

Digest paper

## Carboranes meet photochemistry: Recent progresses in light-mediated cage functionalisation

Alberto Lanfranco, Polyssena Renzi, Marco Rusconi, Annamaria Deagostino\*

Department of Chemistry, University of Turin, Via Giuria 7, 10125 Torino, Italy



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## ABSTRACT

Carboranes are intriguing structures which show an excellent *in vivo* stability and high chemical versatility. Furthermore, thanks to their structural and electronic properties they find many applications in several fields, as smart materials, bioisosters of aryl rings in known drugs and BNCT (Boron Neutron Capture Therapy) agents, for example. Recently, the reactivity of these boron rich icosahedral cages, promoted by UV-visible light, has encountered the interest of some research groups, which described new pathways based on the formation of B- and C-centred radicals. In these way, properly functionalised carboranes have been prepared, increasing the applications of these precious moieties.

Carboranes are icosahedral clusters, with a high boron (B) content, which are considered three dimensional aromatic rings thanks to their electronic and structural properties [1]. Moreover, because of their stability and chemical versatility, they find many applications ranging from medicine to functional materials. In the pharmaceutical field, carboranes are *in vivo* stable thus they are employed as pharmacophores of aromatic moieties in known drugs, or as promising Boron Neutron Capture Therapy (BNCT) agents [2–8]. As functional building blocks, they are applied for the design of nanomaterials, and also find applications in coordination and organometallic chemistry as valuable ligands [9–13]. One of the more interesting aspects of these intriguing structures is their peculiar and rich reactivity. In fact, B-H and C-H vertices display an orthogonal behaviour: the latter react with electrophiles after deprotonation, on the contrary the boron counterpart has a reactivity comparable to the electrophilic substitution of aromatics. Nowadays, organometallic chemistry plays an important role allowing for the site-selective functionalisation of carboranes at both C-H and B-H vertices without the need of any protection [2,14–18]. In addition to heterolytic B-H transformations, which generally require quite harsh reaction conditions, more recently methodologies involving radical pathways exploiting both the B-H or/and C-H homolysis of organoboranes has been proposed [19–21]. The development of new synthetic strategies involving B- and C-centered radicals is challenging and allows carborane cages to be functionalised *via* pathways which are orthogonal to classical closed-shell reactions, thus increasing the number of protocols available for obtaining substituted carboranes. The possibility of

finely tuning the properties of the carborane by a precise design of suitable moieties to be linked to the cage *via* proper synthetic strategies is then increased. For example, this is relevant for drug selectivity in the design of therapeutic agent.

Visible light-mediated transformations have, indeed, attracted huge interest in the last years, revealing alternative routes to functionalised molecules under mild reaction conditions and with high functional group tolerance [22]. Furthermore, visible light allows radical mediated pathways to be accomplished in a controlled way. Despite the potential of the use of photochemistry in the reactions of carboranes, only few examples have been reported so far [23]. Thus, this field remains still unexplored (12 papers available in the literature). Considering the potential of carborane-clusters functionalisation, in this digest, we will review the light-mediated strategies exploited for the generation of B- and C-centred radicals. From the first example dating back 2016, in the last three years an increasing number of papers have been published and the group of Zuowei Xie is the most active in the field.

### Carboranes functionalisation *via* C-centered radicals

Light-promoted cleavage of aryl C-halide bonds is an established strategy for the generation of reactive C-centered radicals [18,24,25]. In 2017, Xie and co-workers first applied this functionalisation mode to iodo-carboranes **1**, achieving a photo(hetero)arylation with un-activated (hetero)arenes **2** at room temperature [26] (Scheme 1). The reaction was carried out in basic conditions under the irradiation of an 18 W UV

\* Corresponding author.

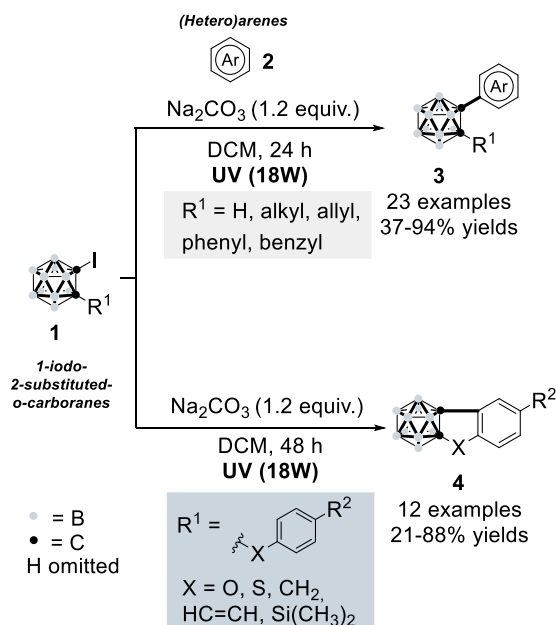
E-mail address: [annamaria.deagostino@unito.it](mailto:annamaria.deagostino@unito.it) (A. Deagostino).

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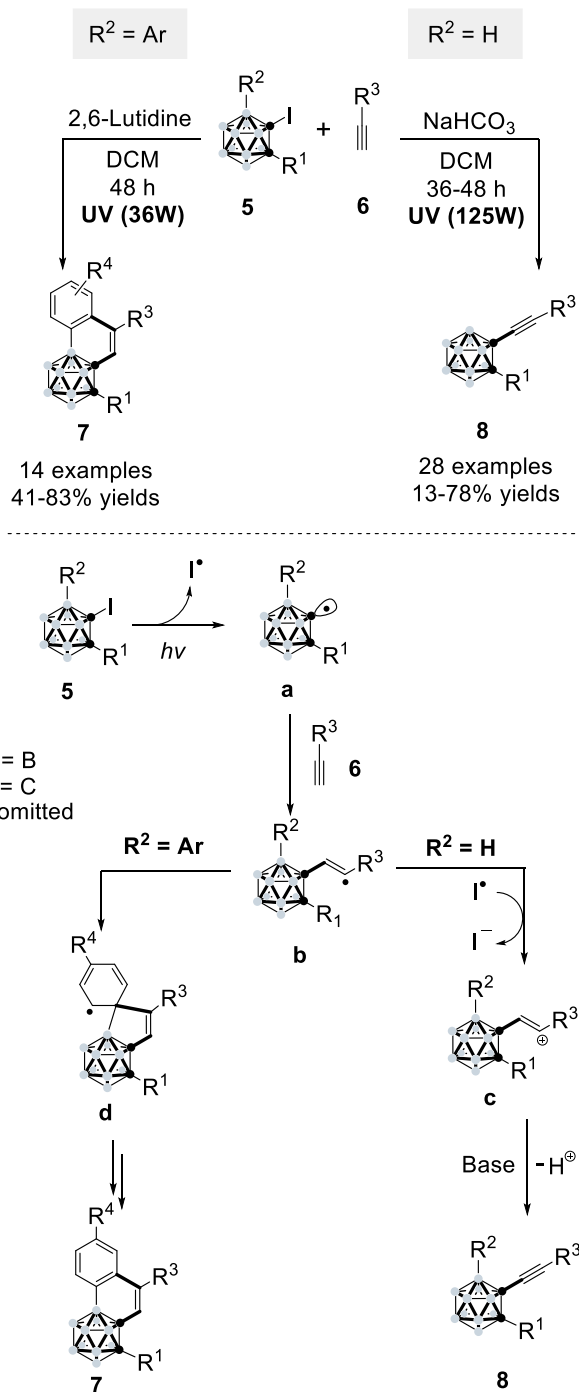
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**Scheme 1.** UV light-promoted inter- and intramolecular photo(hetero)arylation of 1-iodo-*o*-carboranes **1**.

lamp. This procedure afforded a library of 1-(hetero)aryl-*o*-carboranes **3** including a variety of heteroarenes, such as furans and pyrroles. Noteworthy, the reaction proceeded smoothly with electron-rich (hetero)arenes compared to electron-deficient ones, as in the case of pyridines. Furthermore, the authors also reported a di(hetero)arylation under the same reaction conditions from 1,2-diiodo-*o*-carboranes, producing five different di(hetero)arylated compounds in good yields. The presence of substituents on the C(2)-position of the cage did not affect considerably the intermolecular (hetero)arylation reaction. An intramolecular photo(hetero)arylation was observed with aromatic rings sufficiently spaced from the cage by one or two (hetero)atoms (**Scheme 1 bottom**). This cyclisation reaction afforded *o*-carboranes-fused (hetero)cycles **4**, thus allowing the efficient construction of five- and six-membered rings systems under very mild reactions conditions.

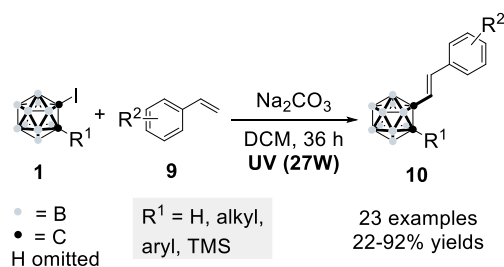
Later, Xie *et al.* also reported the UV light-promoted functionalisation of 1-iodocarboranes **5** with terminal alkynes **6** at room temperature in the presence of a base (**Scheme 2**) [27]. Depending on the nature of the substituent on the adjacent B(3)-position, under similar conditions, the reaction could either yield the *o*-carborane-fused cycle **7** or the alkynylated product **8**. The synthesis of 1-alkynyl-*o*-carboranes **8** gave better results with electron-poor alkynes but it was limited to arylalkynes. Indeed, the authors did not observe any alkynylation product in absence of an aryl group. It was speculated that with alkylalkynes, the resulting reactive alkenyl radical would rather capture an iodine atom from the reaction environment, as it was observed in the case of 1-hexyne. Meanwhile, the synthesis of *o*-carborane-fused cycle **7** in the presence of an adjacent aryl group in 1-iodo-*o*-carboranes was compatible with terminal alkyl- and aryl-alkynes. The reaction was also applied to C(2)-aryl 1-iodo-*o*-carboranes affording three *o*-carborane-fused cycles in moderate to good yields in the reaction with 1-hexyne. Control experiments and the identification of key intermediates/by-products allowed a reaction mechanism to be proposed by authors (**Scheme 2 bottom**). UV light-mediated homolytic cleavage of the C-I bond of 1-iodo-*o*-carborane **5** would generate the corresponding C-centered carboranyl radical **a**. The reaction with the terminal alkyne **6** produces the alkenyl radical **b** as suggested by the identification of the corresponding iodinated product when  $R^2$  is a hydrogen atom. In this case, **b** would be oxidised by an iodine atom, generating the vinyl carbocation **c**. Then, the latter participates in a base-promoted elimination reaction to produce the alkynylated product **8**. Meanwhile, with an aryl group either on the B(3)- or



**Scheme 2.** UV light promoted alkynylation of 1-iodo-*o*-carboranes **5** and its subsequent cyclisation reaction.

C(2)-positions, **b** is supposed to undergo a cyclisation reaction to give the spirointermediate **d** as suggested by the isolation of its dimeric by-product. Lastly, subsequent ring expansion and rearomatisation in the presence of a base affords the *o*-carborane-fused cycle **7**.

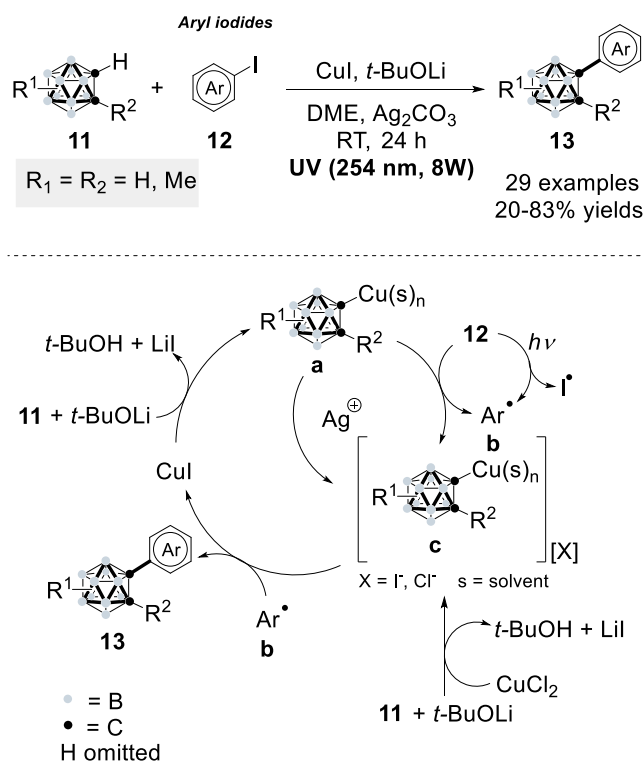
Following their achievements in the activation of the C-I bond in the carborane cage, the same group later reported the alkynylation of iodocarboranes **1** with un-activated styrenes **9** by the means of UV light for the synthesis of 1-alkenyl-*o*-carboranes **10** (**Scheme 3**) [28]. The reaction was carried under mild conditions in the presence of a small excess of Na<sub>2</sub>CO<sub>3</sub> as the base. A wide scope was presented, comprising halide, trifluoromethyl, pyridinyl and methoxy groups. Higher yields were observed with electron-poor alkenes. Substituents on the C(2)



**Scheme 3.** Synthesis of 1-alkenyl-*o*-carboranes **10** via UV light promoted alkenylation reaction of 1-iodo-*o*-carboranes **1**.

position greatly influenced the reactivity, as loss in yields was observed with bulkier aryl substituents compared to the smaller methyl and ethyl groups. However, reduced reactivity was noted in the case of C(2)-H *o*-carboranes. The authors hypothesised that the enhanced acidity of the C—H group in the cage would hinder the alkenylation reaction [29,30]. Control experiment with the radical scavenger TEMPO suggested a radical mechanism, presumably involving photoinduced homolytic cleavage of the C-I bond, as seen in Scheme 2 for the similar system.

Xie *et al.* exploited a copper catalyst in combination with an excess of *t*-BuOLi and Ag<sub>2</sub>CO<sub>3</sub>, to avoid the carborane pre-functionalisation and allow 1-aryl-*o*-carboranes **13** to be synthesised under light irradiation. *Ortho*-carboranes **11** were reacted with aryl iodides **12** under UV light irradiation, at room temperature, in DME as the solvent (Scheme 4). [31] As suggested by control experiments with CuCl<sub>2</sub>, the reaction can be mediated both by Cu(I) and Cu(II). Moreover, the inhibition of the process in the presence of TEMPO suggested the involvement of radicals which can be generated either *via* the homolysis of the C-I bond of the aryl iodide **12** or *via* SET (Single Electron Transfer) from the Cu(I) complex **a** to halide **12**. The introduction of an oxidant as Ag<sub>2</sub>CO<sub>3</sub> was required to promote the formation of the Cu(II)-complex **c**. The latter can react with the aryl radical **b** to form the desired product **13**. The



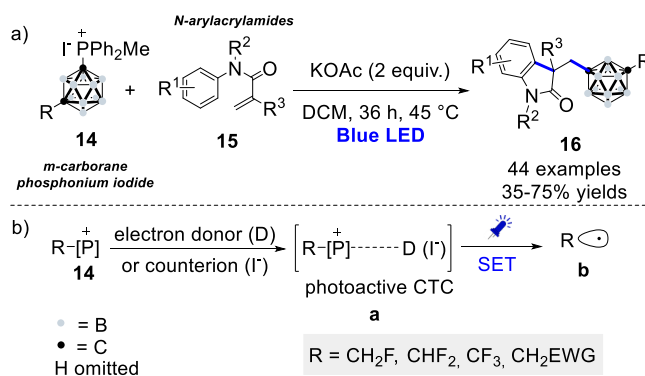
**Scheme 4.** Light-promoted Cu-catalysed synthesis of 1-aryl-*o*-carboranes **13** under UV irradiation.

protocol tolerated a good range of functional groups on the aryl iodide **12**, but a pronounced decrease on yield was observed with strong electron-withdrawing groups such as 3,5-bis(trifluoromethyl)iodobenzene and 2-iodothiophene. The scope of *o*-carboranes **11** was limited to un-substituted cages, indeed, the introduction of a methyl group on position 1 reduced the yield to 20 %, while 9,10-dimethyl-*o*-carborane gave very satisfactory results with yields up to 76 %. The intramolecular arylation/cyclisation reaction was also explored affording five- or six-membered fused *o*-carboranes, although with a marked sensitivity towards steric effects (from 20 to 57 % yields).

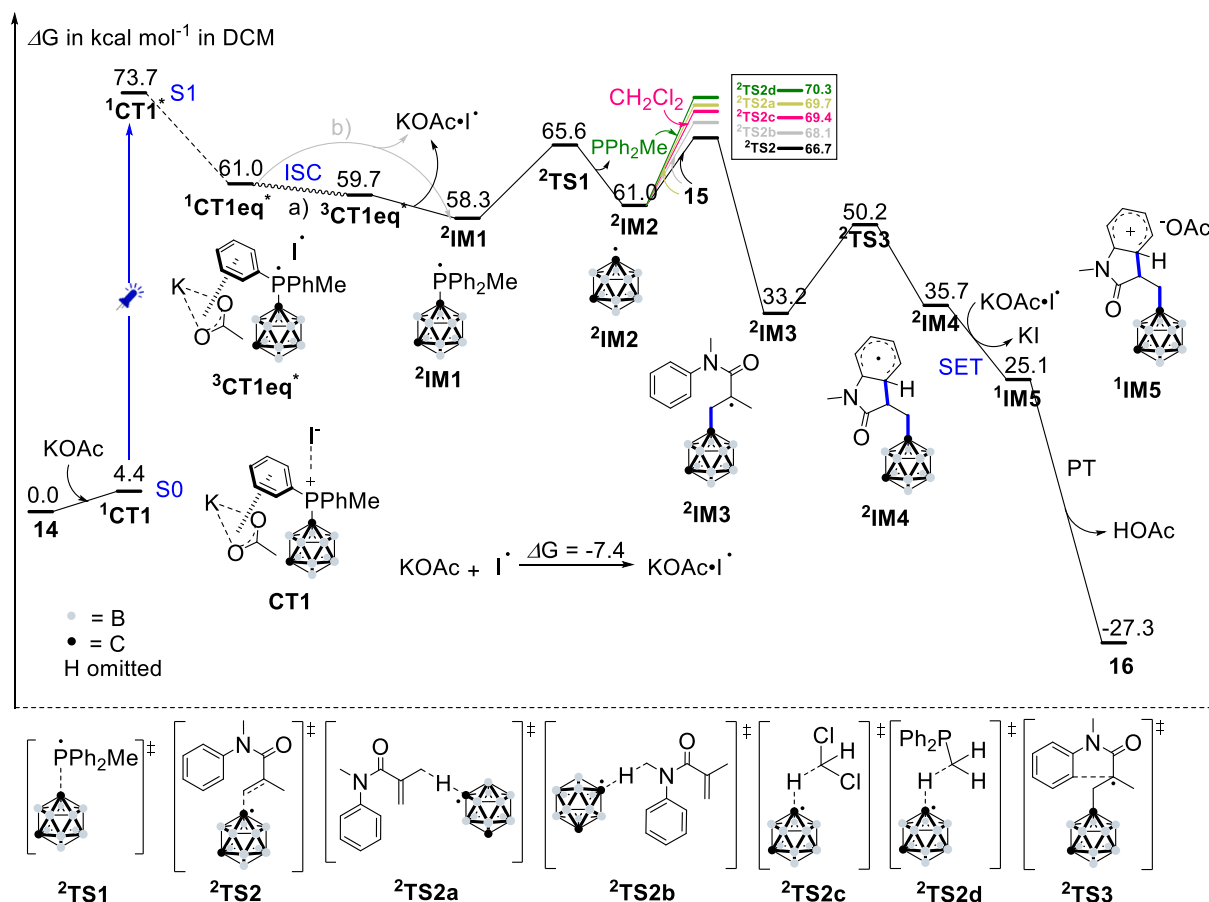
A different approach based on the visible light-mediated photo-reduction of carborane phosphonium salts **14** was recently developed by the group of Chen [32]. Phosphonium salts **14** formed photoactive charge-transfer-complexes **a** (CTC) when substituted with suitable electron-donors substituents, which undergo SET under visible light irradiation thus affording C-centered radicals **b** (Scheme 5b). Following this methodology, the authors synthesised several carborane oxindoles **16** by reacting *m*-carborane phosphonium iodide salts **14** and *N*-arylacrylamides **15** using KOAc as the base, in DCM at 45 °C under blue light irradiation (Scheme 5a).

An extensive reaction scope was investigated, however more limited regarding the carborane moiety. Good to modest yield were obtained with both electron-withdrawing and electron-donating groups on the *N*-arylacrylamide aryl rings **15**, changing the R<sup>2</sup> group. Also the modification of the R group on the carborane cage was well tolerated, even if substituted with ethers. Since the oxindole moiety is embedded in several natural products and drugs, this methodology has been applied to the synthesis of different carborane-oxindole-pharmaceutical/bioactive molecule hybrids, such as Ibuprofen and Flurbiprofen *inter alia*. Mechanistic investigations confirmed the crucial role of the base, probably necessary to form a more active CTC **a** with **14** and to stabilise the iodine radical. Moreover, trapping experiments with TEMPO led to a complete inhibition of the reaction, corroborating the existence of a radical process. The authors gave an astonishing explanation of the reaction mechanism, as shown in the free energy diagram reported in Scheme 6.

A large number of experiments were carried out to gain insights on the reaction mechanism which could be summarised as follows. KOAc and **14** form a key photoactive complex <sup>1</sup>CT1 able to reach its first excited state <sup>1</sup>CT1\* under blue light irradiation. A relaxation process leads to the formation of an equilibrium structure <sup>1</sup>CT1eq\* in its S1 state. The intersystem crossing occurs to form the equilibrium structure <sup>3</sup>CT1eq\* in its triplet state, which releases I<sup>•</sup> affording <sup>2</sup>IM1. This latter could also be obtained directly from <sup>1</sup>CT1eq\* by the release of KOAc·I<sup>•</sup>. The P—C bond cleavage releases PPh<sub>2</sub>Me and the radical intermediate <sup>2</sup>IM2. At this point, different pathways are possible, since the C-centered carboranyl radical is strong enough to follow a HAT (Hydrogen Atom



**Scheme 5.** a) blue light-induced synthesis of carborane oxindoles **16** via radical cascade reactions. b) CTC-mediated photoreduction of phosphonium salts **14**.



Scheme 6. Proposed mechanism for the synthesis of carborane oxindole 16.

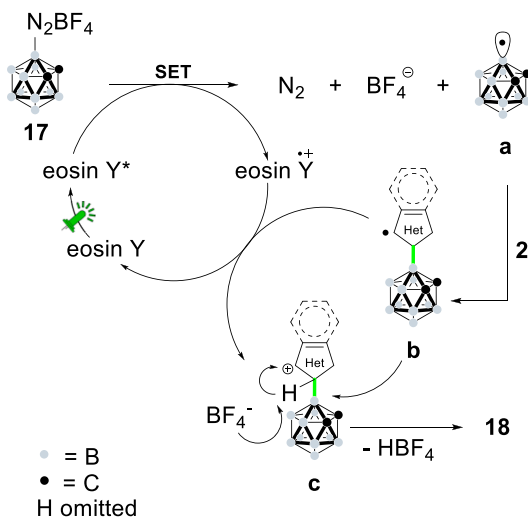
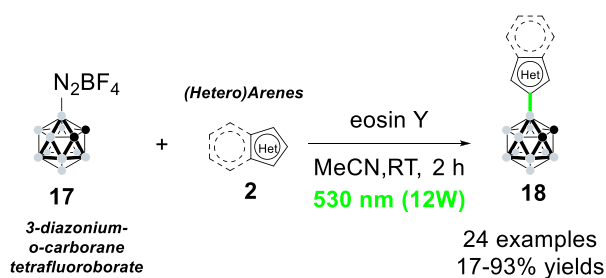
Transfer) process. Indeed, hydrogen abstraction could involve diverse species affording <sup>2</sup>TS2a-d, with a slight difference in the energy barrier. However, the lowest one is related to the exoergonic radical addition of <sup>2</sup>IM2 to the double bond of 15, therefore this pathway seems to be the most favoured. Once <sup>2</sup>IM3 is formed, it undergoes intramolecular cyclisation to produce <sup>2</sup>IM4 via <sup>2</sup>TS3. The above generated KOAc·I<sup>-</sup> and <sup>2</sup>IM4 are involved in a SET and proton transfer processes to afford 16, releasing KI and HOAc.

### Carboranes functionalisation via B-centered carboranyl radicals

Carboranes functionalisation can be realised also through the generation of B-centered carboranyl radicals, a poorly developed field up to recent years. Indeed, the number of methodologies available for the photo-generation of cage B-based radicals is quite limited. The first example dates back to 2016, when the group of Xie reported 3-diazonium *o*-carborane tetrafluoroborates 17 to be suitable starting materials for the generation of the B-centered carboranyl radical under irradiation with green light. In the absence of any other additives, the process is mediated by eosin Y as the photocatalyst (Scheme 7) [33]. B(3)-arylated *o*-carboranes 18 were easily obtained upon coupling with (hetero)arenes 2 at room temperature in MeCN as the solvent. Moreover, the reaction is regioselective with the functionalisation at the C(2)-position in the heteroarene. When the C(2)-position is not available, a new bond is selectively formed at the C(3)-position. In general, higher yields were obtained with electron-rich arenes suggesting an electrophilic nature for the boryl radical. In order to obtain moderate yields with simple arenes, their loading should be increased from 2 to 10 equivalents. The authors did not explore the scope of the 3-diazonium *o*-carborane tetrafluoroborates 17. According to the proposed mechanism

based on the experimental evidence (Scheme 7), the irradiation with green light caused the excitation of eosin Y, which can engage a SET with the diazonium salt 17 to afford the B-centered carboranyl radical a upon release of N<sub>2</sub> and BF<sub>4</sub><sup>-</sup>. The following addition of the key radical a to the arene 2 generates radical b which upon oxidation by eosin Y radical cation formed c. In the last step, a rearomatisation process followed the deprotonation of c, thus the formation of the product 18. A radical-chain transfer could be also active for the generation of cation c.

A more versatile strategy for the generation of B-centered carboranyl radicals at the different positions of the *o*-carborane cage (B(3), B(4) or B(9)) was reported in 2022 by the group of Xie [34]. In this case iodo-carboranes 19 were coupled with (hetero)arenes 2 exploiting a light-mediated palladium-catalysed cross coupling (Scheme 8). With respect to the previously reported methodology employing iodocarboranes as starting materials, the usage of a palladium-mediated reaction allowed to move from UV to visible light, thus the generation of the carboranyl radicals is feasible in milder reaction conditions. Indeed, a photoactive Pd(0) catalyst is formed, mixing Pd<sub>2</sub>(dba)<sub>3</sub> with a phosphine in ratio 1:3.5. Upon the absorption of blue light, the excited state of the catalyst can undergo a SET with iodocarborane 19, thus forming a B-centered carboranyl radical and a Pd(I) species a (Scheme 8). Once the radical is generated, it can react with 2 to afford radical complex b. Its oxidation by the Pd(I) species, through a SET, regenerated the Pd(0) catalyst thus providing the cation d. Deprotonation in the presence of a base such as Cs<sub>2</sub>CO<sub>3</sub> afforded the arylated product 20. No reaction was observed with Br or Cl-*o*-carboranes. As observed also with 3-diazonium *o*-carborane salts 17, the more electron-donating is the (hetero)arene the higher are the yields, implying B-centered carboranyl radicals to be electrophiles. The highest electrophilicity was observed for radicals centered at the B(3) position and decreasing in the order B(3) > B(4) > B(9). As a matter



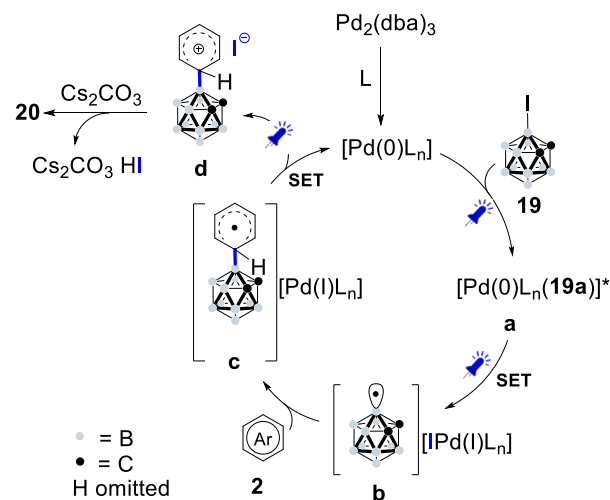
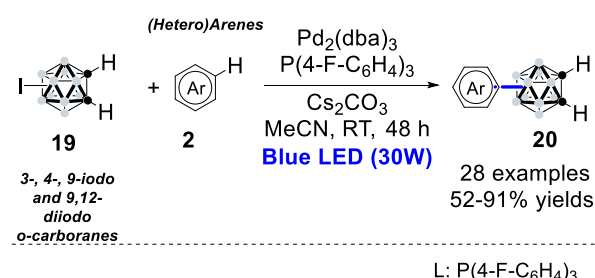
**Scheme 7.** Visible light-generation of B-centered carboranyl radical **a** from 3-diazonium *o*-carborane tetrafluoroborate **17** and its functionalisation.

of facts, electron-deficient arenes reacted better with 9-iodo-*o*-carboranes (e.g. 1,4-difluoro benzene gave 63 % yield at B(3), 71 % at B(4) and 81 % at B(9)). The authors reported also a stepwise difunctionalisation of 9,12-diiodo-*o*-carborane with two different arenes.

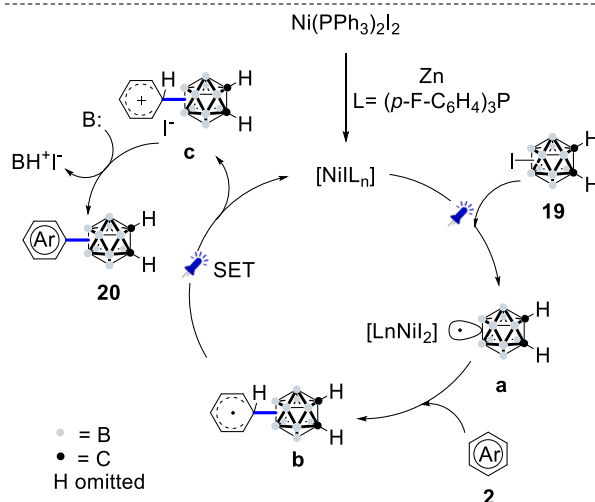
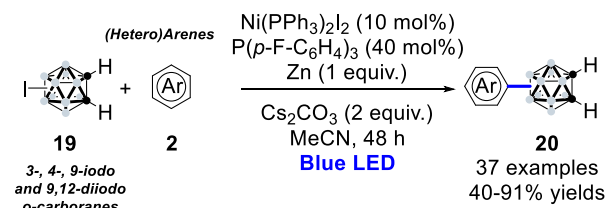
The same research group proposed the B-C bond formation *via* a visible light-mediated arylation of iodocarboranes **19** using Ni(I) as metal catalyst (Scheme 9) [35]. Exploring the scope of the reaction, the authors mainly played with the substitution on the aryl ring confirming the electrophilicity trend of B-centered carboranyl radicals to be B(3) > B(4) > B(9). Indeed, electron deficient (hetero)arenes gave higher yields for the B(9) functionalisation while the B(3) position was better substituted in presence of electron-donating groups on the aromatic ring. This methodology worked well, also, in presence of disubstituted (hetero)arenes **2** and diiodo-*o*-carboranes **19**. To gain some insights into the mechanisms, control experiments were carried out confirming the crucial role of both the metal catalyst and the visible light, while the presence of TEMPO completely suppressed the reaction, indicating a radical process.

As far as the mechanism is concerned, Ni(II) could be reduced by Zn to both Ni(I) and Ni(0) species, but it is worth noting that the latter does not undergo oxidative addition reaction with iodo-*o*-carboranes **19**. Therefore, iodocarboranes **19** undergo iodine abstraction by the active Ni(I) complex under blue light irradiation affording the B-centered radical **a**. This latter attacks (hetero)arenes **2** giving **b** which is oxidised to the corresponding cation **c** by Ni(II) in a SET process regenerating the active catalyst Ni(I). The deprotonation of **c** might produce the desired product **20**.

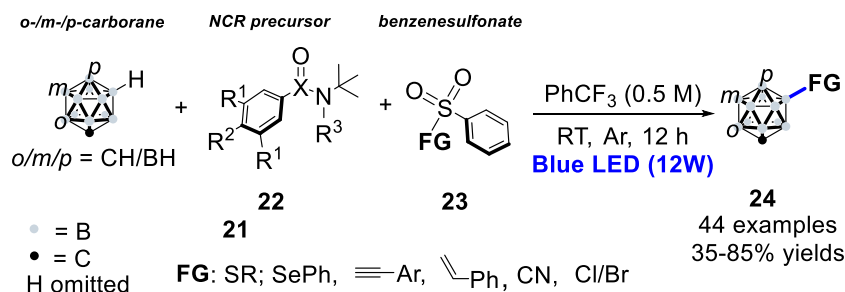
A cutting-edge work on the direct B-H functionalisation of carboranes was recently published by the group of Yan (Scheme 10) [36]. The reaction was carried out on *ortho*-, *meta*- or *para*-carboranes **21** obtaining the B-centered radical thanks to a HAT process induced by a strong *in situ* generated *N*-centered radical (NCR from **22**). These two compounds



**Scheme 8.** Visible-light mediated palladium-cross-coupling of iodo-*o*-carboranes **19**.



**Scheme 9.** Visible light-mediated nickel-catalysed cross-coupling of iodo-*o*-carboranes **19**.



**Scheme 10.** Blue light-mediated functionalisation of carboranes **21** via hydrogen atom transfer.

were reacted with a SOMO-phile **23** using PhCF<sub>3</sub> as the solvent, at room temperature under blue light irradiation.

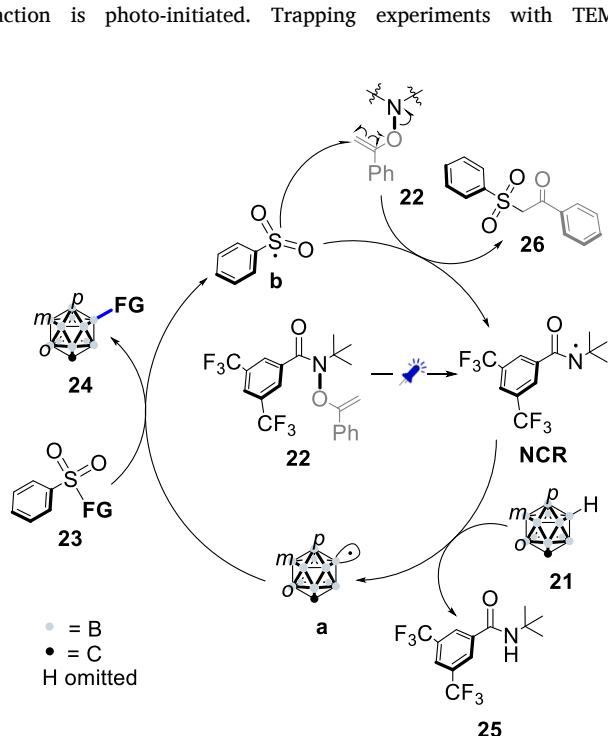
A mixture of regioisomers was obtained using the optimised reaction conditions. However, the B(9)-substitution was favoured leading to a 14:1:1 ratio of B(9):B(5):B(4)-functionalised carboranes. Focusing on *m*-carboranes, the authors investigated the reaction scope by varying the *S*-aryl benzenethiosulfonate partners obtaining **24** in modest to good yields with *ortho*-, *meta*- and *para*-substituted (hetero)arenes **23**. To strengthen the methodology, a substrate derived from indomethacin was also coupled with *m*-carborane. The reaction was scaled up to 1 mmols giving the product in 60 % yield. *p*-Carboranes are also suitable, but longer reaction times are needed, while the functionalisation of *o*-carboranes led to a 2.4:1 mixture of B(9):B(8)-substituted products. The protocol could be applied to the metal-free alkylation of *m*-carboranes, in the presence of both electron-withdrawing and electron-donating groups and direct B-H alkenylation, selenylation, trifluoromethylation, cyanation and halogenation were also carried out.

A mechanistic explanation was shown in **Scheme 11** starting from the N—O bond homolysis of **22** under blue light illumination to obtain the highly reactive NCR species. This latter promotes HAT from the carborane cage releasing the amide **25**. The so-formed radical **a** could interact with a SOMO-phile **23** affording the desired product **24** while the sulfonyl radical **b** reacts with **22** regenerating the active NCR to continue the cycle. Indeed, ON/OFF experiments pointed out that the reaction is photo-initiated. Trapping experiments with TEMPO

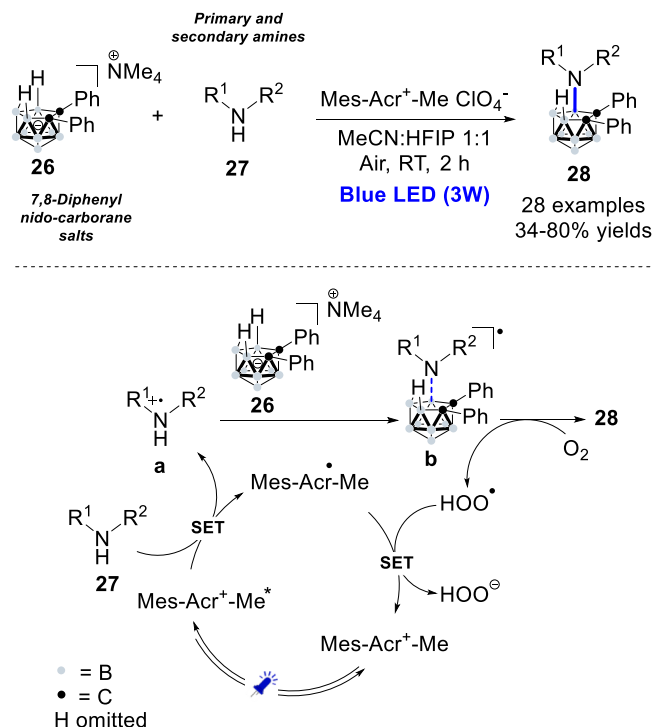
corroborated the radical pathway as the adduct with carboranyl radical was observed by HRMS.

### *nido*-Carboranes functionalisation

A seminal work on the photocatalysed functionalisation of *nido*-carboranes **26** was reported in 2021 by the groups of Lu and Yan (**Scheme 12**) [37]. A B-N(sp<sup>3</sup>) coupling was realised in the presence of mesityl acridinium perchlorate as the photocatalyst, a primary or secondary amine **27** as the nucleophilic coupling partner in MeCN/HFIP (hexafluoroisopropanol) as the solvent mixture at room temperature under irradiation with a blue LED. The protocol could be applied to alkyl or heteroaryl functionalised amines **27a** as well as to sulphonamides **27b**, although the scope of *nido*-carboranes **26** was limited to compound **26**. Control experiments proved the formation of radicals during the process. According to the authors, the interaction of the amine **27** with the excited state of the acridinium catalyst generated the radical cation **a**, which attacking the *nido*-carborane **26** formed intermediate **b**. To furnish the product **28** should be oxidised, thus the presence of O<sub>2</sub> in the reaction mixture revealed to be essential. The reduction of oxygen generated the peroxide radical was then exploited to regenerate the catalyst in the ground-state.



**Scheme 11.** Proposed mechanism for the direct B-H functionalisation of carboranes **24**.



**Scheme 12.** Photoredox B-H functionalisation of *nido*-carboranes **26** mediated by a mesityl acridinium catalyst.

## Conclusions

The reactivity of *nido*- and *closo*-carboranes in the presence of UV-visible light is here reported. This chemistry is a new approach based on the formation of B- or C-centred radicals, which allows new chemical pathways for the synthesis of properly functionalised carboranes to be optimised. Despite the youth of this field and the limited number of papers published until now, several reactivities are described. First of all, B- or C-centred radical protocols have to be distinguished, but among these two classes, the activation of different bonds is described. Radicals are formed from C-halide, C–P, C–N or C–H bonds, in addition to B-halide or B-H bonds as the sources of the radical key intermediates. A lot of work has still to be done, *i.e.* many papers report methods applied to very small amounts of reagents (0.1 mmols) and the scope of carborane derivatives in the reactions is often limited. For these reasons, we think that the light-mediated functionalisation of carboranes deserves attention and it is going to have an interesting future.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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