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Correction: Functionalization of *o*-carboranes via carboryne intermediates

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 Correction for 'Functionalization of *o*-carboranes via carboryne intermediates' by Zaozao Qiu et al., *Chem. Soc. Rev.*, 2022, **51**, 3164–3180, <https://doi.org/10.1039/D2CS00024E>.

Through this correction, *Chem. Soc. Rev.* notifies readers that this review article is an update of a previous review published in *Coord. Chem. Rev.*¹ Due to this, some lines of text overlap with the earlier publication, particularly in the conclusions. To rectify this, an updated version of the conclusions section has been provided below:

Carborynes, three-dimensional relatives to benzyne, can be generated *in situ* from 1-X-2-Li-1,2-C₂B₁₀H₁₀ (X = Br, I, OTs, OTf), or 1-Me₃Si-2-[Ph(OAc)]-1,2-C₂B₁₀H₁₀ or [1-Li-3-N₂-1,2-C₂B₁₀H₁₀][BF₄]. Two kinds of carborynes have been known, *o*-carboryne (1,2-dehydro-*o*-carborane) and 1,3-dehydro-*o*-carborane. The former exists in two resonance forms, a bonding form (C=C double bond) vs. a biradical form, showing diverse reactivity patterns. The latter can also be presented in two resonance forms, a bonding form (C=B double bond) vs. a zwitterionic form (Fig. 1). *o*-Carboryne is a versatile intermediate, readily participating in pericyclic processes with substrates such as dienes and (hetero)aromatics, ene reactions with unsaturated systems, and regioselective insertions into sp³ or sp² C–H bonds (e.g., in ethers, amines, ferrocenes, indoles). In contrast, 1,3-dehydro-*o*-carborane demonstrates superior efficiency in [4+2] cycloaddition/aromatic ene reactions with aromatics, and ene reactions with alkenes and alkynes. This enhanced reactivity is attributed to the highly polarized nature of the cage C–B multiple bond. Although these reactivities suggest parallels between carboryne and benzyne chemistry, carborynes clearly possess unique characteristics, as detailed in this review.

Notwithstanding these advances, several challenges have yet to be overcome. The study of carborynes, especially 1,3-dehydro-*o*-carborane, lags behind the well-established field of arynes. Consequently, there is a pressing need for the design of more efficient precursors and the expansion of their reaction scope to uncover novel transformations. It has been documented that the highly symmetrical 3D structure of *o*-carborane can be transformed to chiral-at-cage molecules with the addition of substituents to lower the symmetry of its icosahedral structure.^{95,96} For example, the presence of a substituent at the position B(3/6) of C(1)-substituted *o*-carborane results in the chirality of the molecule.⁹⁷ The development of a (C,B)-carboryne with an inherent chirality is of great interest as well as challenge. Transition metal (BB)-carboryne complex has been reported with concomitant increase of the bond order between the two metalated boron atoms.^{40–42} The carboryne analogues containing B–B multiple bond (the (BB)-carboryne) still remain unrevealed. Meanwhile, (C,B)-, and (B,B)-carborynes derived from *m*- and *p*-carboranes need to be explored. Though pericyclic reactions of *o*-carborynes with a series of unsaturated substrates have been intensively developed in recent years, the dipolar reactions involving carborynes remain much less studied. The reaction chemistry based on carborane centered radicals derived from carborynes are awaiting exploration. A great progress has been made in the construction of C_{cage}–C and B_{cage}–C bonds, however, direct C_{cage}/B_{cage}–heteroatom bond formation from carboryne intermediates remains a significant challenge. Novel reaction modes are expected from the multi-component or cascade reactions involving carborynes through a proper design of the starting materials. Finally, the extension of carboryne chemistry to supra-icosahedral cages (those with > 12 vertices) stands as a significant unresolved challenge.^{98,99} It is anticipated that advances in such research field will provide functionalized

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carborane molecules with important applications in different fields such as medicine, materials science, catalysis and more. As the field progresses, we expect that other carbonyne precursors will be invented, and the results detailed in this review will promote these efforts.

The Royal Society of Chemistry apologizes for these errors and any inconvenience caused to authors and readers.

References

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