TENMAK BOREN
BOR ARAŞTIRMA ENSTİTÜSÜ

BOR DERGİSİ
JOURNAL OF BORON
https://dergipark.org.tr/boron

Isolation and stabilization of aryldiazonium cations with boron clusters

Ozan Unver [1], **Akin Akdag** [1,*]

[1]*Middle East Technical University, Department of Chemistry, Ankara, 06800, Türkiye*

ARTICLE INFO

Article history:
Received September 8, 2023
Accepted October 15, 2023
Available online December 29, 2023

Research Article

DOI: 10.30728/boron.1338235

Keywords:
Aryl diazonium
Boron clusters
Carborone
Reactive intermediate

ABSTRACT

Diazonium salts were found to be useful intermediates for many applications. Although few salts were isolated, they were found to be short-lived. Charged boron cages have been known to be weakly coordinating anions. The cages were used to isolate short lived cations for characterizations and further reactions. In this study, we have facilitated dodecaborate dianion and carborate anion to isolate and characterize diazonium cations. With these cages, it was found that diazonium cation was stable more than a month at ambient conditions.

1. Introduction

Since the discovery of aryl diazonium salts by Griefs in 1858 [1], they have been used in numerous application areas. The most common one is dyeing. When diazonium salts undergo diazo-coupling reactions, diazo compounds are produced with great coloring features [2,3], and some of the important diazo dyes are shown in Figure 1a. Other than dyeing, some of the diazo compounds have antimicrobial, anticancer, antibacterial, antioxidant, antibiotic, antifungal and anti-HIV activity (Figure 1b) [4-7]. Moreover, some diazo compounds are known to be used in photoelectronics, optical recording and gas storage [8,9]. Also, aryl diazonium salts which have strong electrophilic character arising from the reactivity of diazonium group, can be used in Sandmeyer reactions, Balz-Schiemann reaction, Pschorr reaction, Meerwein reaction, Gomberg-Bachmann reaction and palladium catalyzed cross-coupling reactions [10-18].

The syntheses of aryl diazonium salts are straightforward. Starting with acidifying an aniline derivative and proceeding through addition of a nitrite resulting an aryl diazonium salt (Figure 2) [19,20]. Due to the high reactivity of diazonium cation, they must be kept at low temperature [21]. In the literature, there are many incidents reported coming from the unstable nature of aryl diazonium cations such as wild decomposition or explosion [22]. In order to use aryl diazonium cations in further reactions, they should be treated with the nucleophile in the same environment where they were formed [17,23-28]. Meanwhile, these cations can be stabilized by tosylates, disulfonamides,

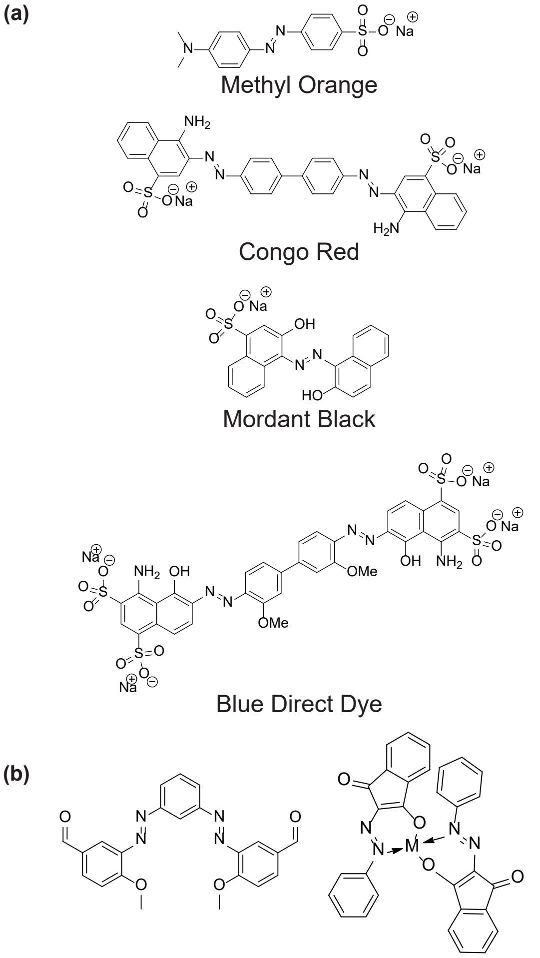

Figure 1. Examples of diazo compounds produced from diazonium salts a). used as dyes and b). that have biological activity.

---

*Corresponding author: aakdag@metu.edu.tr hexafluorophosphates and tetrafluoroborates which are considered as the most effective anions to stabilize aryl diazonium cations but not as good as expected [22,29].

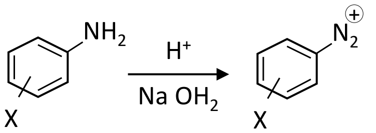

Figure 2. Synthesis of aryl diazonium cations.

The famous stabilized diazonium salt is the salt of tetrafluoroborate anion. However, this salt could lead to fluoroaryl compounds upon heating. (Figure 3a) [11]. Besides, this compound is not as stable as it is advertised. A new stabilizing anion is needed. Charged boron clusters are known to stabilize cationic intermediates [30,31]. For this purpose, dodecahydro-*closo*-dodecaborate, dodecachloro-*closo*-dodecaborate and mono-carba-*closo*-dodecaborate (Figure 3b-d) could be used which are synthesized in our laboratory according to the literature [32-35]. These boron clusters are accepted as weakly coordinating anions which have low affinity for coordination to their counter cations [36]. Also, these anions have high thermal stability and high chemical stability [37].

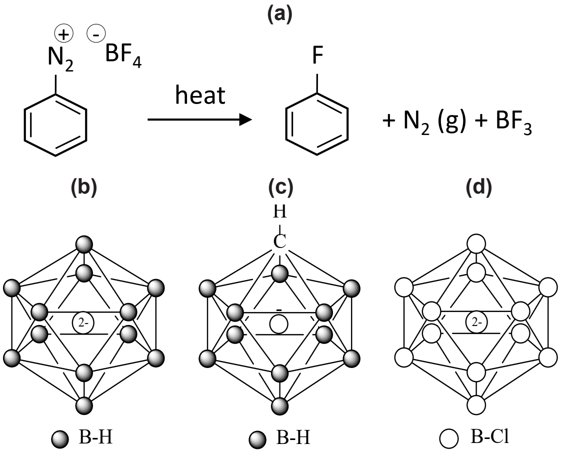

Figure 3. a). Conversion of benzenediazonium tetrafluoroborate into fluorobenzene upon heating. b). dodecahydro-*closo*-dodecaborate, c). mono-carba-*closo*-deodecaborate and d). dodecachloro-*closo*-dodecaborate.

2. Materials and Methods

2.1. Materials

All chemicals were purchased from Sigma-Aldrich (USA). IR spectrums were measured with Thermo Scientific Nicolet iS10 Atr-IR (USA).

2.2. Synthesis of Boron Clusters

2.2.1. Synthesis of triethylammonium salt of dodecahydro-closo-dodecaborate

A 3-necked round bottom flask equipped with a condenser (connected to an acetone trap), a dropping funnel and a stopper was charged with 30 g (0.793 mol) NaBH$_4$ and 150 mL of diglyme under Ar atmosphere. The silicon oil bath was heated to 120ºC to dissolve the sodium borohydride in the reaction mixture. 62.5 g (0.246 mol) I$_2$ was dissolved in 200 mL of diglyme and added to the dropping funnel. The solution of iodine in diglyme was added to the solution containing sodium borohydride dropwise in 6 hours. After the addition, the solution was stirred overnight at 120ºC. Temperature of the oil bath was increased to 185ºC and the solution was stirred for 1 day. The solvent was removed with distillation. 143 mL of distilled water was added to the residue and 84 mL 37% HCl was added to the reaction mixture slowly. The reaction vessel was stored in refrigerator overnight for completion of the formation of boric acid. The reaction mixture was filtered and boric acid was collected. To the filtrate, 150 mL Et$_3$N was added and white crystals of triethylammonium salt of dodecahydro-*closo*-dodecaborate were started to form immediately. The expected product was collected by filtering the reaction mixture. (15.728 g, 0.046 mol, 68.9%) IR: 2473 cm^{-1} (B-H str.), 3125 cm^{-1} (N-H str.)

2.2.2. Synthesis of sodium salt of dodecahydro-closo-dodecaborate

2.2 equivalent of NaOH was dissolved in distilled water and 1 equivalent of triethylammonium salt of dodecaborate was added into the solution. The solution was heated and stirred until it became clear. Then, the solvent was removed and the obtained solid was the expected sodium salt of dodecaborate.

2.2.3. Synthesis of sodium salt of dodecachloro-closo-dodecaborate

0.51 g (12.7 mmol, 2.2 eqv.) NaOH was dissolved in water and 2 g (5.8 mmol, 1 eqv.) (Et$_3$NH)$_2$B$_{12}$H$_{12}$ was added to the solution. The solution was heated and stirred until it became clear. Solvent was removed and Na salt of B$_{12}$H$_{12}^{2-}$ was obtained. Obtained Na$_2$B$_{12}$H$_{12}$ was mixed with MeCN (~60 mL) and SO$_2$Cl$_2$ (~60 mL) was added to the suspension dropwise and the solution became yellow. The solution was stirred for 20 minutes without applying heat and then, refluxed for 1 day. Solvent was removed and the residue was the expected compound. IR: 1031 cm^{-1} (B-Cl str.) Also, disappearance of the belonging to B-H stretching proved the product formation.

2.2.4. Synthesis of trimethylammonium salt of tetradecahydro-nido-undecaborate

30 g (0.793 mol) NaBH4 and 150 mL of diglyme were charged into a 3-necked round bottom flask equipped with a dropping funnel, a condenser (connected to an acetone trap) and a stopper under Ar atmosphere. Temperature of the silicon oil bath was raised to 120ºC for complete dissolution of sodium borohydride. 125 mL (0.995 mol) BF$_3$.OEt$_2$ was added to the solution dropwise with dropping funnel in 5 hours. Then, the reaction mixture was cooled to room temperature

(RT) and suction filtration was applied. During the filtration process, both the reaction flask and the solid were washed with diglyme until the solid becomes white. To the filtrate, solvent exchange procedure was applied with portions of 150 mL distilled water (total 1050 mL) and the evaporated liquid was nearly 1060 mL. Resulting solution was cooled to RT and 6.5 g (0.068 mol) trimethylammonium chloride was added to the solution. The solution was stored in refrigerator overnight and filtered. Obtained solid was dissolved in acetone and heated to reflux. Distilled water was added to the solution until cloudiness was observed. The solution was cooled to RT and stored in refrigerator overnight. The solution was filtered and the collected solid was dried yielding 5.8 g (0.03 mol, 41.7%) $(CH_3)_3NHB_{11}H_{14}$. IR: 2501 cm^{-1} (B-H str.), 3169 cm^{-1} (N-H str.).

2.2.5. Synthesis of trimethylammonium salt of mono-carba-closo-dodecaborate

5.0 g (0.026 mol) trimethylammonium salt of tetradecahydro-*nido*-undecaborate was dissolved in freshly distiled THF under Ar atmosphere and cooled to 0ºC in an ice bath. 17.5 g (0.648 mol) NaH was washed with hexane and added to the solution slowly. The solution was stirred for 1 hour at RT and solvent was removed. After evaporation, freshly distilled THF was added to the flask to dissolve the solid. Then, 12.5 mL (0.156 mol) $CHCl_3$ was added slowly at 0ºC. The solution was stirred for 1 hour at RT and EtOH was added to the solution dropwise at 0ºC and allowed to stir overnight. Next day, the solvent was removed and distilled water was added to the residue. The solution was acidified with 40 mL of 37% HCl + 80 mL of distilled water. After the acidification process, trimethylammonium chloride was added to the solution and filtered. Obtained solid was dissolved with minimum amount of MeOH with heating and after all the solid was dissolved, distilled water was added to the solution and filtered. To the filtrate, trimethylammonium chloride was added and some precipitation occurred. The desired product was collected with filtration yielding 0.18 g (0.9 mmol, 3.41%). IR: 3172 cm^{-1} (N-H str.), 3037 cm^{-1} (C-H str.), 2525 cm^{-1} (B-H str.).

2.2.6. Synthesis of sodium salt of mono-carba-closo-dodecaborate

2.2 equivalent of NaOH was dissolved in distilled water and 1 equivalent of triethylammonium salt dodecahydro-*closo*-dodecaborate was added into the solution. The solution was heated and stirred until it became clear. Then, the solvent was removed and the obtained solid was the expected sodium salt of dodecahydro-*closo*-dodecaborate.

2.3. General Synthesis of Different Benzenediazonium Salts of Boron Clusters

2.3.1. Synthesis of diazonium salts of dodecahydro-closo-dodecaborate, dodecachloro-closo-dodecaborate

2 equivalent of an aniline derivative was mixed with 2 M HCl solution. 2.5 equivalent of $NaNO_2$ was dissolved in distilled water and added to the solution slowly at 0ºC. The solution was stirred for 1 hour. 1 equivalent of sodium salt of dodecaborate was dissolved in distilled water and added to the solution slowly at 0ºC. The solution was stirred for 2 hours and after the filtration, expected compound was obtained by filtration. IR: *ca*. 2200 cm^{-1} (-N≡N str.), *ca*. 2400 cm^{-1} (B-H str.), *ca*. 1030 cm^{-1} (B-Cl str.)

2.3.2. Synthesis of diazonium salts of mono-carba-closo-dodecaborate

1 equivalent of an aniline derivative was mixed with 2 M HCl solution. 1.25 equivalent of $NaNO_2$ was dissolved in distilled water and added to the solution slowly at 0ºC. The solution was stirred for 1 hour. 1 equivalent of sodium salt of dodecaborate was dissolved in distilled water and added to the solution slowly at 0ºC. The solution was stirred for 2 hours and after the filtration, expected compound was obtained by filtration. IR: *ca*. 2200 cm^{-1} (-N≡N str.), *ca*. 2520 cm^{-1} (B-H str.), *ca*. 3030 cm^{-1} (C-H str.).

3. Results and Discussion

Dodecahydro-*closo*-dodecaborate was synthesized according to the reported literature with modifications (Figure 4a) [32]. The procedure starts with ensuring the reaction setup was under inert atmosphere by flushing Argon through setup. Sodium borohydride was suspended in diglyme. Before addition of iodine to the borohydride, the complete dissolution of $NaBH_4$ was attained at 105-110ºC. Then, iodine in diglyme was added dropwise at this temperature. Faster addition resulted in lower yields for the dodecaborate. With the iodine addition over, the reaction mixture was stirred for 12 hours at this temperature to ensure that the conversion of all BH_3 to $B_3H_8^-$. Then, the reaction mixture was brought to reflux temperature and kept at that temperature for 24 hours. The cooled reaction mixture was added water to quench the reaction. With solvents removed, the formed $B(OH)_3$ was separated, and $B_{12}H_{12}^{2-}$ was precipitated as triethylammonium salt. The IR spectrum of triethylammonium salt of dodecahydro-*closo*-dodecaborate (Figure 4b) shows the characteristic peaks as 2475 cm^{-1} for B-H stretching and 3125 cm^{-1} for N-H stretching in the cation.

With dodecaborate in hand, perchlorination of the dodecaborate was performed with refluxing the dodecaborate with sulfuryl chloride (Figure 5a). The perchlorinated dodecaborate was separated as sodium salt. This salt was characterized with IR spectroscopy. The IR spectrum of the obtained compound (Figure 5b) shows B-Cl stretching at 1030 cm^{-1}. Also, disappearance of the peak belonging to B-H stretching proves the product formation.

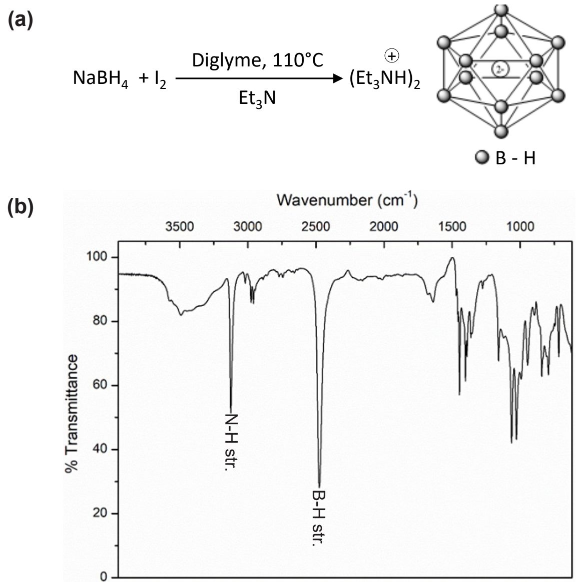

Figure 4. a). Synthesis of triethylammonium salt of dodecahydro-*closo*-dodecaborate, b). IR Spectrum of triethylammonium salt of dodecahydro-*closo*-dodecaborate.

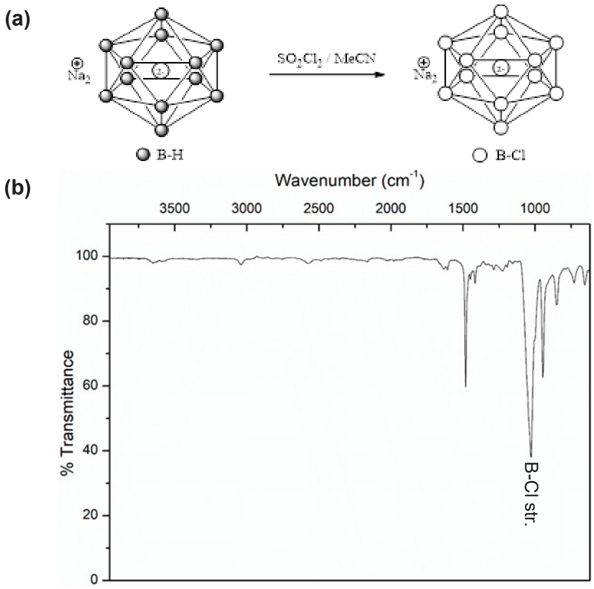

Figure 5. a). Synthesis of dodecahloro-*closo*-dodecaborate, b). IR Spectrum of dodecachloro-*closo*-dodecaborate.

For the synthesis of mono-carba-*closo*-dodecaborate, Michl's method was followed with modifications (Figure 6a). For that, tetradecahydro-*nido*-undecaborate was synthesized by following Dunk's method from NaBH$_4$ treated with BF$_3$.OEt$_2$ and characterized by IR Spectroscopy (Figure 6b). The undecaborate anion was then treated with dichlorocarbene which was generated *in situ* from chloroform yielded the carborate. The carborate was characterized by IR spectroscopy and HRMS. The characterization of the salt was done with IR Spectroscopy which shows characteristic B-H stretching at 2525 cm^{-1} and C-H stretching at 3037 cm^{-1} (Figure 6c).

It is known that the charged borate cages could be used to stabilize cationic intermediates [38].

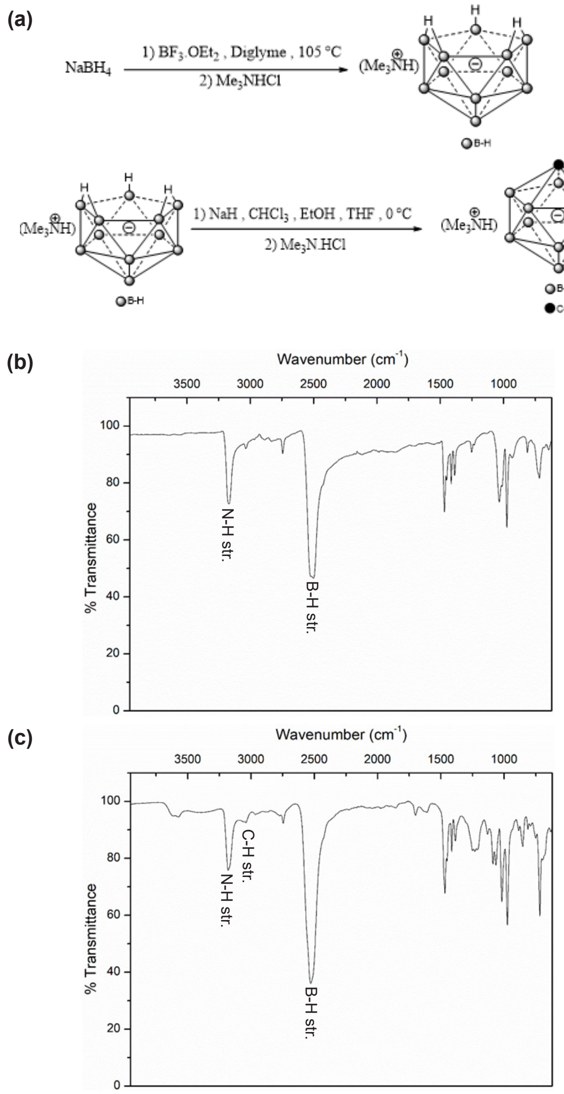

Figure 6. a). Synthesis of mono-carba-*closo*-dodecaborate, b). IR Spectrum of undecahydro-*nido*-undecaborate, c). IR Spectrum of mono-carba-*closo*-dodecaborate.

With that in mind, they could also be used to stabilize aryldiazonium cations. In order to test this hypothesis, first, aniline was converted into benzenediazonium cation by reacting with NaNO$_2$ in the presence of an acid at 0ºC. As soon as the sodium salt of dodecaborates (dodecahydro-*closo*-dodecaborate, dodecachloro-*closo*-dodecaborate and mono-carba-*closo*-dodecaborate) were added onto benzenediazonium cation, precipitates were formed (Figure 7). The precipitates were characterized with IR spectroscopy. The spectra showed characteristic peaks for diazonium cations ca. 2200 cm^{-1} and for $B_{12}H_{12}^{2-}$, B-H str., *ca*. 2480 cm^{-1}, for $B_{12}Cl_{12}^{2-}$, B-Cl str., *ca*. 1030 cm^{-1}, for $CB_{11}H_{12}^{-}$, B-H str., *ca*. 2520 cm^{-1} and C-H str., *ca*. 3000 cm^{-1}. However, in the IR spectra of 1b and 1c, peaks belonging to diazo group (-N=N-) were also observed. Figure 7 shows the IR spectra for the benzenediazonium salts (Figure 8).

After stabilizing benzenediazonium cation with dodecahydro-*closo*-dodecaborate (1a),

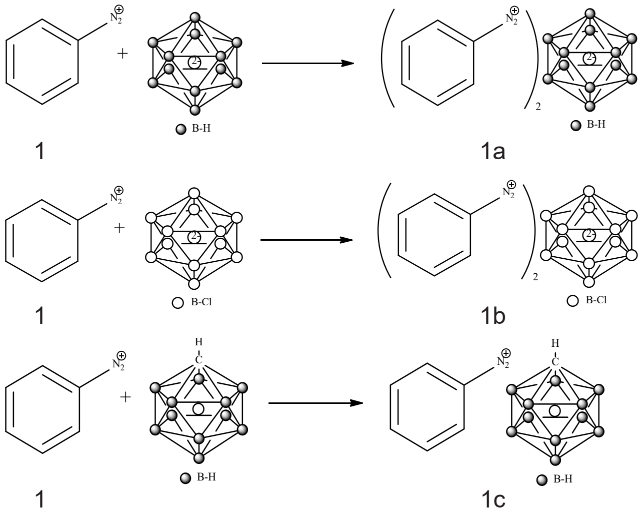

Figure 7. Stabilization of benzenediazonium cation with a). dodecahydro-*closo*-dodecaborate, b). dodecachloro-*closo*-dodecaborate and c). mono-carba-*closo*-dodecaborate

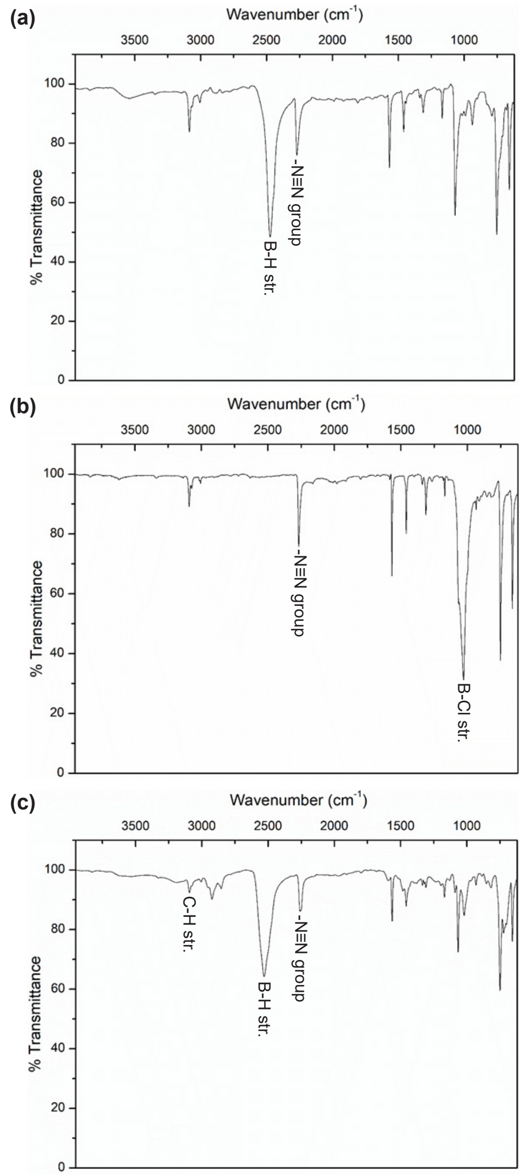

Figure 8. Benzenediazonium salts of a). dodecahydro-*closo*-dodecaborate, b). dodecachloro-*closo*-dodecaborate and c). mono-carba-*closo*-dodecaborate

dodecachloro-*closo*-dodecaborate (1b) and mono-carba-*closo*-dodecaborate (1c), some of the aniline derivatives (Figure 9) were also converted into aryldiazonium compounds and stabilized with dodecaborates.

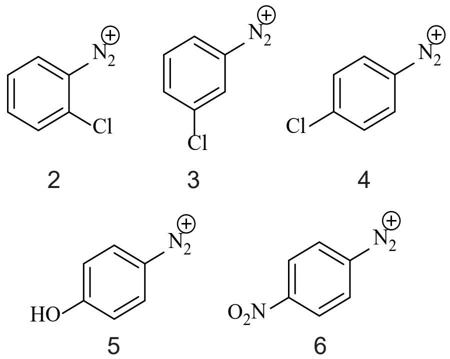

Figure 9. Some of the aniline derivatives that were stabilized with dodecaborates.

First, compounds 2,4 and 5 were stabilized with dodecahydro-*closo*-dodecaborate (the salts forms numbered as 2a,4a and 5a) with the same procedure which aniline was subjected. Then, these compounds and also compound 1a were subjected into a stability test. The tests were applied with the help of IR spectroscopy. These compounds were characterized immediately after they were synthesized. Then, for 4 weeks, they were characterized after each week ended. The results showed that dodecahydro-*closo*-dodecaborate was a good stabilizer since all the IR spectra showed the same result (Figure 10). Apart from these compounds, compound 6 was also tried to be stabilized with the same procedure with dodecahydro-*closo*-dodecaborate (6a). The compound 6a was immediately characterized with IR spectroscopy (Figure 10) but when it was fully dried under vacuum and tried to be transferred into a vial, it exploded.

After obtaining meaningful results from 4-week stability tests with dodecahydro-*closo*-dodecaborate, it was decided to stabilize *o*-chlorobenzenediazonium (2), *m*-chlorobenzenediazonium (3) and *p*-chlorobenzenediazonium (4) cations with dodecachloro-*closo*-dodecaborate (2b, 3b and 4b). Same procedure was applied for stabilization process and characterizations of these salts were performed with IR spectroscopy. In IR spectra of these compounds (Figure 12), there were peaks for both diazonium salt ca. 2200 cm^{-1} and diazo compound ca. 1500 cm^{-1} as observed in IR spectrum of 1b.

Next, these three cations were also tried to be stabilized with mono-carba-*closo*-dodecaborate (2c, 3c and 4c). Same procedure was applied for stabilization process. The resulting compounds were characterized with IR spectroscopy. IR spectra of these compounds (Figure 13) show peaks for diazonium salt *ca*. 2200 cm^{-1} and diazo compound *ca*. 1500 cm^{-1} as observed in the IR spectrum of 1c.

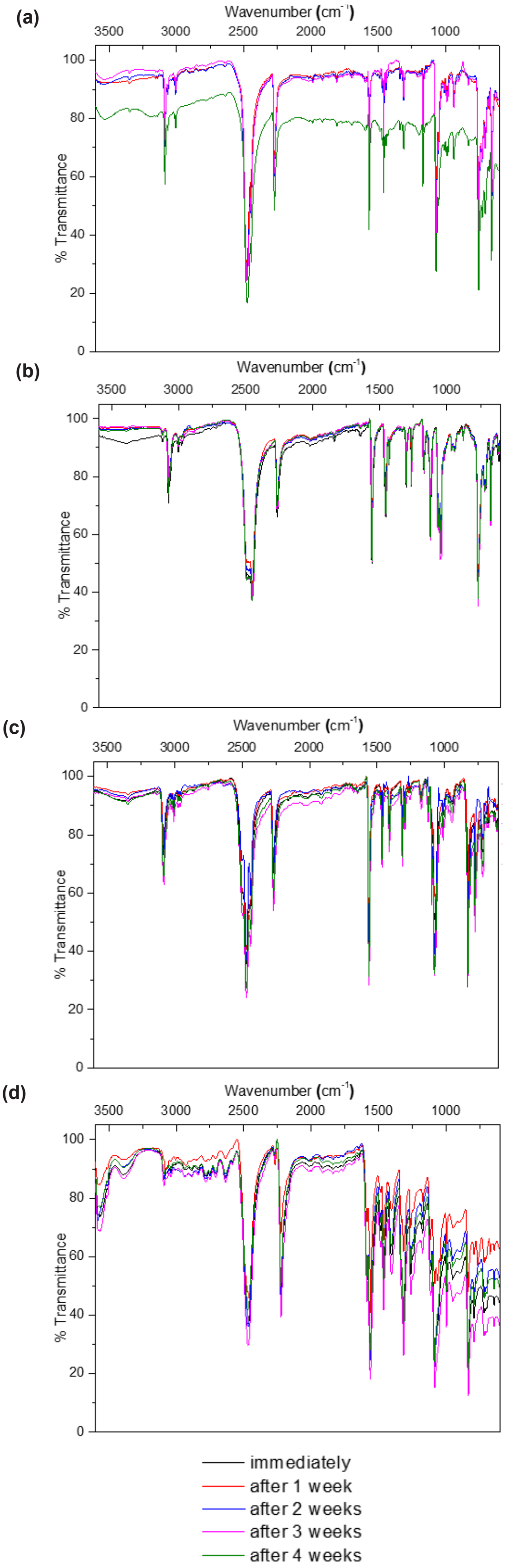

Figure 10. Stability test results of a). benzenediazonium cation, b). *o*-chlorobenzenediazonium salt, c). *p*-chlorobenzenediazonium cation and d). *p*-hydroxybenzenediazonium cation with dodecahydro-*closo*-dodecaborate

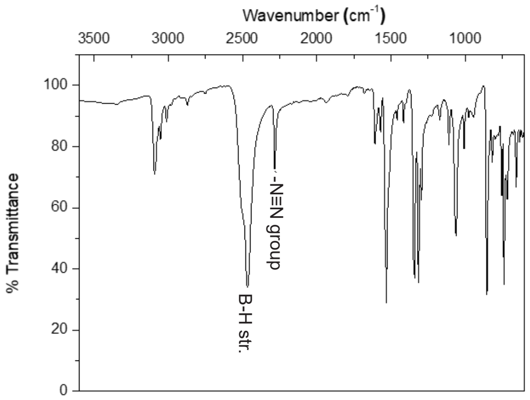

Figure 11. IR spectrum of *p*-nitrobenzenediazonium salt of dodecahydro-*closo*-dodecaborate.

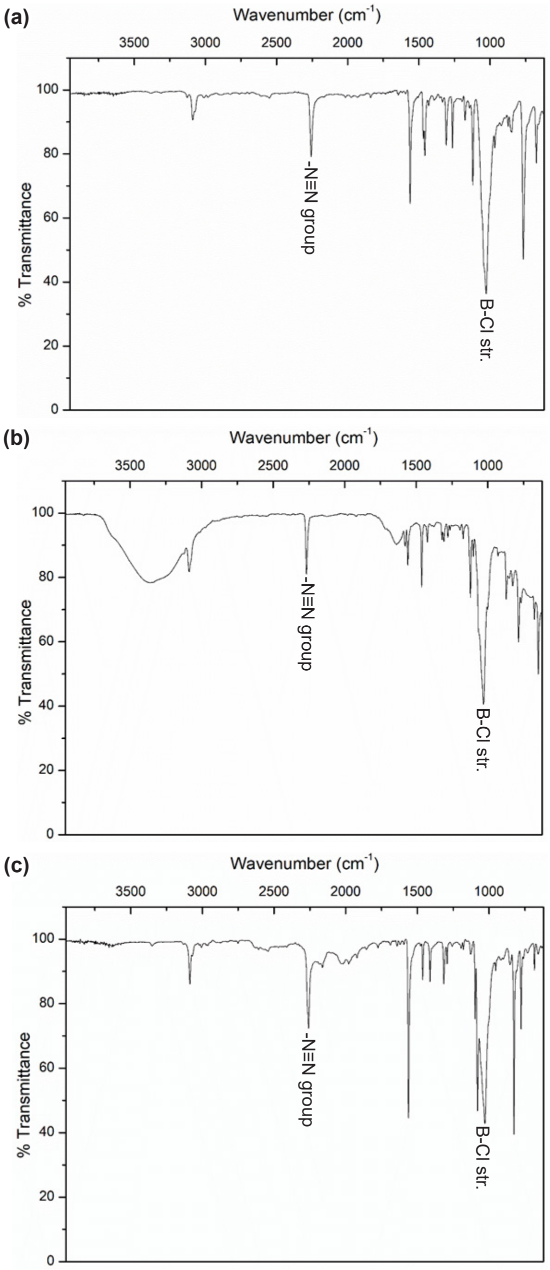

Figure 12. IR spectra of a). *o*-chlorobenzenediazonium cation, b). *m*-chlorobenzenediazonium cation and c). *p*-chlorobenzenediazonium cation stabilized with dodecachloro-*closo*-dodecaborate.

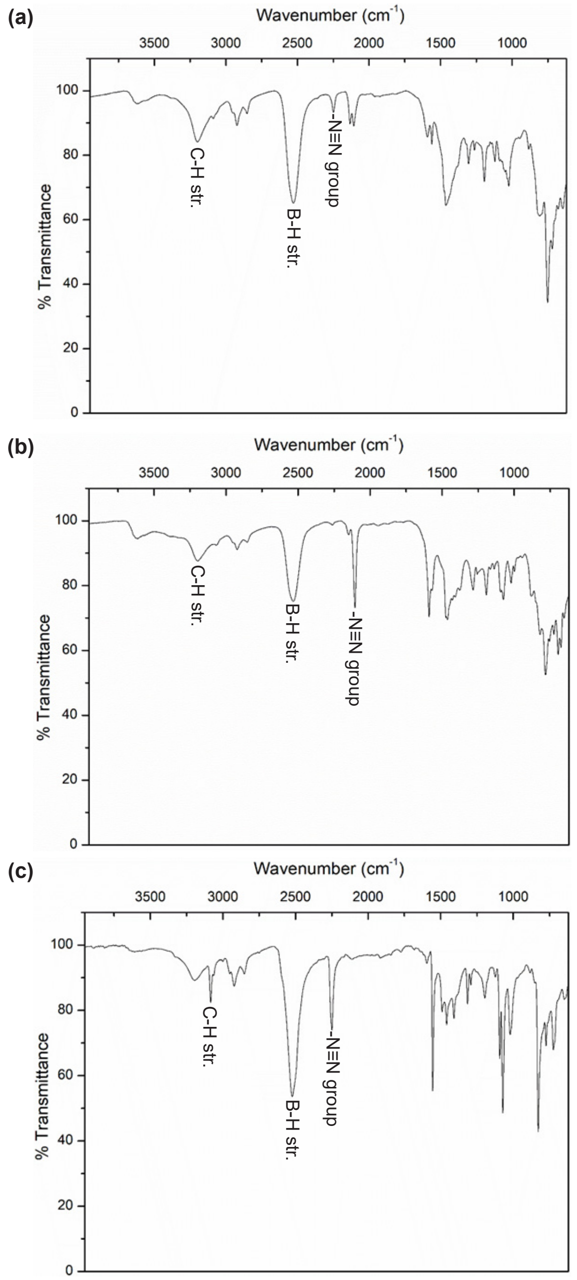

Figure 13. IR spectra of a). *o*-chlorobenzenediazonium cation, b). *m*-chlorobenzenediazonium cation and c). *p*-chlorobenzenediazonium cation stabilized with mono-carba-*closo*-dodecaborate.

4. Conclusions

In this study, dodecaborate and carborate anions are synthesized successfully in our laboratories. These anions were known to be weakly coordinating anions. With this in mind, we employed these anions to stabilize and capture aryldiazonium cations. The aryldiazonium borate salts were found to be stable for months under ambient conditions as judged by IR spectroscopy.

5. Acknowledgements

We would like to thank Fatma Nur Aydemir for initial studies. Also, Oğuzhan Albayrak and Sevban Doğan are acknowledged for helpful discussions. Turkish Energy Nuclear Mineral Research Agency (TENMAK) Boron Research Institute (BOREN) is acknowledged for partially funding this study (Project Number 2018-30-06-30-004).

Competing interests

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

Authors' contributions

A.A. conceived the idea. O.U. performed the experiments. O.U. and A.A. analyzed the results. O.U. and A.A. wrote and edited the manuscript together.

References

[1]. Griefs, P. (1858). Vorläufige notiz über die einwirkung von salpetriger säure auf amidinitro- und aminitrophenylsäure. *Justus Liebigs Annalen der Chemie*, *106*, 123-125. https://doi.org/10.1002/jlac.18581060114.

[2]. de Souza Ferreira, I. L., de Medeiros, J. I., Steffens, F., & Oliveira, F. R. (2020). Seawater as an alternative to dye cotton fiber with reactive dyes. *Textile Research Journal*, *91*(9-10), 1184-1193. https://doi.org/10.1177/0040517520972482.

[3]. Hanor, A. (1942). Dyes and dyeing. *Journal of Chemical Education*, *19*(10), 460. https://doi.org/10.1021/ed019p460.

[4]. Mahmoud, W. H., Omar, M. M., & Sayed, F. N. (2016). Synthesis, spectral characterization, thermal, anticancer and antimicrobial studies of bidentate azo dye metal complexes. *Journal of Thermal Analysis and Calorimetry*, *124* (2), 1071-1089. https://doi.org/10.1007/s10973-015-5172-1.

[5]. Sharma, R., Rawal, R. K., Gaba, T., Singla, N., Malhotra, M., Matharoo, S., & Bhardwaj, T. R. (2013). Design, synthesis and ex vivo evaluation of colon-specific azo based prodrugs of anticancer agents. *Bioorganic & Medicinal Chemistry Letters*, *23*(19), 5332-5338. https://doi.org/10.1016/j.bmcl.2013.07.059.

[6]. Ahmad, K., Naseem, H. A., Parveen, S., Shah, H.-R., Shah, S. S. A., Shaheen, S., … & Ashfaq, M. (2019). Synthesis and spectroscopic characterization of medicinal azo derivatives and metal complexes of Indandion. *Journal of Molecular Structure*, *1198*, 126885. https://doi.org/10.1016/j.molstruc.2019.126885.

[7]. Mutlu, H., Geiselhart, C. M., & Barner-Kowollik, C. (2018). Untapped potential for debonding on demand: the wonderful world of azo-compounds. *Materials Horizons*, *5*(2), 162-183. https://doi.org/10.1039/C7MH00920H.

[8]. Li, X., Wu, Y., Gu, D., & Gan, F. (2010). Spectral, thermal and optical properties of metal(II)-azo complexes for optical recording media. *Dyes and Pigments*, *86*(2), 182-189. https://doi.org/10.1016/j.dyepig.2010.01.002.

[9]. Arab, P., Rabbani, M. G., Sekizkardes, A. K., İslamoğlu, T., & El-Kaderi, H. M. (2014). Copper(I)-catalyzed

synthesis of nanoporous azo-linked polymers: Impact of textural properties on gas storage and selective carbon dioxide capture. *Chemistry of Materials*, *26*(3), 1385-1392. https://doi.org/10.1021/cm403161e

[10]. Hodgson, H. H. (1947). The sandmeyer reaction. *Chemical Reviews*, *40*(2), 251-277. https://doi.org/10.1021/cr60126a003.

[11]. Balz, G., & Schiemann, G. (1927). Über aromatische fluorverbindungen, I.: Ein neues verfahren zu ihrer darstellung. *Berichte der Deutschen Chemischen Gesellschaft (A and B Series)*, *60*(5), 1186-1190. https://doi.org/10.1002/cber.19270600539.

[12]. Pschorr, R. (1896). Neue synthese des phenanthrens und seiner derivate. *Berichte der Deutschen Chemischen Gesellschaft*, *29*(1), 496-501. https://doi.org/10.1002/cber.18960290198.

[13]. Meerwein, H., Büchner, E., & van Emster, K. (1939). Über die einwirkung aromatischer diazoverbindungen auf α,β-ungesättigte carbonylverbindungen. *Journal für Praktische Chemie*, *152*(7-10), 237-266. https://doi.org/10.1002/prac.19391520705.

[14]. Gomberg, M., & Bachmann, W. E. (1924). The synthesis of biaryl compounds by means of the diazo reaction. *Journal of the American Chemical Society*, *46*(10), 2339-2343. https://doi.org/10.1021/ja01675a026.

[15]. Roglans, A., Pla-Quintana, A., & Moreno-Mañas, M. (2006). Diazonium salts as substrates in palladium-catalyzed cross-coupling reactions. *Chemical Reviews*, *106*(11), 4622-4643. https://doi.org/10.1021/cr0509861.

[16]. Mo, F., Dong, G., Zhang, Y., & Wang, J. (2013). Recent applications of arene diazonium salts in organic synthesis. *Organic & Biomolecular Chemistry*, *11*(10), 1582. https://doi.org/10.1039/C3OB27366K.

[17]. Oger, N., d'Halluin, M., Le Grognec, E., & Felpin, F. X. (2014). Using aryl diazonium salts in palladium-catalyzed reactions under safer conditions. *Organic Process Research & Development*, *18*(12), 1786-1801. https://doi.org/10.1021/op500299t.

[18]. Felpin, F. X., & Sengupta, S. (2019). Biaryl synthesis with arenediazonium salts: Cross-coupling, CH-arylation and annulation reactions. *Chemical Society Reviews*, *48*(4), 1150-1193. https://doi.org/10.1039/C8CS00453F.

[19]. Naseem, H. A., Aziz, T., Shah, H. R., Ahmad, K., Parveen, S., & Ashfaq, M. (2021). Rational synthesis and characterization of medicinal phenyl diazenyl-3-hydroxy-1h-inden-1-one azo derivatives and their metal complexes. *Journal of Molecular Structure*, *1227*, 129574. https://doi.org/10.1016/j.molstruc.2020.129574.

[20]. Oger, N., Le Grognec, E., & Felpin, F. X. (2015). Handling diazonium salts in flow for organic and material chemistry. *Organic Chemistry Frontiers*, *2*(5), 590-614. https://doi.org/10.1039/c5qo00037h.

[21]. Hu, T., Baxendale, I., & Baumann, M. (2016). Exploring flow procedures for diazonium formation. *Molecules*, *21*(7), 918. https://doi.org/10.3390/molecules21070918.

[22]. Firth, J. D., & Fairlamb, I. J. S. (2020). A need for caution in the preparation and application of synthetically versatile aryl diazonium tetrafluoroborate salts. *Organic Letters*, *22*(18), 7057-7059. https://doi.org/10.1021/acs.orglett.0c02685.

[23]. Filimonov, V. D., Trusova, M., Postnikov, P., Krasnokutskaya, E. A., Lee, Y. M., Hwang, H. Y., & Chi, K. W. (2008). Unusually stable, versatile, and pure arenediazonium tosylates: Their preparation, structures, and synthetic applicability. *Organic Letters*, *10*(18), 3961-3964. https://doi.org/10.1021/ol8013528.

[24]. Callonnec, F. L., Fouquet, E., & Felpin, F. X. (2021). Unprecedented substoichiometric use of hazardous aryl diazonium salts in the heck-matsuda reaction via a double catalytic. *Cycle Organic Letters*, *13*(10), 2646-2649. https://doi.org/10.1021/ol200752x.

[25]. Susperregui, N., Miqueu, K., Sotiropoulos, J. M., Le Callonnec, F., Fouquet, E., & Felpin, F. X. (2012). Sustainable heck–matsuda reaction with catalytic amounts of diazonium salts: An experimental and theoretical study. *Chemistry-A European Journal*, *18*(23), 7210-7218. https://doi.org/10.1002/chem.201200444.

[26]. Oger, N., Le Callonnec, F., Jacquemin, D., Fouquet, E., Le Grognec, E., & Felpin, F. X. (2014). Heck–matsuda arylation of olefins through a bicatalytic approach: Improved procedures and rationalization. *Advanced Synthesis & Catalysis*, *356*(5), 1065-1071. https://doi.org/10.1002/adsc.201301144.

[27]. Mihelac, M., Siljanovska, A., & Kosmrlj, J. (2021). A convenient approach to arenediazonium tosylates. *Dyes and Pigments*, *184*, 108726. https://doi.org/10.1016/j.dyepig.2020.108726.

[28]. Honraedt, A., Raux, M. A., Grognec, E. L., Jacquemin, D., & Felpin, F. X. (2014). Copper-catalyzed free-radical C-H arylation of pyrroles. *Chemical Communications*, *50*(40), 5236-5238. https://doi.org/10.1039/C3CC45240A.

[29]. Bonin, H., Fouquet, E., & Felpin, F. X. (2011). Aryl diazonium versus iodonium salts: Preparation, applications and mechanisms for the suzuki–miyaura cross-coupling reaction. *Advanced Synthesis & Catalysis*, *353*(17), 3063-3084. https://doi.org/10.1002/adsc.201100531.

[30]. Reed, C. A. (2009). H+, CH3+, and R3Si+ Carborane reagents: When triflates fail. *Accounts of Chemical Research*, *43*(1), 121-128. https://doi.org/10.1021/ar900159e.

[31]. Reed, C. A. (2000) Taming superacids: Stabilization of the fullerene cations HC60+ and C60·+. *Science*, *289*(5476), 101-104. https://doi.org/10.1126/science.289.5476.101.

[32]. Geis, V., Guttsche, K., Knapp, C., Scherer, H., & Uzun, R. (2009). Synthesis and characterization of synthetically useful salts of the weakly-coordinating dianion [B12Cl12]2-. *Dalton Transactions*, *2009*(15), 2687-2694. https://doi.org/10.1039/b821030f.

[33]. Knoth, W. H., Miller, H. C., Sauer, J. C., Balthis, J. H., Chia, Y. T., & Muetterties, E. L. (1964). Chemistry of boranes. IX. Halogenation of B10H10-2 and B12H12-2.

Inorganic Chemistry, *3*(2), 159-167. https://doi.org/10.1021/ic50012a002.

[34]. Gu, W., & Ozerov, O. V. (2011). Exhaustive chlorination of [B12H12]2- without chlorine gas and the use of [B12Cl12]2- as a supporting anion in catalytic hydrodefluorination of aliphatic C-F bonds. *Inorganic Chemistry*, *50*(7), 2726-2728. https://doi.org/10.1021/ic200024u.

[35]. Rempala, P., & Michl, J. (2003). A proposed mechanism of [closo-CB11H12]- formation by dichlorocarbene insertion into [nido-B11H14]-. A computational study by density functional theory. *Collection of Czechoslovak Chemical Communications*, *68*(3), 644-662. https://doi.org/10.1135/cccc20030644.

[36]. Mueller, L.O. (2008). *Weakly coordinating anions and lewis superacidity* [Doctoral dissertation, Albert Ludwig University of Freiburg]. Retrieved from https://d-nb.info/988804875/34.

[37]. Pecyna, J., Rončević, I., & Michl, J. (2019). Insertion of carbenes into deprotonated nido-undecaborane, B11H13(2-). *Molecules*, *24*(20), 3779. https://doi.org/10.3390/molecules24203779.

[38]. Douvris, C., & Michl, J. (2013). Update 1 of: Chemistry of the carba-closo-dodecaborate(-) Anion, CB11H12-. *Chemical Reviews*, *113*(10), PR179-PR233. https://doi.org/10.1021/cr400059k.