early as the 1970s by Kaska and co-workers and Schmidbaur.<sup>15,16</sup> Subsequent theoretical studies of carbodiphosphoranes by Frenking and co-workers beginning in 2006 revitalized interest in zerovalent carbon chemistry and supported a bonding model in which there are donor-acceptor interactions between the central carbon and two ligands (L),  $L \rightarrow C \leftarrow L$ , placing two lone pair orbitals on carbon with  $\sigma$  and  $\pi$  symmetry.<sup>17–19</sup> The extent to which back-donation from the carbone center occurs depends on the flanking ligands. Weak back-bonding occurs to phosphorus donors  $PR_3$ , whereas carbones with flanking carbene donors have more allene-like  $C=C=C$  character.<sup>18,19</sup> In-depth discussions of the frontier orbitals and the nature of the donor-acceptor interactions in carbones are available in review articles from Frenking and co-workers.<sup>3,20</sup>

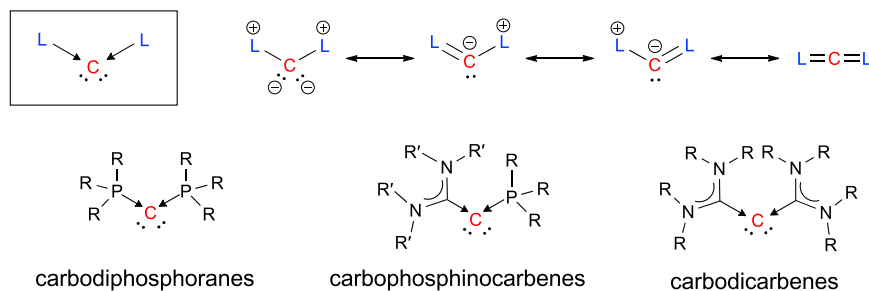
The structures of zerovalent carbon compounds have also sparked considerable interest, as both linear<sup>21–23</sup> and bent<sup>24–36</sup> geometries are known. Indeed, for the

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**Figure 1. Bonding depictions and classes of zerovalent carbon compounds**

The preferred bonding model shows dative interactions between the flanking donor groups and the carbene center. Alternative bonding depictions show C=L double-bonded structures. The most common classes of zerovalent carbon compounds are carbodiphosphoranes, carbophosphinocarbenes, and carbodicarbenes.

carbodiphosphorane  $C(PPh_3)_2$  (1), experimental P–C–P bond angles range from  $130.1^\circ$  to  $180^\circ$  depending on the crystallization conditions.<sup>22,23</sup> Density functional theory (DFT) calculations revealed that the energy required to expand the P–C–P bond angle of 1 from  $136.9^\circ$  to  $180^\circ$  is only 3.1 kcal/mol, which is small enough that dispersion interactions with co-crystallized benzene could cause the linear arrangement to be favored.<sup>22,23</sup>

Varied terminology for carbene compounds has been used. While carbenes are frequently referred to as carbon(0) compounds,<sup>3,37–40</sup> the electronegativity of the flanking groups relative to carbon impacts the calculated oxidation state, making this descriptor unreliable. Using the definition of valence as the number of electrons that an atom uses in bonding, carbene centers are classified as zerovalent.<sup>41,42</sup> However, an alternative method has been used of assigning valence by counting the number of bonds an atom forms within a molecule,<sup>43</sup> leading to examples of carbene species being referred to as divalent in the literature.<sup>3,39,40,44</sup>

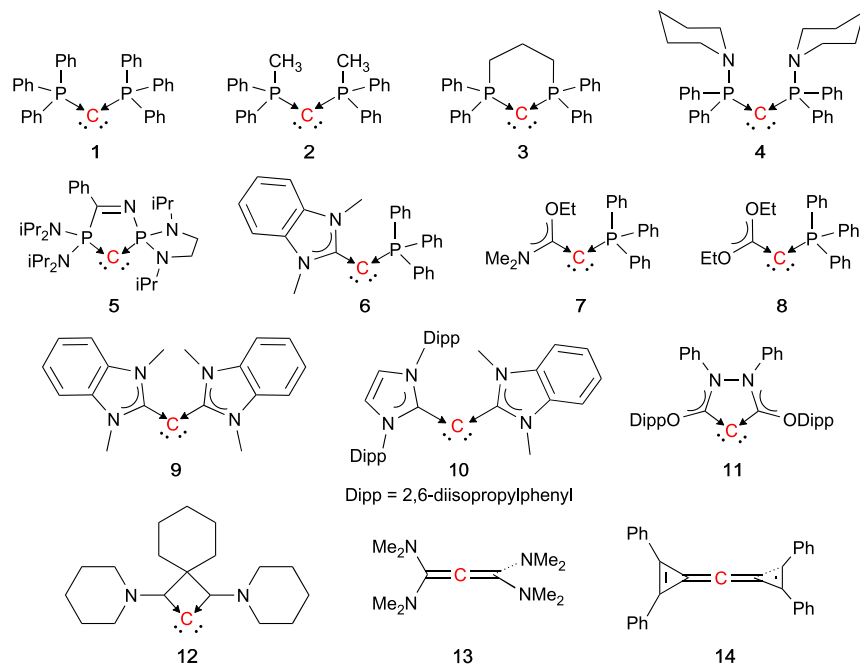
The three most prominent classes of zerovalent carbon compounds feature phosphine or carbene donors flanking the central carbene center. These species are termed carbodiphosphoranes (for compounds featuring two phosphine donors), carbophosphinocarbenes (one phosphine and one carbene donor), and carbodicarbenes (two carbene donors). Synthetic routes to access carbene compounds are available in a review article by Mézailles and co-workers.<sup>45</sup> This perspective compares the properties of carbene compounds, describes their unique reactivity patterns, and discusses recent examples of organocatalytic applications of these low-valent species.

## DONOR STRENGTH MEASUREMENTS

Understanding the electronic properties of ligands can facilitate the rational design of novel transition metal and main group compounds.<sup>46</sup> In addition to DFT studies of zerovalent carbon properties,<sup>44,47</sup> a range of experimental metrics have been used to parametrize carbene donor strengths (Table 1).

- (1) The  $A_1$  stretch for carbene- $Ni(CO)_3$  complexes has been measured, which is termed the Tolman electronic parameter (TEP).<sup>48</sup> The synthesis of nickel carbonyl compounds to obtain TEP values is relatively uncommon due to the high toxicity of the  $Ni(CO)_4$  precursor.<sup>49</sup>

**Table 1. Donor properties of zerovalent carbon compounds**



Carbon compound	Average $\nu_{CO}$ for carbone-Rh(CO) <sub>2</sub> Cl (cm <sup>-1</sup> )	$\sum \text{ClGaCl}$ for carbone-GaCl <sub>3</sub> (°)	Tolman Electronic Parameter (TEP)	Reference
<b>Carbodiphosphoranes</b>				
1	–	315.40(3)	2,033 <sup>a</sup> 2,035 <sup>b</sup>	El-Hellani et al., Petz et al. <sup>52,53</sup>
2	–	–	2,029 <sup>a</sup>	Flösdorf et al. <sup>54</sup>
3	–	312.64(3)	2,031 <sup>b</sup>	El-Hellani et al. <sup>52</sup>
4	–	313.31(2)	2,032 <sup>b</sup>	Kroll et al. <sup>34</sup>
5	2,001	–	2,021 <sup>c</sup>	Marrot et al. <sup>55</sup>
<b>Carbophosphinocarbenes</b>				
6	–	320.00(2)	2,043 <sup>b</sup>	Liu et al. <sup>35</sup>
7	–	315.97(3)	2,036 <sup>b</sup>	Alcarazo et al. <sup>56</sup>
8	2,007	319.74(1)	2,042 <sup>b</sup> 2,026 <sup>c</sup>	El-Hellani et al., Alcarazo et al. <sup>52,56</sup>
<b>Carbodicarbenes</b>				
9	2,014	–	2,031 <sup>c</sup>	Dyker et al. <sup>30</sup>
10	2,005	–	2,024 <sup>c</sup>	Chen et al. <sup>36</sup>
11	2,019	–	2,035 <sup>c</sup>	Lavallo et al. <sup>57</sup>
12	2,016	–	2,033 <sup>c</sup>	Melaimi et al. <sup>58</sup>
13	–	310.85(8)	2,028 <sup>b</sup>	El-Hellani et al. <sup>52</sup>
14	–	320.78(4)	2,045 <sup>b</sup>	Pranckevicius et al. <sup>59</sup>

<sup>a</sup>The A<sub>1</sub> stretching frequency of the carbone-Ni(CO)<sub>3</sub> complex.

<sup>b</sup>Calculated from the sum of Cl–Ga–Cl bond angles ( $\sum \text{ClGaCl}$ ) for the carbone-GaCl<sub>3</sub> complex based on the following relationship: TEP = 1.7231( $\sum \text{ClGaCl}$ ) + 1,491.9.

<sup>c</sup>Calculated from the average CO stretching frequency ( $\nu_{CO,av}$ ) for the carbone-Rh(CO)<sub>2</sub>Cl complex based on the following relationship: TEP = 0.8001( $\nu_{CO,av}$ ) + 420.

(2) The average carbonyl stretching frequency for carbone-Rh(CO)<sub>2</sub>Cl complexes has been measured.<sup>50</sup> However, this method has not been successful with carbodiphosphoranes that can undergo orthometallation. For example, Cavell and co-workers have observed phenyl orthometallation upon treatment of hexaphenylcarbodiphosphorane **1** with [RhCl(cod)]<sub>2</sub> (cod = 1,5-cyclooctadiene), which hampered the synthesis of a (Ph<sub>3</sub>P)<sub>2</sub>C-Rh(CO)<sub>2</sub>Cl complex.<sup>51</sup>

- (3) The sum of the Cl–Ga–Cl bond angles for carbene-GaCl<sub>3</sub> compounds has been determined by X-ray crystallography.<sup>52</sup>

Equations to convert data for (L)Rh(CO)<sub>2</sub>Cl or (L)GaCl<sub>3</sub> complexes into TEP values are available<sup>50,52</sup>; however, comparing data collected across different measurement methods is challenging. For example, the  $\pi$ -accepting ability of the flanking NHC donors of carbophosphinocarbenes and carbodicarbenes may influence GaCl<sub>3</sub> bond angles due to interactions between chlorine and the NHC center. Indeed, for carbophosphinocarbene **8**, the TEP values calculated by different methods differ substantially (2,026 from the rhodium carbonyl method versus 2,042 from the gallium trichloride method).<sup>52,56</sup> Despite this limitation, a few general trends in donor properties are suggested for the carbene compounds in [Table 1](#).

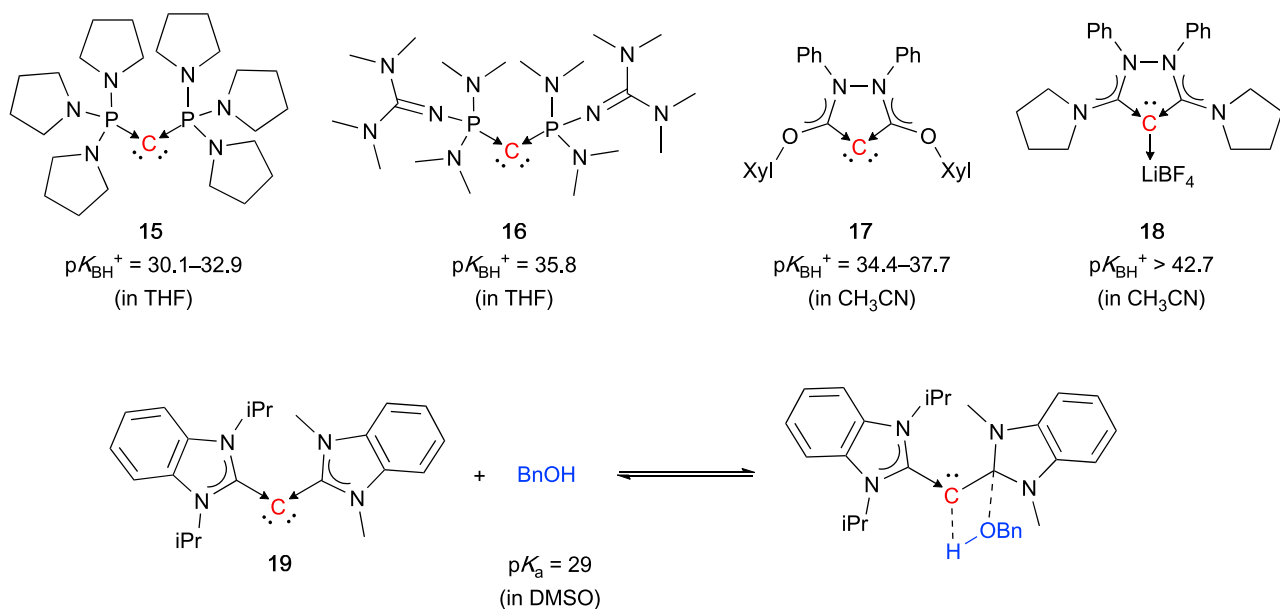
Within the carbodiphosphorane family, cyclic compounds (**3** and **5**) have lower TEP values than acyclic variants (**1**, **2**, and **4**). Furthermore, the carbophosphinocarbenes tend to have higher TEP values than either carbodiphosphoranes or carbodicarbenes. Interestingly, the carbophosphinocarbene **6** has a higher TEP value than the carbodiphosphorane and carbodicarbene analogs featuring the same flanking substituents (**1** and **9**, respectively). All zerovalent carbon compounds in [Table 1](#) have lower TEP values than NHCs (typical TEP values of 2,045–2,050) or cyclic(alkyl)(amino)carbenes (TEP approximately 2,046–2,050).<sup>52</sup>

Caution is needed when interpreting TEP values, as these are a *thermodynamic* measurement of the net  $\sigma$ -donating and  $\pi$ -accepting interactions of a ligand with a metal. The TEP does not reveal the *kinetic* properties of a ligand, such as the propensity toward ligand dissociation. Two reports suggest that carbenes can dissociate relatively easily from transition metals. Petz, Frenking, and co-workers demonstrated that triphenylphosphine can displace carbodiphosphorane **1** from a (Ph<sub>3</sub>P)<sub>2</sub>C–Ni(CO)<sub>2</sub> complex,<sup>53</sup> although phosphines have higher TEP values than carbodiphosphoranes. In addition, Liberman-Martin and Grubbs reported ruthenium benzylidene complexes containing both *N*-heterocyclic carbene and carbodicarbene ligands.<sup>60</sup> In these complexes, the carbodicarbene ligand is labile and dissociates to generate active olefin metathesis catalysts. Similar to *N*-heterocyclic olefins,<sup>61</sup> the weak  $\pi$ -accepting ability of the carbene center may be responsible for the greater lability of these compounds relative to NHCs or phosphines.

## BRØNSTED BASICITY MEASUREMENTS

Computed first and second proton affinities have been used to quantify zerovalent carbon character.<sup>62</sup> The first proton affinity values for carbodiphosphoranes and carbodicarbenes are very high, ranging from 285 to 298 kcal/mol, and the second proton affinities for these compounds are also large (165–193 kcal/mol).<sup>37</sup> In contrast, NHCs have large first proton affinities (262–275 kcal/mol) and significantly smaller second proton affinities (72–106 kcal/mol), consistent with the single lone pair character of carbenes.<sup>62</sup>

Experimental Brønsted basicities have been measured for a limited number of carbenes ([Figure 2](#)). Sundermeyer and co-workers reported the synthesis of aminophosphine-flanked carbodiphosphoranes and performed <sup>31</sup>P NMR titration experiments in THF to quantify the basicities of compounds **15** and **16**.<sup>32</sup> From experiments with the phosphazenes (tmg)P<sub>1</sub>-tBu (pK<sub>BH</sub><sup>+</sup> = 29.1 in THF) and (dma)P<sub>4</sub>-tBu (pK<sub>BH</sub><sup>+</sup> = 33.9 in THF), the pK<sub>BH</sub><sup>+</sup> for **15** was determined to be between 30.1 and 32.9.



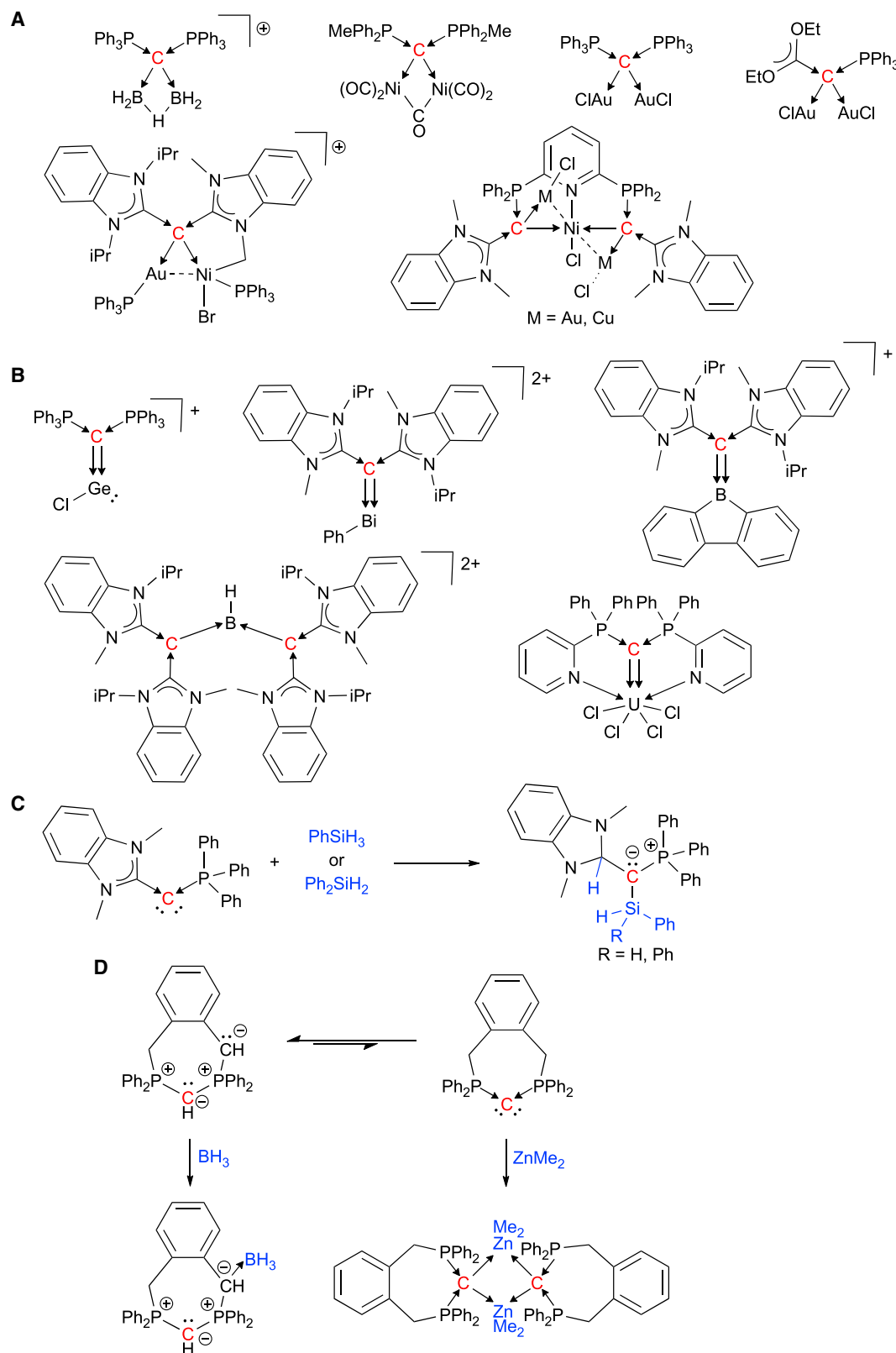
**Figure 2. Experimental Brønsted basicity measurements for zerovalent carbon compounds**

The  $pK_{\text{BH}}^+$  values for carbenes 15–18 have been determined using NMR spectroscopy. For carbodiphosphorane 19, a hydrogen-bonding interaction was observed with benzyl alcohol.

Treatment of carbodiphosphorane 16 with  $(\text{pyrr})\text{P}_4\text{-tBu}$  ( $pK_{\text{BH}}^+ = 35.3$  in THF) resulted in a mixture of protonated and basic forms of both compounds, corresponding to a  $pK_{\text{BH}}^+$  value of 35.8 for 16. These measurements provided the first experimental basicity metrics for carbodiphosphoranes, which indicated that 15 and 16 are stronger bases than many unstabilized phosphorus ylides ( $pK_{\text{BH}}^+$  of 26–33)<sup>63</sup> and most NHCs ( $pK_{\text{BH}}^+$  of 20–24).<sup>64–66</sup>

Bertrand, Jazzar, and co-workers recently reported basicity measurements for carbodiphosphoranes 17 and 18 as determined by  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy.<sup>67</sup> From titration experiments with the phosphorus ylides  $\text{Ph}_3\text{PCH}_2$  and  $(\text{Me}_2\text{N})_3\text{P}(\text{C}(\text{CH}_3)_2)$ , the  $pK_{\text{BH}}^+$  value for 17 was found to be between 34.4 and 37.7. Impressively, the  $\text{LiBF}_4$  adduct of pyrrolidiny-substituted 18 can fully deprotonate the conjugate acid of the phosphazene  $\text{P}_4\text{-tBu}$  ( $pK_{\text{BH}}^+ = 42.7$  in acetonitrile). These results uncovered the strong basicity of cyclic carbodiphosphoranes and suggested that these species may be efficient superbase organocatalysts.<sup>68</sup>

Ong, Zhao, Chen, and co-workers have investigated the reactivity of acyclic carbodiphosphorane 19 with benzyl alcohol (BnOH).<sup>69</sup> Upon treatment with 19 in benzene- $d_6$  solvent, the hydroxyl signal of BnOH (a sharp triplet at  $\delta = 1.70$  ppm) broadens and shifts downfield to  $\delta = 9.50$  ppm, suggesting a hydrogen-bonding interaction. Nuclear Overhauser effect spectroscopy data are also consistent with this non-covalent interaction, with cross-peaks observed between BnOH and carbodiphosphorane 19. The observation of a hydrogen-bonding interaction indicates that carbodiphosphorane 19 is insufficiently basic to deprotonate BnOH ( $pK_{\text{a}} = 29$  in DMSO). Furthermore, no interaction was observed between 19 and benzylamine or *tert*-butanol, which are weaker acids than benzyl alcohol. The behavior of 19 is comparable to that of NHCs, which also exhibit hydrogen-bonding interactions with alcohols.<sup>70,71</sup> These observations reveal that acyclic carbodiphosphorane 19 is significantly less Brønsted basic than cyclic carbodiphosphoranes 17 and 18.





**Figure 3. Distinctive reactivity patterns for zerovalent carbon compounds**

- (A) Geminal dimetallation involving double dative bonding.
- (B) Simultaneous  $\sigma$ - and  $\pi$ -donation to main group and *f*-block elements.
- (C) 1,2-addition reactions of silanes.
- (D) Tautomerization between unsymmetrical bisylide and carbodiphosphorane binding modes.

### DISTINCTIVE REACTIVITY PATTERNS

A significant difference between divalent and zerovalent carbon compounds is the number of dative interactions possible at the low-valent carbon center. Due to the presence of one lone pair on a carbene, these species can only form a single dative interaction with a Lewis acid. In contrast, zerovalent carbon compounds can behave as 2-fold Lewis bases at the central carbon.<sup>72</sup>

Representative complexes exhibiting simultaneous coordination of a carbene center to two main group or transition metal centers are presented in Figure 3A. An adduct between carbodiphosphorane **1** and a  $B_2H_5^+$  fragment has been verified by X-ray crystallography.<sup>73</sup> A dinuclear  $Ni_2(CO)_4$  carbonyl derivative was prepared upon treatment of carbodiphosphorane **2** with  $Ni(CO)_4$ .<sup>54</sup> Carbodiphosphorane **1** and carbophosphinocarbene **8** react with two equivalents of gold(I) chloride to form geminally diaurated adducts.<sup>56,74</sup> It is worth noting that not all carbones are capable of gem-dimetallation. For example, although compounds **7** and **13** can coordinate to a single gold center, attempts to prepare gem-diaurated adducts of these species were unsuccessful, which was attributed to the shape of these ligands.<sup>56</sup>

Geminal bimetallic Pd-Pd, Pd-Au, and Ni-Au coordination to a carbodicarbene was reported by Ong, Chen, Zhao, and co-workers.<sup>75</sup> In all complexes, intramolecular C–H activation of a methyl group on the carbodicarbene furnishes a cyclometallated ligand. This ligand chelation provides a covalent bond to hold one metal center in place, enabling bimetallic coordination. Subsequently, Ong, Zhao, and co-workers described a bis(carbene) pincer ligand featuring two carbophosphinocarbenes flanking a central pyridine donor.<sup>76</sup> This pincer platform supports trimetallic Au-Pd-Au, Au-Ni-Au, and Cu-Ni-Cu complexes, with each carbene center coordinated to two metals. Although short metal-metal distances are observed, computational studies indicate that metal-metal interactions are not responsible for the stability of these multimetallic complexes; instead, the strongest orbital interactions are from carbene-metal dative bonding.

Carbones can also provide both  $\sigma$  and  $\pi$  donation to a single metal or main group element center. For example, Alcarazo and co-workers demonstrated chloride abstraction from a carbodiphosphorane- $GeCl_2$  compound to generate a  $[(Ph_3P)_2C-GeCl][AlCl_4]$  compound.<sup>77</sup> DFT calculations revealed double dative C=Ge bonds in this cationic germanium compound. Gilliard and co-workers have recently reported mono-, di-, and tri-cationic antimony and bismuth compounds supported by carbodicarbene ligands.<sup>78,79</sup> For the [carbodicarbene-BiPh]<sup>2+</sup> compound,  $\pi$  donation from the carbodicarbene to bismuth accounts for 19% of the total orbital interactions between these components, indicating that a double dative interaction is present, with a strong  $\sigma$  and weaker  $\pi$  component. Carbodiphosphoranes and carbodicarbenes have also stabilized cationic<sup>80–83</sup> and dicationic<sup>84</sup> boron species. The air-stable carbodicarbene-borafluorenium ions prepared by Gilliard, Wilson, and co-workers are thermoluminescent and exhibit temperature-controlled white-light emission.<sup>83</sup> Ong and co-workers have utilized carbodicarbene ligands to support a dicationic three-coordinate hydrido boron compound.<sup>84</sup> Carbodiphosphoranes have also been reported to engage in double dative interactions with

beryllium,<sup>85</sup> iron,<sup>86</sup> rhenium,<sup>87</sup> and uranium,<sup>88</sup> extending this bonding motif to the s-, d-, and f-blocks.

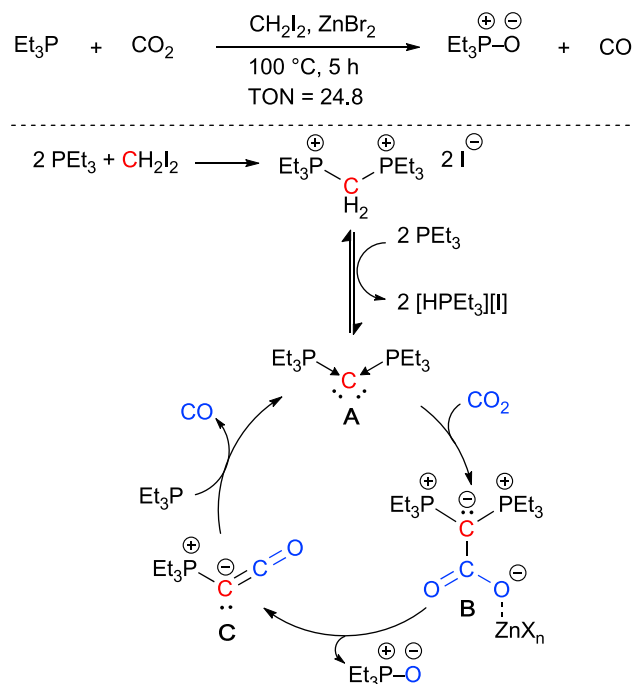
Another distinctive reactivity pattern for carbophosphinocarbenes and carbodicarbenes is 1,2-addition across the carbene and a supporting carbene center (Figure 3C). Additions of silane and borane reagents have been observed, with the Si or B atom adding to the carbene and the hydridic hydrogen attaching to the flanking carbene position.<sup>36,89</sup> In contrast, divalent carbene compounds undergo 1,1-addition reactions.<sup>90–96</sup> The 1,2-addition pattern for carbophosphinocarbenes and carbodicarbenes is enabled by the  $\pi$ -accepting ability of the NHC donors supporting the carbene center of these species. Carbodiphosphoranes have not been observed to undergo 1,2-addition reactions, presumably due to the lower  $\pi$ -acidity of the flanking phosphine groups.

Tautomerization is a final reactivity pattern that has, so far, been observed exclusively for carbodiphosphoranes (Figure 3D). For compounds with suitable  $\alpha$  positions, tautomerization between carbodiphosphorane and unsymmetrical bisylide forms can occur, and these tautomers can be trapped as Lewis acid-base adducts. Tautomerization behavior was initially implicated in the coordination chemistry of  $C(PMe_3)_2$ .<sup>97,98</sup> Rather than binding at the central carbene position, Group 10–13 metals (Ni, Pd, Pt, Au, Zn, Cd, Al, and Ga) reacted with  $C(PMe_3)_2$  to generate complexes with symmetrical bidentate methanido-bis(dimethylphosphoniummethylide) ligands. If resonance-stabilizing substituents are present on the phosphorus donors,<sup>99</sup> as is the case for  $BnPh_2P=CH-PPh_2=CHPh$ <sup>100</sup> (Bn = benzyl) and the cyclic structure in Figure 3D,<sup>101</sup> fluxional bisylide species are observed spectroscopically instead of symmetrical carbodiphosphorane structures. In the case of the cyclic bisylide in Figure 3D,  $BH_3$  coordination occurs to the unsymmetrical ylide form, while dimethylzinc coordination is observed at the central carbene position, suggesting tautomerization behavior.

## ORGANOCATALYTIC APPLICATIONS

Carbenes are widespread in homogeneous catalysis, with NHCs and related classes of stable carbenes serving as both ligands and organocatalysts.<sup>102</sup> In contrast, carbenes are less frequently applied in catalytic studies, though the double lone pair character at the carbene position makes these species promising Lewis and Brønsted base catalysts. Examples of transition metal catalysts supported by carbene ligands are discussed in several book chapters and review articles.<sup>37–40,45,103</sup> Instead, this perspective highlights applications in which zerovalent carbon species serve as organocatalysts.

In 2013, the Stephan group described an *in situ*-generated carbodiphosphorane catalyst for reducing  $CO_2$  to CO (Figure 4).<sup>104</sup> Under the optimal conditions, treatment of  $CH_2I_2$ ,  $ZnBr_2$ , and  $CO_2$  (2 atm) with a 25-fold excess of triethylphosphine at  $100^\circ C$  led to 99% conversion to triethylphosphine oxide ( $Et_3PO$ ) and CO after 5 h, corresponding to a turnover number (TON) of 24.8. In the absence of  $ZnBr_2$ , catalytic turnover was still observed, although the reaction was less efficient (TON = 14 after 56 h at  $100^\circ C$ ). Carbodiphosphorane  $C(PEt_3)_2$  (A) is proposed to form by the nucleophilic attack of  $CH_2I_2$  by  $PEt_3$  and subsequent deprotonation of the resulting bis(phosphonium) salt by excess  $PEt_3$ . The authors propose that carbodiphosphorane A reacts with  $CO_2$  to generate  $(Et_3P)_2C-CO_2$  (B), which undergoes a Wittig-type reaction to form the phosphaketene  $Et_3PCCO$  (C) and  $Et_3PO$ . Nucleophilic attack of intermediate C by  $Et_3P$  and loss of CO results in the regeneration of carbodiphosphorane A. Analogous  $CO_2$  adduct formation<sup>105,106</sup> and thermal cleavage<sup>107</sup> reactions have been previously

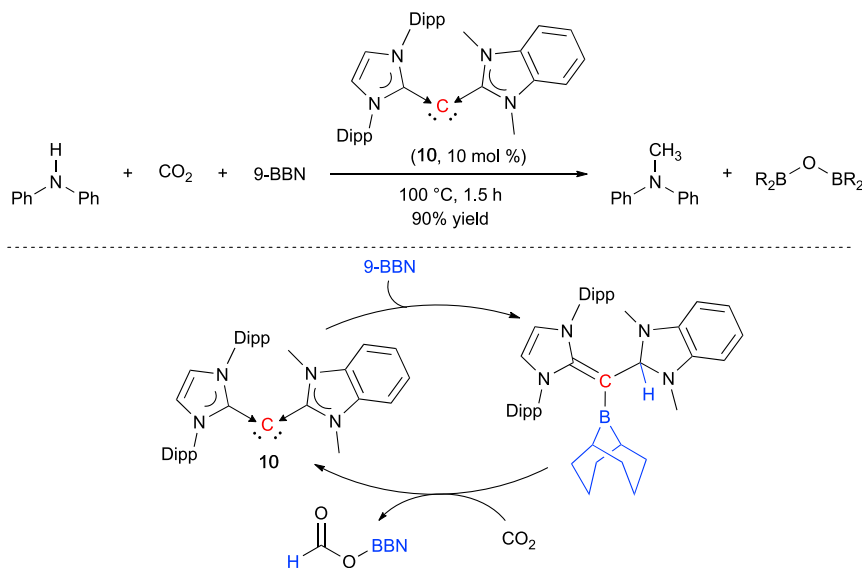


**Figure 4. Catalytic reduction of  $\text{CO}_2$  to  $\text{CO}$  by an *in situ*-generated carbodiphosphorane**

The carbodiphosphorane  $\text{C}(\text{PEt}_3)_2$  catalyzes the conversion of carbon dioxide and triethylphosphine into carbon monoxide and triethylphosphine oxide. The mechanism is proposed to involve carbon dioxide binding to the carbene center, followed by formation of a phosphaketene  $\text{Et}_3\text{PCCO}$  and subsequent loss of carbon monoxide.

observed with  $\text{C}(\text{PPh}_3)_2$  (1). The zinc Lewis acid is proposed to facilitate the nucleophilic attack of phosphaketene  $\text{C}$  by  $\text{Et}_3\text{P}$ , which was supported by DFT calculations for the model carbodiphosphorane  $\text{C}(\text{PMe}_3)_2$ . This work presents a catalyst that cycles between carbodiphosphorane and phosphaketene forms, which is a unique approach that may enable other atom transfer reactions.

In 2015, Ong and co-workers reported carbodicarbene and carbophosphinocarbene catalysts for amine methylation using  $\text{CO}_2$  (Figure 5).<sup>36</sup> Six catalysts were compared for diphenylamine methylation with 9-borabicyclo[3.3.1]nonane (9-BBN) and  $\text{CO}_2$  (1 atm). The highest activity was observed using 10 mol % of carbodicarbene 10 (90% yield in 1.5 h at  $100^\circ\text{C}$  in toluene solvent). For comparison, a mesoionic *N*-heterocyclic olefin catalyst was reported by Mandal and co-workers that provides similar yields of *N*-methylation products using 5 mol % catalyst loading at  $40^\circ\text{C}$  with reaction times of 24 h.<sup>108</sup> With carbodicarbene catalyst 10, Ong and co-workers explored the reaction scope with fifteen amines and obtained methylated products in yields between 35% and 97%. In a stoichiometric experiment, treatment of 10 with 9-BBN resulted in 1,2-addition of the B–H bond across the central carbene and the neighboring benzimidazole carbon. The resulting 9-BBN adduct exhibited comparable catalytic activity to carbodicarbene 10. The authors present a mechanism analogous to a pathway described by Cantat and co-workers for amine methylation using a proazaphosphatrane catalyst.<sup>109</sup> The carbodicarbene is proposed to activate the borane reagent by 1,2-addition and catalyze (1) the reduction of  $\text{CO}_2$  to a boryl formate intermediate and (2) the reduction of a formamide intermediate to the methylamine product. Given the ability of carbodicarbenes and carbophosphinocarbenes to activate a range of borane and silane substrates (Figure 3C), these



**Figure 5. Amine methylation using CO<sub>2</sub> and 9-BBN catalyzed by carbodicarbene 10**

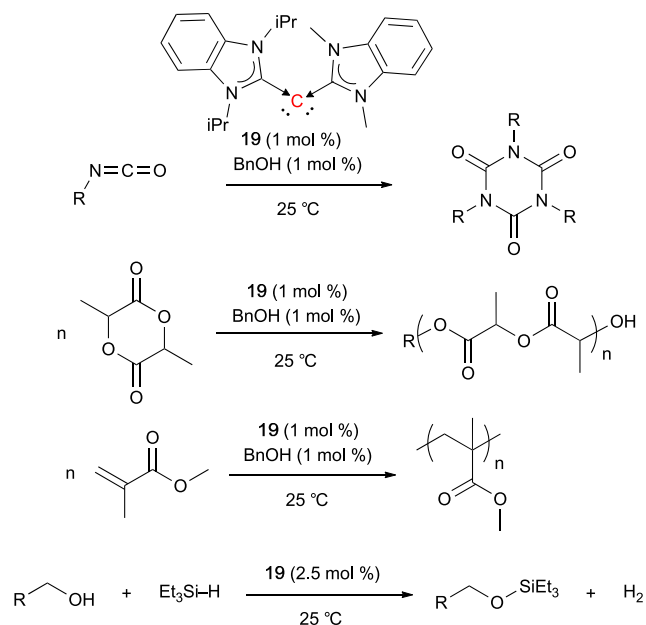
Methylation of secondary amines is catalyzed at 100°C. The borane reagent is proposed to be activated by 1,2-addition to carbodicarbene catalyst 10 during catalysis.

classes of zerovalent carbon compounds may be able to catalyze hydrosilylation and hydroboration of substrate classes beyond CO<sub>2</sub>.

The catalytic activity of carbenes in the presence of benzyl alcohol (BnOH) has also been investigated by Ong, Chen, Zhao, and co-workers (Figure 6).<sup>69</sup> In this study, hydrogen bonding between the carbene and BnOH (Figure 2) is proposed to render the flanking carbene center more  $\pi$ -acidic. The authors compared the catalytic activity of two carbodicarbenes and one carbophosphinocarbene to prototypical *N*-heterocyclic carbene and *N*-heterocyclic olefin (NHO) organocatalysts in four types of transformations: (1) isocyanate cyclotrimerization, (2) lactide ring-opening polymerization, (3) methyl methacrylate polymerization, and (4) alcohol dehydrosilylation (Figure 6).

For 4-methoxyphenyl isocyanate cyclotrimerization, the highest catalytic activity (92% yield after 30 min) was observed using carbodicarbene 19 (1 mol %) in combination with BnOH (1 mol %). The NHC and NHO compounds tested were inactive under these reaction conditions; however, NHCs and NHOs are both highly active isocyanate cyclotrimerization catalysts in the absence of BnOH.<sup>110,111</sup> Six isocyanate substrates were examined, which formed cyclotrimerization products in high yields (89%–97%). An X-ray structure of an adduct between carbodicarbene 19 and 4-nitrophenylisocyanate revealed an interaction between the isocyanate nitrogen and a flanking carbene donor position ( $N_{\text{isocyanate}}\text{---}C_{\text{carbene}}$  distance = 2.723 Å). DFT calculations of the complete cyclotrimerization pathway for 19 in the presence of BnOH indicate that this  $N_{\text{isocyanate}}\text{---}C_{\text{carbene}}$  interaction, hydrogen bonding, and  $\pi$ - $\pi$  stacking are all important factors in enabling rapid catalytic turnover.

To expand upon this promising carbodicarbene catalytic activity in the presence of BnOH, the authors explored ring-opening polymerization of *L*-lactide (*L*-LA). Carbodicarbene 19 exhibited higher catalytic activity toward lactide polymerization than the two other carbene catalysts tested, with 90% conversion observed within 1 min to produce poly(lactide) with a moderate dispersity ( $D = M_w/M_n = 1.44$ ) using [LA]:[19]:[BnOH] = 100:1.5:1. Pre-mixing 19 with BnOH for 5 min before addition of



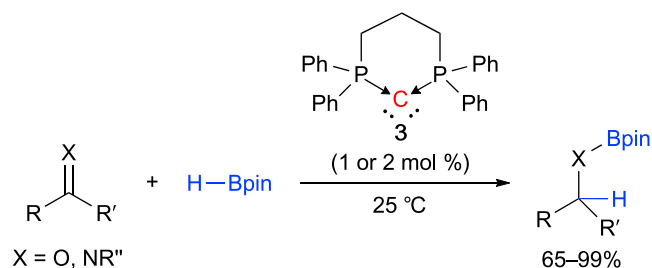
**Figure 6. Catalytic reactions of carbodicarbene 19 in the presence of alcohols**

Cyclotrimerization of isocyanates is catalyzed by carbodicarbene **19** in the presence of benzyl alcohol. Catalyst **19** promotes lactide ring-opening polymerization and methyl methacrylate polymerization using benzyl alcohol as an initiator. Dehydrosilylation of primary and secondary alcohols is catalyzed by **19**.

LA led to a narrower dispersity product ( $\bar{D} = 1.26$ ). Significant epimerization of *L*-LA was observed in the absence of BnOH ( $P_m = 0.66$ ), which likely occurs by deprotonation of lactide to form the lactide enolate.<sup>112</sup> The BnOH initiator is proposed to attenuate the basicity of the carbene center, preventing deprotonation of the lactide monomer and enabling high isotacticity.

The combination of carbodicarbene **19** and BnOH also mediated methyl methacrylate (MMA) polymerization. Using  $[MMA]:[19]:[BnOH] = 100:1:1$ , 99% conversion of MMA was achieved in toluene solvent within 12 min to afford poly(methyl methacrylate) with moderate dispersity ( $\bar{D} = 1.79$ ). Polymer molecular weight increased as the amount of MMA relative to **19** and BnOH was increased between 100 and 600 equiv of MMA. A very broad dispersity poly(methylmethacrylate) product ( $\bar{D} = 3.50$ ) was observed in the absence of BnOH for a polymerization with  $[MMA]:[19] = 100:1$ . In previous studies, NHCs were found to be catalytically inactive for MMA polymerization in toluene solvent in the absence of Lewis acid co-catalysts.<sup>113</sup> The results for carbodicarbene catalyst **19** reveal that zerovalent carbon species may offer advantages over NHC catalysts for polymerization mechanisms involving conjugate addition pathways.

Carbodicarbene **19** also efficiently catalyzed the dehydrosilylation of alcohols at room temperature. Silylation of benzyl alcohol was complete within 0.5 h using  $Et_3SiH$  and 2.5 mol % of **19**, while the bulkier silanes  $t-BuMe_2SiH$  and  $iPr_3SiH$  required longer reaction times (5–12 h) and higher catalyst loading (5 mol %). For comparison, dehydrosilylation of alcohols with an NHO catalyst reported by Nguyen and co-workers used higher catalyst loading (12 mol %), higher temperature (50°C), and longer reaction times (24 h).<sup>114</sup> A scope of nineteen alcohols was investigated using catalyst **19** (2.5 mol %) and  $Et_3SiH$ , with high yields (>80%) observed for both primary and secondary alcohol substrates. Dehydrosilylation of tertiary



**Figure 7. Catalytic ketone and imine hydroboration by cyclic carbodiphosphorane 3**

Hydroboration of ketone and imine reagents is observed at 25°C using a pinacolborane reductant.

alcohols was not observed, which was attributed to steric interference of these bulky alcohols preventing interaction with the carbene center of **19**. This reactivity suggests that zerovalent carbon compounds may be capable catalysts for broader classes of dehydrocoupling reactions.

Last, our group reported that cyclic carbodiphosphorane **3** catalyzes ketone and imine hydroboration using pinacolborane, HBpin (Figure 7).<sup>115</sup> Reactions with ketones were rapid (15–30 min at 25°C using 1 mol % of **3**) to achieve high yields of boronate ester products (86%–98% yield). Imine hydroboration reactions required longer reaction times (1 h) and higher catalyst loading (2 mol % of **3**). The ketone and imine hydroboration activity of carbodiphosphorane **3** exceeded the reactivity of the NHC and NHO catalysts tested.<sup>116</sup> For all substrates, the catalytic activity of cyclic carbodiphosphorane **3** was compared to the unstabilized phosphorus ylide  $\text{Ph}_3\text{PCH}_2$ , and **3** exhibited higher hydroboration activity toward both ketones and imines than  $\text{Ph}_3\text{PCH}_2$ . Preliminary mechanistic experiments were inconclusive, as carbodiphosphorane **3** reacted with both benzophenone and pinacolborane substrates. Furthermore, a ring-opened unsymmetrical bisylide product was formed upon treatment of carbodiphosphorane **3** with benzophenone, raising the possibility that a tautomerized form of **3** may be catalytically active. Wittig-type reactivity has been previously observed between  $\text{C}(\text{PPh}_3)_2$  (**1**) and hexafluoroacetone<sup>117,118</sup>; however, **1** does not react with benzophenone.<sup>119</sup>

### Summary and outlook

Zerovalent carbon compounds, termed carbones, have intriguing electronic structures that render them more electron donating than divalent carbon species. While the donor properties of carbones have been exploited to support main group and transition metal elements, organocatalysis with carbones is nascent yet promising. At present, the catalytic activity of carbones appears to exceed the reactivity of NHC and NHO catalysts in alcohol dehydrosilylation reactions as well as ketone and imine hydroboration reactions.<sup>69,115</sup>

For catalytic applications of persistent carbenes, the rational selection of NHC catalysts is aided by extensively cataloged nucleophilicities,<sup>120,121</sup> Brønsted basicities,<sup>122,123</sup> donor properties,<sup>50</sup> and steric profiles.<sup>124</sup> In contrast, zerovalent carbon nucleophilicities have not yet been measured, and Brønsted basicities have only been reported for a small subset of known carbones. Extending the systematic parameterization of the steric and electronic properties of carbones<sup>54</sup> to a wider range of these compounds would allow for the identification of promising catalytic applications for which the distinctive electronic properties of these zerovalent carbon species are well suited.

At present, there are only a handful of reported organocatalytic applications that showcase the Lewis or Brønsted basic properties of carbones. Within these reports,

it is rare for catalysts across multiple classes of carbones (carbodiphosphoranes, carbophosphinocarbenes, and carbodicarbenes) to be compared for the same catalytic reaction. Understanding zerovalent carbon reactivity would be improved by comparison of a broader range of catalysts for each catalytic application. Likewise, more extensive mechanistic and computational studies could help to establish the precise elementary steps possible for carbone catalysts and if these species remain zerovalent during catalysis, convert to divalent species or cycle between valence states during catalysis. Many opportunities exist for further development of novel carbone compounds and catalytic applications of these unique low-valent carbon species.

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## DECLARATION OF INTERESTS

The author declares no competing interests.

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