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Computations illuminate emerging reactivity of metal-free carbones

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Carbones, formal zerovalent carbon centers, exhibit reactivity that distinguishes them from other reactive carbon species. Recent computational studies have provided mechanistic insights into how carbones can facilitate ligand exchange and leverage the π-acidity of coordinating fragments to catalyze chemical transformations, highlighting their potential as unique contributors in organocatalysis.

The emerging reactivity of carbones

Carbones ($L \longrightarrow C \longleftarrow L$), a unique class of formally zerovalent carbon compounds, have attracted significant attention in recent years due to their bonding characteristics, intriguing donor–acceptor properties, and potential applications in catalysis. Central to the properties of carbones is the behavior of the central carbon atom, which exhibits a double lone-pair character and consequently has high electron density. This characteristic has been leveraged through the use of carbones as strongly electron-donating ligands in organometallic complexes [1].

Recent studies have revealed the reactivity of metal-free carbones, particularly in their capacity for ligand exchange and as organocatalysts. Review articles that focus on experimental advancements in this area can be found here [2,3]. Computational studies using density functional theory (DFT) have supported these experimental findings, providing in-depth insights into the bonding characteristics of carbones, the mechanisms for ligand exchange, and substrate activation mode in chemical transformations. In this forum article, we gather these computational studies and illuminate the current hypotheses about the reactivity of these species. We emphasize that mechanistic studies of carbone reactivity are still in their early stages. As carbone chemistry progresses, both computational and experimental investigations will show that carbones are not just structural oddities, but also important reactive carbon species, potentially placing them alongside carbenes as key players in organocatalysis research.

Donor–acceptor reactivity

Carbones may be represented in the dative form, zwitterionic form, or in an allene configuration (Figure 1). In the dative form, the central carbon retains two lone pairs and is flanked by two L-type ligands. In the zwitterionic form, a sigma bond is depicted between the central carbon (–2 charge) and coordinating fragments (+1 charge). As an allene, the lone pairs on the central carbon are delocalized into π networks with the coordinating fragments. The literature provides extensive studies and discussions regarding which form is the most plausible. The actual bonding situation for carbones likely relies on the structural and electronic characteristics of the backbone. For instance, computations suggest that carbodiphosphoranes (R_3P C PR_3) are best represented as zwitterions, while carbodicarbenes ($R_2C \longrightarrow C \longleftarrow CR_2$) fit the allene model (Figure 1A) [4]. Regardless, computational and crystallographic data reveal that carbones can bind up to two protons or small Lewis acids [1,4], thus supporting the double lone-pair characteristics at the central carbon.

The donor–acceptor model describing the interaction between the central carbon and the coordinating fragments, commonly phosphines or carbenes, has been supported by DFT calculations of natural charges around the carbones [4]. The central carbon retains most of its negative charge when coordinating with one or two H^+ ions or other Lewis acids. The ligands surrounding the central carbon effectively compensate for the potential loss of electron density by significantly donating electron density, as evidenced by the increase in positive charge at these atoms when the central carbon transfers charge to protons, metals, or organic Lewis acids.

Recent studies have highlighted that carbones can undergo ligand exchange, a type of donor–acceptor reactivity typically associated with metal-coordinating ligands [5–9]. Initial work in this area by Hansmann and coworkers has shown that diazoalkenes, a family of carbones flanked by carbene and N_2 fragments ($R_2C \longrightarrow C \longleftarrow N_2$), can exchange the coordinating N_2 with carbon monoxide (CO) or isocyanides (CNR) through N_2/CO and N_2/CNR ligand exchanges [5,6]. DFT studies reveal that an associative mechanism is favored for these exchanges, attributed to the significant stabilization achieved via sigma donation from the ligands to the central carbon. A one-step substitution transition state was calculated for the N_2/CO exchange and verified by intrinsic reaction coordinate analysis (Figure 1B). The electronics at the computed transition state geometry is the reverse of a traditional S_N2 mechanism; in this case, the central carbon is donating orbital density to the antibonding π orbital (π*) of the CO. N_2/CNR exchange proceeds through the initial formation of a [3+2] cycloaddition intermediate, followed by fragmentation to release N_2 from the carbone center. More recently, Severin and coworkers reported the exchange of N_2 in diazoalkenes with phosphines and Fischer carbenes [7,8]. Hansmann and coworkers also reported the synthesis of diazoalkenes through the exchange of carbenes in carbodicarbenes with N_2O [9].

π-Acidity of carbones in catalysis

Initially regarded as structural curiosities and ligands in organometallic complexes,

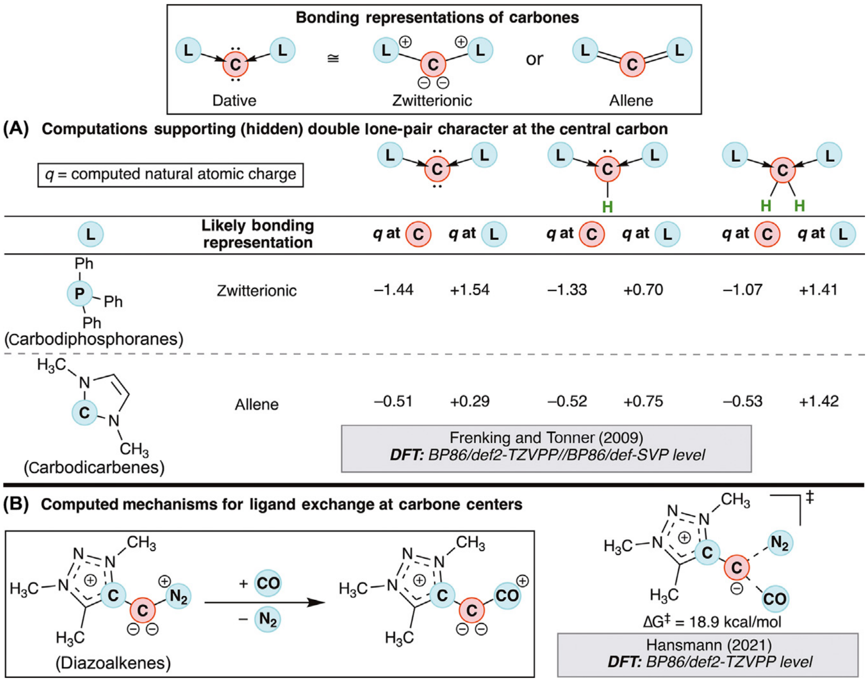

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Figure 1. Zerovalent carbon centers (carbones) shown in dative, zwitterionic, and allene forms, with L denoting the coordinating fragment. (A) Computations by Frenking and Tonner reveal the natural atomic charge (q) at the central carbon and coordinating phosphorus or carbon atoms in carbodiphosphoranes and carbodicarbenes, respectively, in three scenarios: unbound to a proton, bound to one proton, and bound to two protons [4]. (B) A computed model of the associative mechanism for N_2/CO ligand exchange at diazoalkenes by Hansmann and coworkers [5]. The density functional theory (DFT) method and basis set used for each reported calculation are presented in gray boxes.

carbones are now being explored as metal-free catalysts in carbonyl and heteroallene reductions [3]. All reported DFT studies indicate that the reactivity of carbones predominantly arises from the Lewis basic characteristics of the central carbone, enabling it to coordinate with weakly Lewis acidic centers in the reactants. Additionally, the coordinating carbone fragments can function as π acceptors, which can facilitate ylide-type reactivity, stabilize the accumulation of negative charge density on the substrate bound to the carbone, or aid in the transfer of groups from the bound substrate to another electrophilic species in the reaction.

In a 2013 pioneering study, Stephan and coworkers demonstrated that hexaethylcarbodiphosphorane, generated *in situ* from the reaction of triethylphosphines with diiodomethane, catalyzes the conversion of carbon dioxide into carbon monoxide (Figure 2A) [10]. DFT calculations reveal that the reaction begins with the formation of a carbodiphosphorane–CO_2 adduct. This adduct then undergoes ylide-type reactivity through the direct involvement of the phosphine ligand, leading to the formation of phosphaketene and triethylphosphine oxide. Finally, the phosphaketene undergoes CO/PEt_3 ligand exchange, releasing CO and regenerating the active carbodiphosphorane catalyst.

In 2017, Chen, Frenking, Ong, and coworkers showed that carbodicarbenes and carbophosphinocarbenes ($R_3P \longrightarrow C \longleftarrow CR_2$) activate organic Lewis acids such as boranes and silanes, through 1,2-addition across the C–C bond of the central and coordinating carbon atoms [11]. The formation of 1,2 addition species was corroborated by ^1H and ^{13}C NMR and confirmed by single-crystal X-ray diffraction studies. DFT calculations revealed that the likely energy profile begins with the formation of a carbone-borane adduct, followed by an intramolecular hydride transfer through a four-membered ring transition state, ultimately yielding a relatively stable 1,2-addition species. This study offered the first insights into how the π-acidity of carbones introduces unexpected activation mechanisms for this class of reactive carbon species.

In 2021, Zhao, Chen, Ong, and coworkers reported on the reactivity of carbodicarbenes, a prominent family of carbones, as catalysts for the cyclotrimerization of isocyanates (Figure 2B) [12]. Their research highlights a synergistic frustrated Lewis pair reactivity involving carbodicarbenes and mildly acidic benzylic alcohols. Solid-state crystallography provided insights into the activation mechanism, revealing the formation of a carbone-isocyanate adduct characterized by an N–C interaction between one of the coordinating carbenes on the carbodicarbene and the nitrogen of the bound isocyanate. This finding suggests that the reactivity of carbodicarbenes can be enhanced by the π-acidity of the coordinating carbene. Complementary DFT studies further elucidate the cooperative activation of isocyanates by both the carbone and the alcohol, with the latter providing hydrogen bonding stabilization of the intermediates and transition state structures along the catalytic cycle.

Also in 2021, Liberman-Martin and coworkers investigated the catalytic reactivity of carbodiphosphoranes. They identified a cyclic carbodiphosphorane as an effective catalyst for the hydroboration of ketones and imines [13]. Two mechanistic pathways were proposed based on whether the carbodiphosphorane forms an adduct with the borane species or

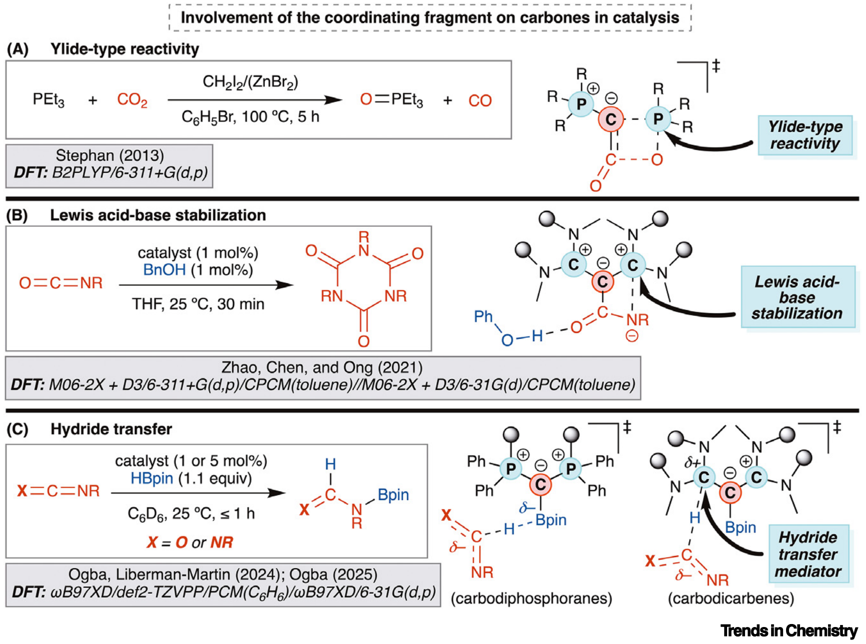

Figure 2. Carbones reported as organocatalysts for heteroallene reductions with computational mechanistic insights revealing the involvement of the coordinating fragment. (A) Stephan and coworkers reported the *in situ* formation of a carbodiphosphorane that catalyzes CO_2 to CO conversion via ylide-type reactivity [10]. (B) Zhao, Chen, Ong, and coworkers reported the carbodicarbene- and benzyl alcohol-catalyzed cyclotrimerization of isocyanates [12]. (C) Ogba, Liberman-Martin, and coworkers reported the carbodiphosphorane-catalyzed hydroboration of isocyanates and carbodiimides [13–15]. The density functional theory (DFT) method and basis set used for each reported calculation are presented in gray boxes.

directly activates the ketone or imine substrates. In a related study in 2024, Ogba, Liberman-Martin, and coworkers demonstrated that cyclic carbodiphosphoranes can catalyze the hydroboration of isocyanates and carbodiimides (Figure 2C) [14]. They explored the two substrate activation pathways previously described using DFT. The cyclic carbodiphosphorane preferentially binds to pinacolborane rather than the heteroallene substrate, enhancing the hydricity of the borane, thereby facilitating the transfer of hydride to the heteroallene in the substrate reduction step. While the alternate pathway is not described here, it is noteworthy that the intermediate formed upon the coordination of isocyanate to the cyclic carbodiphosphorane exhibited a P–O interaction between one of the flanking phosphines and the oxygen in the bound isocyanate, highlighting the π-accepting properties of the phosphine fragment of cyclic carbodiphosphoranes.

Further studies by Ogba and coworkers in 2025 examined the energetic implications of the 1,2-addition pathway and its impact on the catalytic efficiency of carbones in the hydroboration of carbodiimides [15]. They computed catalytic cycles featuring two carbodiphosphoranes and one carbodicarbene. Their results demonstrate that cyclic carbodiphosphoranes exhibited superior catalytic activity, attributed to their preorganized structures that facilitate effective coordination with HBpin while minimizing distortion. Conversely, the carbodicarbene predominantly follows the 1,2-addition pathway. However, this pathway for the carbodicarbene produced a kinetically stable 1,2-addition intermediate, rendering the transfer of hydride to the carbodiimide energetically unfavorable at room temperature during the turnover-determining step. This suggests a potential drawback of the π-acidity of carbones, as it may actually hinder the catalytic activity of carbones at low temperatures.

New frontiers for metal-free carbone reactivity studies

Computational investigations into carbones have significantly advanced our understanding of their unique structure and reactivity patterns. The non-innocent role of the coordinating fragments in carbones, be it in ligand exchange or catalytic reaction pathways, remains a key focus. Investigating the applications of carbones in chemical transformations beyond carbonyl and heteroallene hydroboration is of strong interest. Moreover, prioritizing the design of innovative ligand environments to improve the catalytic efficiency of carbones, particularly in asymmetric catalysis, is crucial. Ultimately, combining synthetic and computational methods collaboratively is vital for developing new chemical processes that utilize these fascinating zerovalent carbon compounds.

Author contributions

M.S. and O.M.O. wrote the paper.

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Declaration of interests

No interests are declared.

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