Lithiacarboranes and 1,2,4-triazine 4-oxides: S_N^H reactions and ring transformations

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The reactions of 1-lithia-1,2- or 1,7-dicarba-*closo*-dodecaborane with 1,2,4-triazine 4-oxides can follow two competitive pathways: deoxygenative nucleophilic substitution of hydrogen to form 1-(1,2,4-triazin-5-yl)-1,2- or 1,7-dicarba-*closo*-dodecaboranes and the transformation of the 1,2,4-triazine ring into the triazoline ring giving rise to 1-(2-acetyl-1-aroyl-3-aryl-1,2,4-triazolin-5-yl)-1,2-dicarba-*closo*-dodecaboranes. Introduction of the electron-withdrawing triazine ring into the carborane cage substantially facilitates deboronation to give 1-(1,2,4-triazin-5-yl)-1,2-1,7-dicarba-*nido*-undecaboranes.

Key words: nucleophilic substitution of hydrogen, ring transformation, 1,2,4-triazine, carborane, hetarylcarboranes.

The construction of new materials possessing unique physicochemical properties is a major endeavor in organic chemistry, which generates a need for new types of organic and organometallic compounds. In the present study, we attempted to combine two radically different and interesting classes of compounds, such as 1,2,4-triazines and carboranes. 1,2,4-Triazines are of interest[1] from the viewpoint of medical and analytical chemistry as well as efficient agents for extraction and separation of rare-earth metals.[2] Carboranes attract attention because of their unique physicochemical properties.[3] In medicine, compounds bearing the carborane cage serve as the basis for boron neutron capture therapy (BNCT) for cancer and proton emission tomography (PET).[4]

The available procedures for the preparation of hetarylcarboranes involve the nucleophilic substitution of halogen or cross-coupling of haloheteroarenes with C-metallacarboranes[5,6] and the addition of metallacarboranes to highly electrophilic heterocycles followed by dehydrogenation of intermediates.[7]

The aim of the present study was to use the nucleophilic substitution of hydrogen in the series of 1,2,4-triazine 4-oxides[8] as a new approach to the synthesis of heteroarylcarboranes.

Results and Discussion

It was found that 1,2,4-triazine 4-oxides **1a—c** readily react with 1-lithia-2-phenyl-*ortho*-carborane **2** and 1-lithia-*ortho*-carborane **3** in THF at low temperatures to form σ^H-adducts **A**, which can be isolated in the free form. For example, 1-(4-hydroxy-3,6-diphenyl-4,5-dihydro-1,2,4-triazin-3-yl)-2-phenyl-1,2-dicarba-*closo*-dodecaborane (**4**) was isolated and characterized upon treatment of the reaction mixture with water. However, σ^H-adducts are unstable and readily undergo aromatization with elimination of a water molecule to form the corresponding 1,2,4-triazinylcarboranes **5a—c** and **6** (Scheme 1). Aromatization occurs even more easily with the use of mild acylating agents, such as dimethylcarbamoyl chloride or acetic anhydride. In this case, σ^H-adducts were not isolated and the acylating agent was added directly to the reaction mixture. Triazinylcarboranes **5** were prepared in 20—40% yields. When performing the reaction with unsubstituted carborane **3**, no precautions[9] were taken to prevent the formation of dilithiacarborane and to ensure against the reaction at both carbon atoms. In spite of this fact, monotriazinylcarborane **6** was isolated from the reaction mixture as the only reaction product.

The structures of compounds **5** and **6** were established by ^1H, ^{13}C, and ^{11}B NMR spectroscopy and mass spectrometry and were confirmed by the independent synthesis using *ipso*-substitution[10] in 5-cyano-3,6-diphenyl-1,2,4-triazine (**7**) with 1-lithia-2-phenyl-*ortho*-carborane **2** resulting in the replacement of the cyano group. New carborane derivatives **5** and **6** are easily crystallizable, which made it possible to study the structures of new compounds **5a,b** by X-ray diffraction analysis (Fig. 1).

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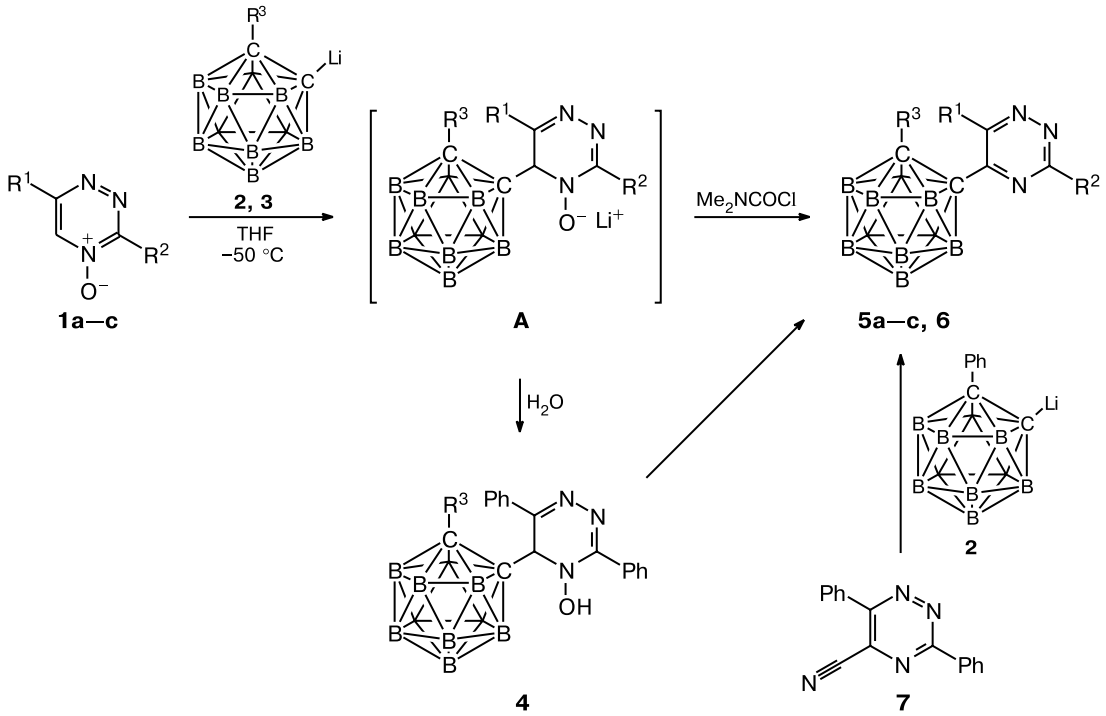
Scheme 1



$R^1 = R^2$ = Ph (**1a**, **5a**, **6**, **7**); $R^1 = R^2$ = *p*-Tol (**1b**, **5b**); R^1 = *p*-Tol, R^2 = Ph (**1c**, **5c**); R^3 = Ph (**2**, **5**), H (**3**, **6**)

It was demonstrated that the 1,2,4-triazine ring bound to the carborane icosahedron substantially changes the properties of the latter. When studying the ^{1}H NMR spectra of triazinylcarboranes **5** in DMSO-d_6, we found that these compounds were slowly transformed into new compounds, which proved to be deboronation products, *viz.*,

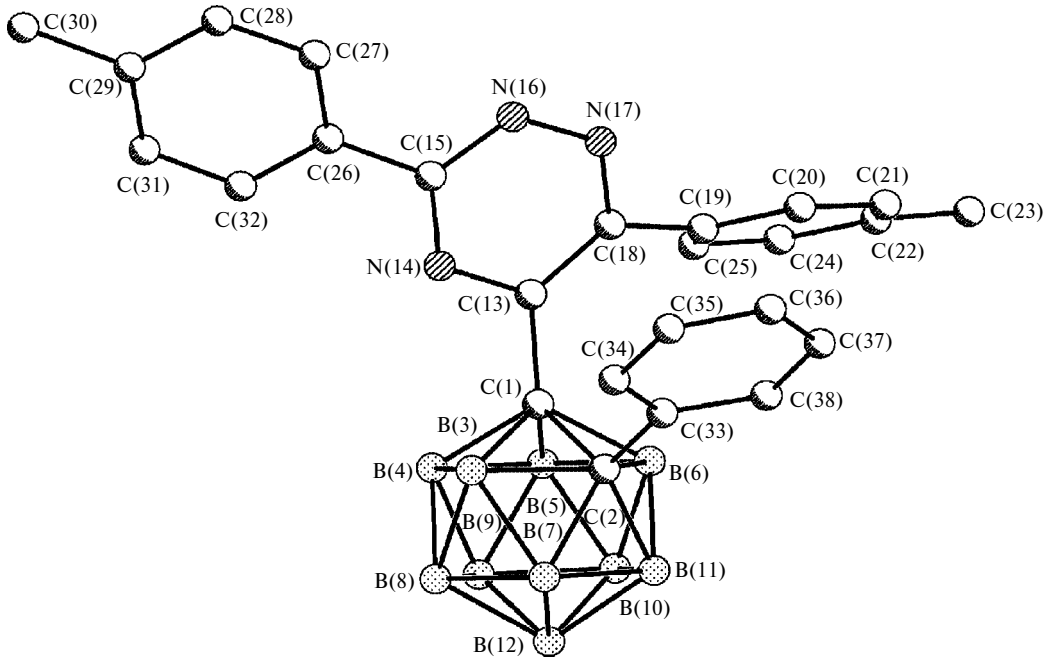
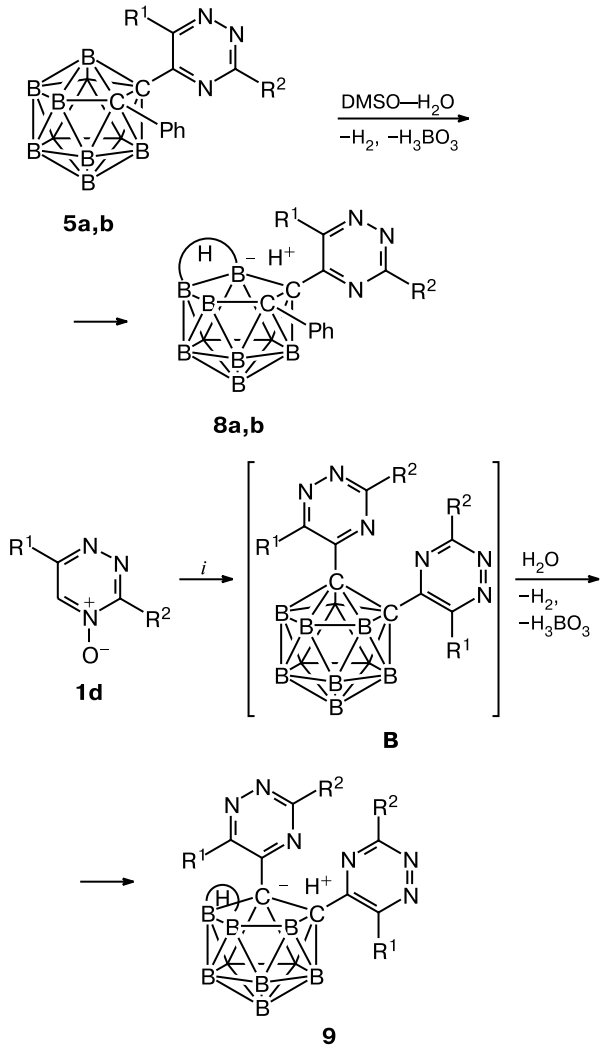


Fig. 1. Crystal structure of triazinyl-*ortho*-carborane **5b**. The H atoms are omitted. Selected bond lengths (Å): C(1)—C(13), 1.525(2); C(1)—C(2), 1.709(3); C(2)—C(33), 1.502(3).

Scheme 2



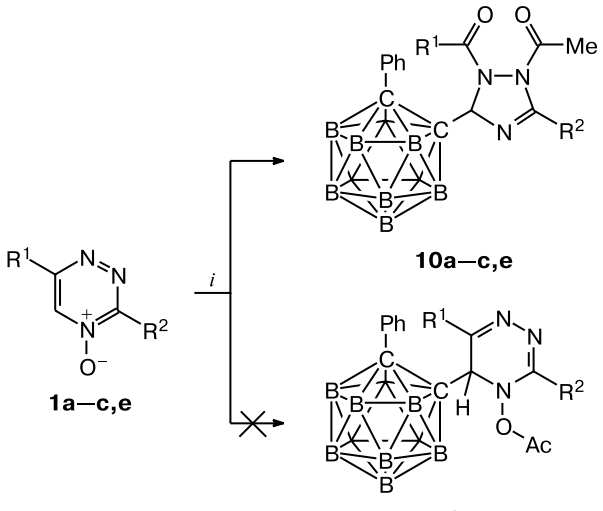
$R^1 = R^2$ = Ph (**a**); $R^1 = R^2$ = *p*-Tol (**b**);
R^1 = 4-Cl-C_6H_4, R^2 = Ph (**1d**, **9**)

Reagents and conditions: *i*. 1) *ortho*-Carborane (0.5 equiv.), Bu^{t}Li (1 equiv.), –50 °C; 2) **1d**; 3) Me_2NCOCl.

1-(1,2,4-triazin-5-yl)-2-phenyl-1,2-dicarba-*nido*-undecaboranes **8a,b** (Scheme 2). Deboronation of triazinylcarboranes **5** occurs very readily on heating in wet (less than 5% of water) DMSO even over a short period. The course of this process is conveniently monitored by ^{1}H NMR spectroscopy. The spectra show the characteristic high-field signal (δ –2.75) of the bridging hydrogen atom and the low-field signal (δ 10) of the "acidic" proton. The fact that deboronation occurred was confirmed by the fact that the ^{1}H NMR spectra show a signal of molecular hydrogen, which was eliminated in this reaction. The signal with the same chemical shift (δ 4.61) was observed in the ^{1}H NMR spectrum in DMSO-d_6 after bubbling of gaseous hydrogen through the reaction solution. It was found that deboronation in DMSO-d_6 containing 5% of water at room temperature was completed in less than one day. Heating of the reaction mixture or an increase in the concentration of water to 20% led to a sharp increase in the reaction rate. The fact that carboranes **5** readily undergo deboronation is attributable to the strong electron-withdrawing properties of the 1,2,4-triazine ring, which facilitates the nucleophilic attack on the boron atom adjacent to the carbon atom of the carborane fragment. An analogous effect of electron-withdrawing substituents on the ease of deboronation has been observed earlier for carbonyl-, alkoxycarbonyl-, and other substituted carboranes.[11] The introduction of two 1,2,4-triazine residues into *ortho*-carborane gives bis(1,2,4-triazinyl)carborane, which cannot virtually be isolated in the *closo* form. 1,2-Bis(1,2,4-triazin-3-yl)-1,2-dicarba-*closo*-dodecaborane **B**, which was formed in the reaction of 1,2,4-triazine 4-oxide **1d** with dilithia-*ortho*-carborane, was rapidly transformed into 1,2-bis[6-(4-chlorophenyl)-3-phenyl-1,2,4-triazin-3-yl]-1,2-dicarba-*nido*-undecaborane (**9**) in the course of isolation.

When studying the reactions of 1,2,4-triazine 4-oxides **1** with lithiacarboranes, we unexpectedly found that the reaction with the use of a more severe acylating agent, *viz*., acetyl chloride, did not afford the expected products of nucleophilic substitution of hydrogen (**5** and **6**). The IR spectra of the reaction products have stretching absorption bands of two (!) carbonyl groups, which cannot be explained in terms of the known concepts. Based on the results of X-ray diffraction analysis and spectroscopic data, we established the structure of one of the reaction

Scheme 3



$R^1 = R^2$ = Ph (**a**); $R^1 = R^2$ = *p*-Tol (**b**); R^1 = *p*-Tol, R^2 = Ph (**c**);
R^1 = Tol, R^2 = 2-furyl (**e**)

Reagents and conditions: *i*. 1) 1-Phenyl-*ortho*-carborane (2 equiv.), Bu^{t}Li (2 equiv.), –50 °C; 2) **1a—c,e**; 3) AcCl.

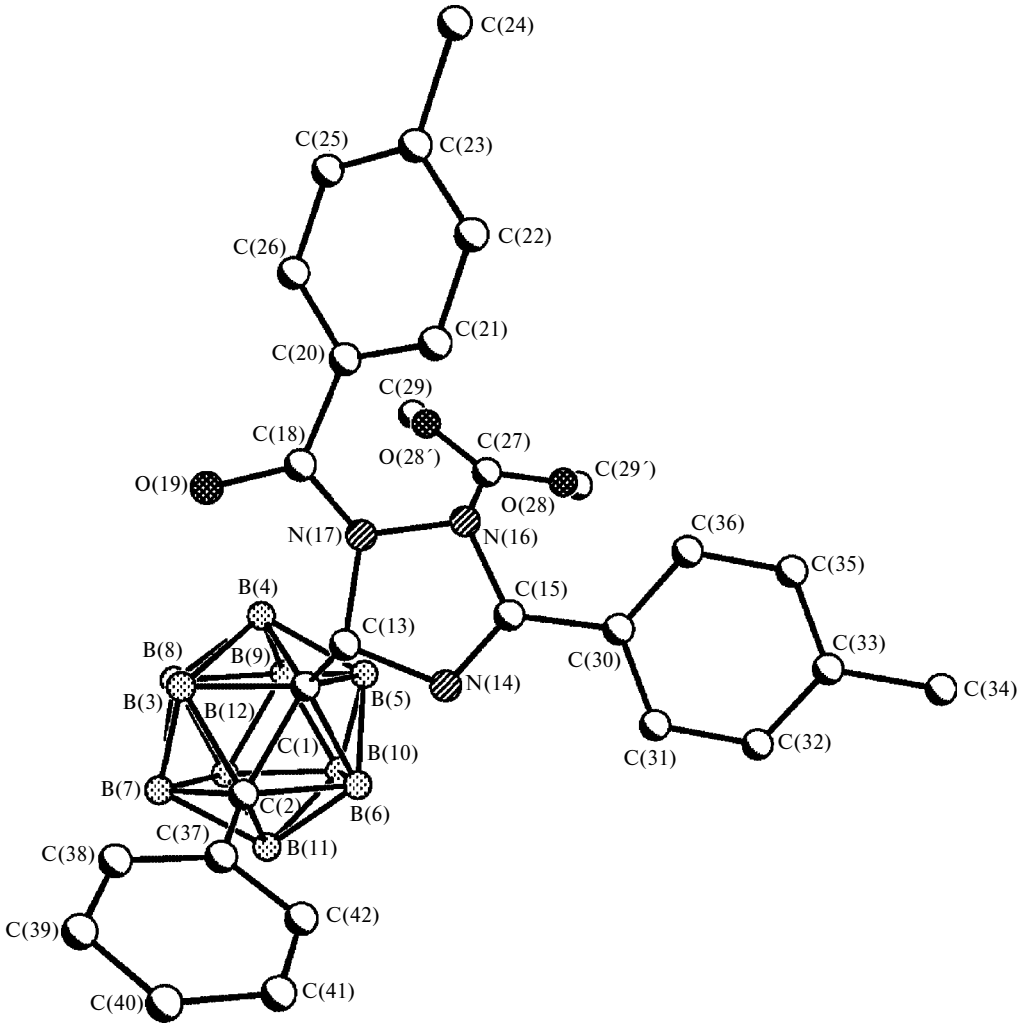


Fig. 2. Crystal structure of triazolinyl-*ortho*-carborane **10b**. The H atoms are omitted. Selected bond lengths (Å): C(1)—C(13), 1.554(3); C(1)—C(2), 1.695(3); C(2)—C(33), 1.515(3). The O(28) and C(29) atoms are disordered over two positions with equal occupancies.

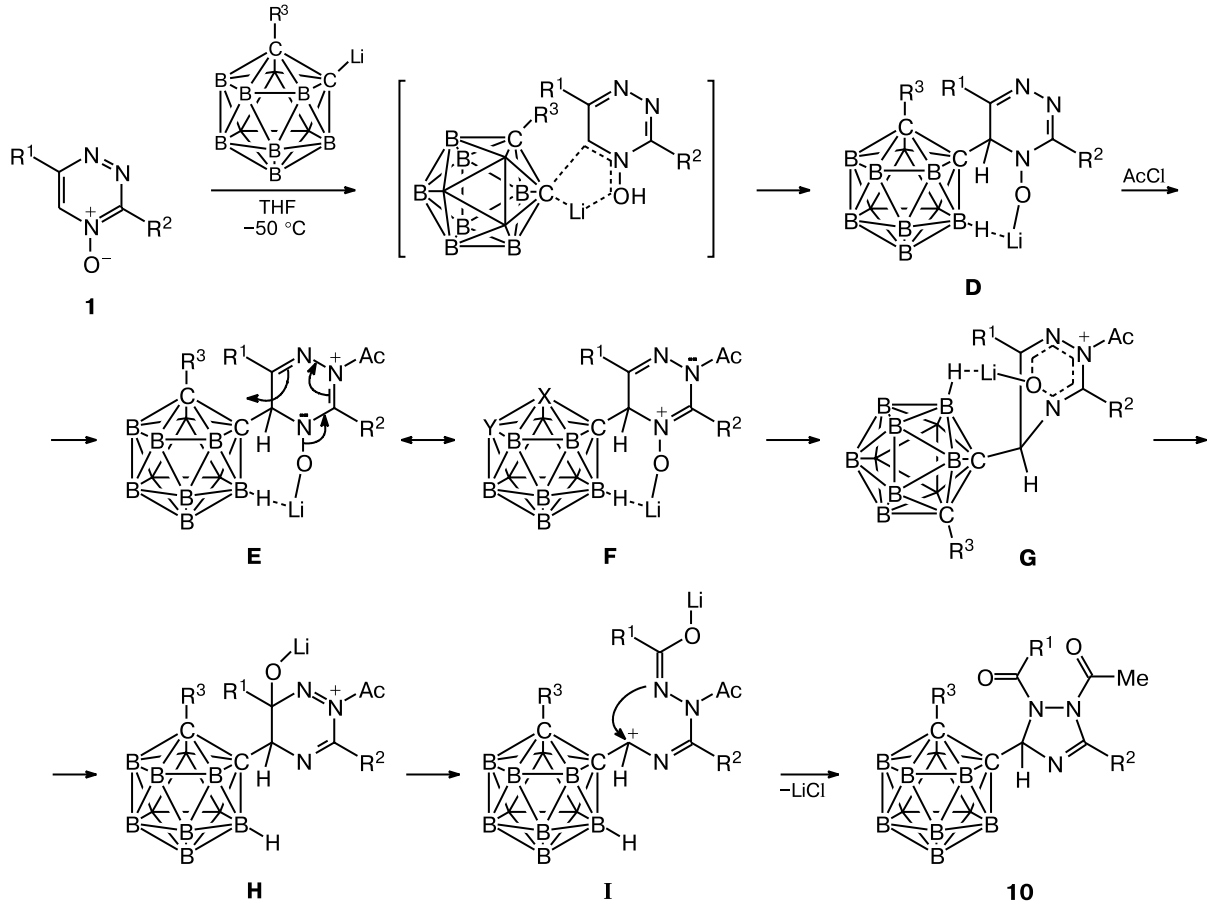
products as 1-(2-acetyl-1-toluoyl-3-tolyl-1,2,4-triazolin-5-yl)-2-phenyl-*ortho*-carborane (**10b**) (Fig. 2).

The following conditions are required for the reaction of 1,2,4-triazine 4-oxides **1a—c,e** with lithiacarborane **2** to proceed as the transformation into the triazoline ring giving rise to 1,2,4-triazolinylcarboranes **10a—c,e**: AcCl as the acylating agent and a 1.5—2-fold excess of lithiacarborane (Scheme 3).

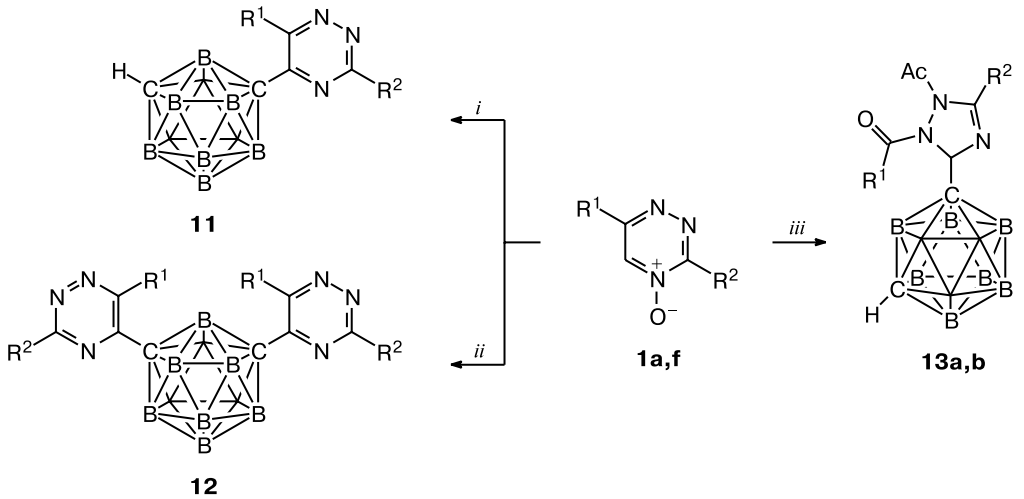
For example, the reactions with the use of equimolar amounts of the reagents and acetyl chloride (only the first condition was fulfilled) did not provide unambiguous results and yielded either products of nucleophilic substitution of hydrogen (**5**) or products of ring transformation (**10**) depending on the nature of substituents in the starting triazine oxide **1**. On the contrary, the reactions with the use of a twofold excess of lithiacarborane and dimethylcarbamoyl chloride (only the second condition was fulfilled) always gave triazinylcarborane **5**.

We propose the mechanism of this transformation (Scheme 4) taking into account that the latter occurs only in the reactions with lithiacarboranes (reactions with phenyllithium, phenylethynyllithium, or Grignard reagents[12] led only to the replacement of hydrogen). The structures of the reaction products are indicative of the transfer of the oxygen atom from the nitrogen atom at position 4 of the heterocycle to the carbon atom at position 6 accompanied by the cleavage of the C(5)—C(6) bond. The addition of lithiacarborane to 1,2,4-triazine 4-oxide **1** results in the formation of intermediate σ-adduct **D**, in which the Li atom is adjacent to the carborane cage and is involved in the Coulomb interaction with the electronegative hydrogen atoms of the B—H groups. Subsequent acylation of the intermediate **D** at the N(2) atom gives a cationic intermediate, which can be represented as two mesomeric structures **E** and **F**. The further **E** → **H** transformation can be considered as the

Scheme 4



Scheme 5



$R^1 = R^2$ = Ph (**1a**, **11**, **13a**); R^1 = *p*-Tol, R^2 = 4-Cl-C_6H_4 (**1f**, **12**, **13b**)

Reagents and conditions: *i*. 1) *meta*-Carborane, Bu^tLi (1 equiv.), −50 °C; 2) **1a**; 3) Ac_2O. *ii*. 1) *meta*-Carborane (0.5 equiv.), Bu^tLi (1 equiv.), −50 °C; 2) **1f**; 3) Me_2NCOCl. *iii*. 1) *meta*-Carborane (2 equiv.), Bu^tLi (2 equiv.), −50 °C; 2) **1a,f**; 3) AcCl.

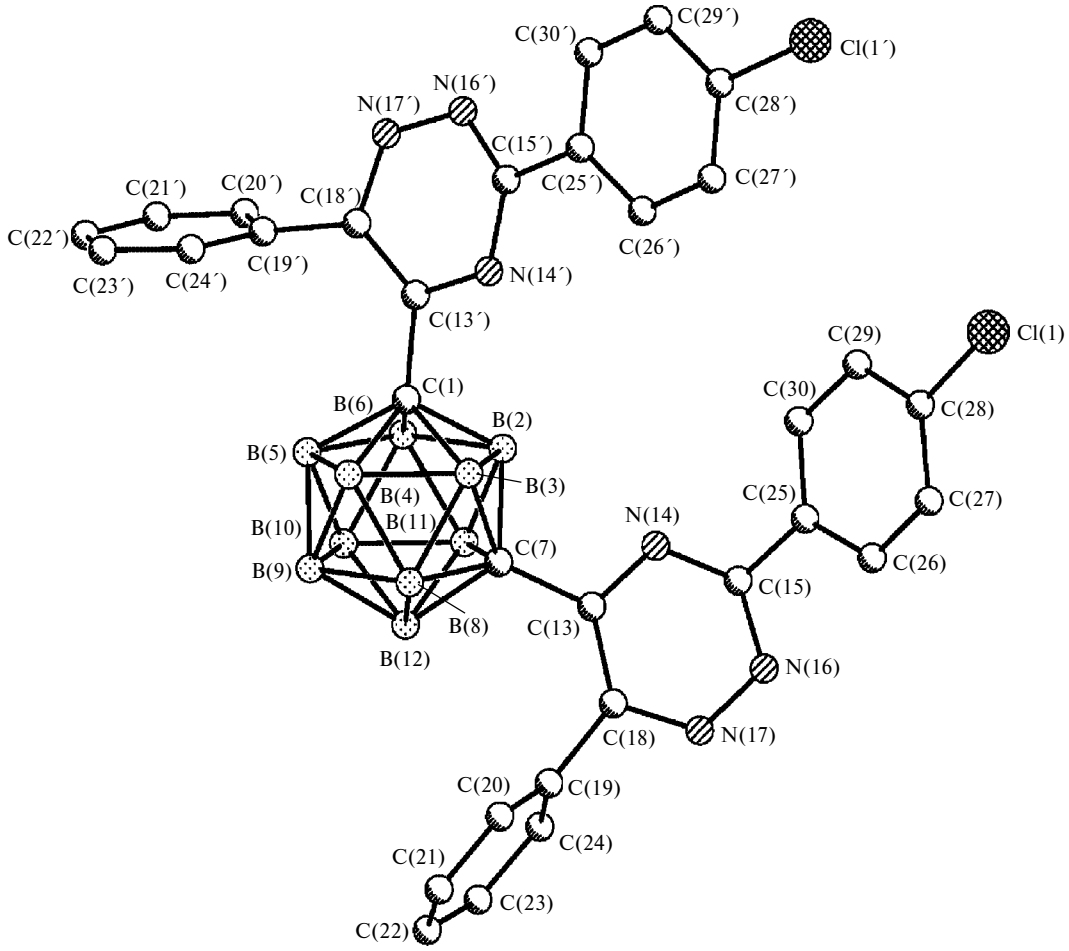


Fig. 3. Crystal structure of bistriazinyl-*meta*-carborane **12**. The H atoms are omitted. Selected bond lengths (Å): C(1)—C(13´), 1.520(3); C(1)—B(3), 1.713(3); C(7)—B(3), 1.719(3); C(7)—C(13), 1.520(3).

sigmatropic shift of OLi proceeding through transition state **G**. The subsequent cleavage of the C(5)—C(6) bond affords the open-chain intermediate **I**, and recyclization gives the final triazoline **10**.

The above-mentioned substitutions of hydrogen and transformations occur also in reactions with the use of the C-lithium derivative of unsubstituted *meta*-carborane as a nucleophile. For example, the reaction of 1,2,4-triazine 4-oxide **1a** with monolithiated *meta*-carborane (equivalent amounts of *meta*-carborane and Bu^{t}Li) followed by treatment of the reaction mixture with acetic anhydride gave 1-(3,6-diphenyl-1,2,4-triazin-3-yl)-1,7-dicarba-*closo*-dodecaborane (**11**). The reaction of a twofold excess of Bu^{t}Li with 1,2,4-triazine 4-oxide **1a** followed by treatment of the reaction mixture with dimethylcarbamoyl chloride afforded 1,7-bistriazinyl-*meta*-carborane **12**. The structure of the latter was studied by X-ray diffraction analysis (Fig. 3). It was established that the above-described transformation of the 1,2,4-triazine ring occurs also in the reactions with *meta*-carborane. Treatment of 1,2,4-triazine 4-oxides **1a,f** with an excess of monolithiated carborane and then with acetyl chloride yielded 1,2,4-triazolin-5-yl-*meta*-carboranes **13a,b** (Scheme 5).

Hence, the reaction pathway can be controlled by varying the conditions. As a result, one can prepare either the products of transformation of the triazine ring, which leads to the ring contraction and the formation of 1,2,4-triazolinylcarboranes, or the products of deoxygenative nucleophilic substitution of hydrogen. The latter pathway provides an approach to the synthesis of a broad spectrum of 1,2,4-triazinylcarboranes. It should be noted that analogous transformations accompanied by the cleavage of the C—C bond have not been described in the literature.

Experimental

The NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz) using DMSO-d_6 as the solvent and Me_4Si as the internal standard. The electron-impact ionization mass spectra were obtained on a Varian MAT-311A instrument. Commercially available carboranes were used as nucleophiles. The

Table 1. Crystallographic data and main details of structure refinement for compounds **5a,b**, **10b**, and **12**

Parameter	**5a**	**5b**	**10b**	**12**
Molecular formula	$C_{23}H_{25}B_{10}N_3$	$C_{25}H_{29}B_{10}N_3$	$C_{27}H_{33}B_{10}N_3O_2$	$C_{32}H_{28}B_{10}Cl_2N_6$
Molecular weight	451.55	479.55	539.69	675.64
Space group	$P4_3$	*Pbca*	*P*1	*P*1(bar)
a/Å	11.3890(6)	11.6446(8)	10.439(6)	8.665(4)
b/Å	—	13.2237	11.925(7)	35.230(3)
c/Å	18.7520(14)	35.230(3)	13.574(7)	16.947(7)
α/deg	90	90	82.664(15)	79.56(3)
β/deg	90	90	77.032(16)	77.11(4)
γ/deg	90	90	64.479(10)	75.39(3)
V/Å^3	2432.3(3)	5424.8(7)	1485.2(14)	1680.2(12)
Z	4	8	2	2
d_{calc}/g cm^{-3}	1.233	1.174	1.207	1.335
μ/cm^{-1}	0.67	0.63	0.070	2.29
Number of measured reflections, R_{int}	7043	5859	5780	5865
Number of reflections with $I > 2\sigma(I)$	6460	1729	4233	4341
Number of parameters in refinement	1.003	0.804	1.142	0.994
$R_1(I > 2\sigma(I))$	0.0464	0.0471	0.0654	0.0477
wR_2	0.1091	0.0865	0.1519	0.1162

starting 1,2,4-triazine 4-oxides **1** were prepared from isonitrosoacetophenone hydrazones according to known procedures.[13] 5-Cyano-3,6-diphenyl-1,2,4-triazine was synthesized by direct cyanation of 3,6-diphenyl-1,2,4-triazine 4-oxide.[14]

X-ray diffraction study. Crystals of compounds **5a,b** were prepared by crystallization from acetonitrile. The intensities of reflections were measured on a Smart 1000 CCD diffractometer at 110 K (**5a,b** and **10b**) and a Nonius CAD4 diffractometer at 298 K (**12**) (λ(MoKα) = 0.71072 Å, ω scanning technique for **5a,b** and **10b**; θ/2θ scanning technique for **12**, 2θ < 60°). The crystallographic data and selected parameters of structure refinement for compounds **5a,b**, **10b**, and **12** are given in Table 1.* The structures were solved by direct methods and refined by the least-squares method with anisotropic and isotropic thermal parameters for nonhydrogen and hydrogen atoms, respectively. All calculations were carried out using the SHELXTL PLUS 5.0 program package.

1-(4-Hydroxy-3,6-diphenyl-4,5-dihydro-1,2,4-triazin-5-yl)-2-phenyl-1,2-dicarba-*closo*-dodecaborane (4). A solution of lithium salt **2** in THF, which was prepared by the addition of a 1.6 *M* Bu^{t}Li solution in pentane (2.5 mL) to a solution of the corresponding carborane (4 mmol) in dry THF (20 mL), was added to a suspension of triazine oxide **1a** (4 mmol) in dry THF (10 mL) under argon at −50 °C. The reaction mixture was kept until the starting triazine oxide was dissolved (~15 min) and then concentrated at ~20 °C. The residue was treated with water. The resulting suspension was extracted with chloroform, the extract was concentrated, the residue was treated with acetonitrile, and the precipitate that formed was filtered off. The yield was 230 mg (11%), m.p. 201 °C. ^{1}H NMR, δ: 1.10—3.10 (m, 10 H, B—H); 4.82 (br.s, 1 H, H(5)); 7.00—8.10 (m, 15 H).

Synthesis of 1-(1,2,4-triazin-5-yl)-1,2- and 1,7-dicarba-*closo*-dodecaboranes-12 (5a—c, 6, 11) (general procedure). A solution of lithiacarborane in THF, which was prepared by the addition of a 1.6 *M* Bu^{t}Li solution in pentane (2.5 mL) to a solution of carborane (4 mmol) in dry THF (20 mL), was added to a suspension of the corresponding triazine oxide (4 mmol) in dry THF (10 mL) under argon at −50 °C. The reaction mixture was kept until the starting triazine oxide was dissolved (~15 min). After 20 min, carbamoyl chloride (4 mmol) was added to the reaction mixture at the same temperature. The reaction mixture was concentrated under reduced pressure, the residue was extracted with toluene, the extract was concentrated, the residue was treated with acetonitrile, and the precipitate that formed was filtered off.

1-(3,6-Diphenyl-1,2,4-triazin-5-yl)-2-phenyl-1,2-dicarba-*closo*-dodecaborane (5a). The yield was 670 mg (37%), m.p. 205 °C. Found (%): C, 61.03; H, 5.65; N, 9.22. $C_{23}H_{25}B_{10}N_3$. Calculated (%): C, 61.17; H, 5.58; N, 9.31 (M = 451.55). ^{1}H NMR, δ: 1.20—3.20 (m, 10 H, B—H); 7.21—7.68 (m, 13 H); 8.33 (m, 2 H). MS (EI, 70 eV), m/z (I_{rel} (%)): 452 [M]$^+$ (100).

1-[3,6-Di(4-methylphenyl)-1,2,4-triazin-5-yl]-2-phenyl-1,2-dicarba-*closo*-dodecaborane (5b). The yield was 750 mg (39%), m.p. 165 °C. Found (%): C, 62.55; H, 6.06; N, 9.00. $C_{25}H_{29}B_{10}N_3$. Calculated (%): C, 62.61; H, 6.09; N, 8.76 (M = 479.55). ^{1}H NMR, δ: 1.20—3.20 (m, 10 H, B—H); 2.43 and 2.46 (both s, 3 H each, Me); 7.18—7.46 (m, 11 H); 8.21 (m, 2 H).

* The crystallographic data were deposited with the Cambridge Structural Database (CCDC 205482—205484; www.ccdc.cam.ac.uk/conts/retrieving.html; the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

1-[6-(4-Methylphenyl)-3-phenyl-1,2,4-triazin-5-yl]-2-phenyl-1,2-dicarba-*closo*-dodecaborane (5c). The yield was 300 mg (21%), m.p. 155 °C. Found (%): C, 62.01; H, 5.93; N, 9.00. $C_{24}H_{27}B_{10}N_3$. Calculated (%): C, 61.91; H, 5.84; N, 9.02 (M = 465.61). ^{1}H NMR, δ: 1.20—3.20 (m, 10 H, B—H); 2.46 (s, 3 H, Me); 7.21—7.68 (m, 12 H); 8.33 (m, 2 H).

1-(3,6-Diphenyl-1,2,4-triazin-5-yl)-1,2-dicarba-*closo*-dodecaborane (6). The yield was 600 mg (40%), m.p. 220 °C. Found (%): C, 54.59; H, 5.64; N, 10.75. $C_{17}H_{21}B_{10}N_3$. Calculated (%): C, 54.38; H, 5.64; N, 11.19 (M = 375.49). ^{1}H NMR, δ: 1.00—3.00 (br.s, 10 H, B—H); 5.95 (br.s, 1 H, C—H); 7.56—7.76 (m, 8 H); 8.46 (m, 2 H).

1-(3,6-Diphenyl-1,2,4-triazin-5-yl)-1,7-dicarba-*closo*-dodecaborane (11). The yield was 300 mg (20%), m.p. 165 °C. Found (%): C, 54.30; H, 5.49; N, 10.95. $C_{17}H_{21}B_{10}N_3$. Calculated (%): C, 54.38; H, 5.64; N, 11.19 (M = 375.49). ^{1}H NMR, δ: 1.00—3.10 (br.m, 10 H, B—H); 4.19 (br.s, 1 H, C—H); 7.50—7.69 (m, 8 H); 8.48 (m, 2 H).

1,7-Bis[3-(4-chlorophenyl)-6-(4-methylphenyl)-1,2,4-triazin-5-yl]-1,7-dicarba-*closo*-dodecaborane (12) was prepared analogously to monotriazinylcarboranes **5** from triazine oxide **1f** (1.13 g, 4 mmol), *meta*-carborane (290 mg, 2 mmol), and a 1.6 *M* Bu^{t}Li solution in pentane (2.5 mL). The yield was 450 mg (16%), m.p. 227 °C. Found (%): C, 56.74; H, 4.27; N, 12.29. $C_{32}H_{28}B_{10}Cl_2N_6$. Calculated (%): C, 56.89; H, 4.18; N, 12.44 (M = 675.64). ^{1}H NMR, δ: 1.20—3.20 (m, 10 H, B—H); 2.43 and 2.46 (both s, 3 H each, Me); 7.18—7.46 (m, 11 H); 8.21 (m, 2 H).

Synthesis of 1-(2-acetyl-1-aroyl-1,2,4-triazolin-5-yl)-1,2- and 1,7-dicarba-*closo*-dodecaboranes (10a—c,e and 13a,b) (general procedure). A solution of lithiacarborane in THF, which was prepared by the addition of a 1.6 *M* Bu^{t}Li solution in pentane (5 mL) to a solution of the corresponding carborane (8 mmol) in dry THF (20 mL), was added to a suspension of triazine oxide (4 mmol) in dry THF (10 mL) under argon at −50 °C. The reaction mixture was kept until the starting triazine oxide was dissolved (~15 min). After 20 min, acetyl chloride (8 mmol) was added to the reaction mixture at the same temperature. Then the reaction mixture was concentrated and extracted with toluene. The extract was concentrated, the residue was treated with acetonitrile, and the precipitate that formed was filtered off.

1-(2-Acetyl-1-benzoyl-3-phenyl-1,2,4-triazolin-5-yl)-2-phenyl-1,2-dicarba-*closo*-dodecaborane (10a). The yield was 1.30 g (63%), m.p. 201 °C. Found (%): C, 58.60; H, 5.76; N, 8.35. $C_{25}H_{29}B_{10}N_3O_2$. Calculated (%): C, 58.69; H, 5.71; N, 8.21 (M = 511.64). ^{1}H NMR, δ: 1.85 (s, 3 H, Me); 1.50—3.10 (m, 10 H, B—H); 5.60 (s, 1 H, H(5)); 7.48—7.80 (m, 15 H).

1-[2-Acetyl-3-(4-methylphenyl)-1-(*p*-toluoyl)-1,2,4-triazolin-5-yl]-2-phenyl-1,2-dicarba-*closo*-dodecaborane (10b). The yield was 890 mg (41%), m.p. 210 °C. Found (%): C, 60.05; H, 6.06; N, 7.71. $C_{27}H_{33}B_{10}N_3$. Calculated (%): C, 60.09; H, 6.16; N, 7.79 (M = 539.69). ^{1}H NMR, δ: 1.86 and 2.39 (both s, 3 H each, Me); 1.50—3.10 (m, 10 H, B—H); 2.41 (s, 3 H, Me); 5.53 (s, 1 H, H(5)); 7.32—7.80 (m, 13 H).

1-[2-Acetyl-3-phenyl-1-(*p*-toluoyl)-1,2,4-triazolin-5-yl]-2-phenyl-1,2-dicarba-*closo*-dodecaborane (10c). The yield was 1.39 g (67%), m.p. 228 °C. Found (%): C, 59.21; H, 5.78; N, 8.02. $C_{26}H_{31}B_{10}N_3O_2$. Calculated (%): C, 59.41; H, 5.94; N, 7.99 (M = 525.67). ^{1}H NMR, δ: 1.86 (s, 3 H, Me); 1.50—3.10 (m, 10 H, B—H); 2.40 (s, 3 H, Me); 5.56 (s, 1 H, H(5)); 7.33—7.80 (m, 14 H).

1-[2-Acetyl-3-furyl-1-(*p*-toluoyl)-1,2,4-triazolin-5-yl]-2-phenyl-1,2-dicarba-*closo*-dodecaborane (10e). The yield was 410 mg (21%), m.p. 193 °C. Found (%): C, 55.79; H, 5.60; N, 8.14. $C_{24}H_{29}B_{10}N_3O_3$. Calculated (%): C, 55.91; H, 5.67; N, 8.15 (M = 515.63). ^{1}H NMR, δ: 1.82 and 2.38 (both s, 3 H each, Me); 1.50—3.10 (m, 10 H, B—H); 5.54 (s, 1 H, H(5)); 6.78 (m, 1 H); 7.28—7.77 (m, 10 H); 8.07 (m, 1 H).

1-(2-Acetyl-1-benzoyl-3-phenyl-1,2,4-triazolin-5-yl)-1,7-dicarba-*closo*-dodecaborane (13a). The yield was 800 mg (50%), m.p. 189 °C. Found (%): C, 52.63; H, 5.76; N, 9.45. $C_{19}H_{25}B_{10}N_3O_2$. Calculated (%): C, 52.40; H, 5.79; N, 9.65 (M = 435.54). ^{1}H NMR, δ: 1.50—3.10 (m, 10 H, B—H); 4.18 (br.s, 1 H, H(2)); 5.99 (s, 1 H, H(5)); 7.53—7.75 (m, 10 H).

1-[2-Acetyl-1-benzoyl-3-(4-chlorophenyl)-1,2,4-triazolin-5-yl]-1,7-dicarba-*closo*-dodecaborane (13b). The yield was 357 mg (19%), m.p. 191 °C. Found (%): C, 48.73; H, 5.36; N, 9.25. $C_{19}H_{24}B_{10}ClN_3O_2$. Calculated (%): C, 48.56; H, 5.15; N, 8.94 (M = 469.98). ^{1}H NMR, δ: 1.98 (s, 3 H, Me); 1.50—3.10 (m, 10 H, B—H); 4.18 (br.s, 1 H, H(2)); 5.98 (s, 1 H, H(5)); 7.56—7.75 (m, 9 H).

Deboronation of triazinylcarboranes 5 (general procedure). The corresponding 1,2,4-triazinylcarborane **5** (1 mmol) was dissolved in DMSO (5 mL). Then water (1 mL) was added to the reaction solution and the mixture was kept at ~20 °C for one day, after which water (10 mL) was added. The precipitate that formed was filtered off and recrystallized from acetonitrile.

1-(3,6-Diphenyl-1,2,4-triazin-5-yl)-2-phenyl-1,2-dicarba-*nido*-undecaborane (8a). The yield was 410 mg (90%), m.p. >250 °C (decomp.). Found (%): C, 62.49; H, 5.81; N, 9.69. $C_{23}H_{26}B_9N_3$. Calculated (%): C, 62.53; H, 5.93; N, 9.51 (M = 441.78). ^{1}H NMR, δ: −2.85 (br.s, 1 H); 1.20—3.20 (m, 9 H, B—H); 6.60—6.80 (m, 5 H, carborane Ph); 7.31—7.67 (m, 8 H); 8.33 (m, 2 H); 10.21 (br.s, 1 H). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 442 $[M]^+$ (100).

1-[3,6-Di(4-methylphenyl)-1,2,4-triazin-5-yl]-2-phenyl-1,2-dicarba-*nido*-undecaborane (8b). The yield was 415 mg (90%), m.p. >250 °C (decomp.). Found (%): C, 63.91; H, 6.44; N, 8.94. $C_{25}H_{30}B_9N_3$. Calculated (%): C, 63.73; H, 6.43; N, 8.81 (M = 469.84). ^{1}H NMR, δ: −2.85 (br.s, 1 H); 1.20—3.20 (m, 9 H, B—H); 6.65—6.89 (m, 5 H, Ph); 7.20—7.46 (m, 6 H); 8.39 (m, 2 H); 11.00 (br.s, 1 H).

1,2-Bis[6-(4-chlorophenyl)-3-phenyl-1,2,4-triazin-5-yl]-1,2-dicarba-*nido*-undecaborane (9). A solution of 1,2-dilithiacarborane in THF, which was prepared by the addition of a 1.6 *M* Bu^{t}Li solution in pentane (2.5 mL) to a solution of carborane (2 mmol, 290 mg) in dry THF (20 mL), was added to a suspension of the corresponding triazine oxide (4 mmol, 1.13 mg) in dry THF (10 mL) under argon at −50 °C. The reaction mixture was kept until the starting triazine oxide was dissolved (~15 min). After 20 min, carbamoyl chloride (4 mmol, 0.5 mL) was added to the reaction mixture at the same temperature. Then the reaction mixture was concentrated under reduced pressure, the residue was extracted with toluene, the extract was concentrated, the residue was treated with acetonitrile, and the precipitate that formed was filtered off. The yield was 330 mg (95%), m.p. >250 °C (decomp.). Found (%): C, 57.73; H, 4.39; N, 12.62. $C_{32}H_{29}B_9Cl_2N_6$. Calculated (%): C, 57.63; H, 4.33; N, 12.51 (M = 665.83). ^{1}H NMR, δ: −2.75

(br.s, 1 H); 1.20—3.20 (m, 9 H, B—H); 7.09—7.44 (m, 14 H); 8.07 (m, 4 H); 11.00 (br.s, 1 H).

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References

1. H. Neunhoeffer, *Compr. Heterocycl. Chem. II*, Eds. A. R. Katritzky, C. W. Rees, and E. F. V. Scriven, Pergamon Press, Oxford, 1996, **6**, 507.
2. Z. Kolarik, U. Mullich, and F. Gassner, *Solv. Extr. Ion Exch.*, 1999, **17**, 23.
3. J. Plesek, *Chem. Rev.*, 1992, **92**, 269.
4. J. F. Valiant, K. J. Guenther, A. S. King, P. Morel, P. Schafer, O. O. Sogbein, and K. A. Stephenson, *Coord. Chem. Rev.*, 2002, **232**, 173; A. H. Soloway, W. Tjarks, B. A. Barnum, F.-G. Rong, R. F. Barth, I. M. Codogni, and J. G. Wilson, *Chem. Rev.*, 1998, **98**, 1515.
5. D. Armspach, E. C. Constable, C. E. Housecroft, M. Neuburger, and M. Zehnder, *J. Organomet. Chem.*, 1998, **550**, 193.
6. W. Gill, P. Herbertson, J. MacBrig, and K. Wade, *J. Organomet. Chem.*, 1996, **507**, 249.
7. A. V. Kazantsev and L. E. Litovchenko, *Zh. Obshch. Khim.*, 1970, **41**, 1057 [*J. Gen. Chem. USSR*, 1970, **41** (Engl. Transl.)].
8. D. N. Kozhevnikov, V. L. Rusinov, and O. N. Chupakhin, *1,2,4-Triazine N-oxides*, in *Adv. Heterocycl. Chem.*, Ed. A. R. Katritzky, 2002, **82**, 261.
9. C. Viñas, R. Benakki, F. Teixidor, and J. Casabó, *Inorg. Chem.*, 1995, **34**, 3844.
10. S. Ohba, S. Konno, and H. Yamanaka, *Chem. Pharm. Bull.*, 1991, **39**, 486.
11. J. J. Schaeck and S. B. Kahl, *Inorg. Chem.*, 1999, **38**, 204.
12. A. M. Prokhorov, D. N. Kozhevnikov, V. L. Rusinov, and O. N. Chupakhin, *Polish J. Chem.*, 2003, **77**, 1157.
13. E. C. Taylor, K. L. Perlman, I. P. Sword, M. Sequin-Frey, and P. A. Jacobi, *J. Am. Chem. Soc.*, 1973, **95**, 6407.
14. S. Ohba, S. Konno, and H. Yamanaka, *Chem. Pharm. Bull.*, 1991, **39**, 486.

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