Acylation of $[B_{12}H_{12}]^{2-}$ dianion by carboxylic acid halides

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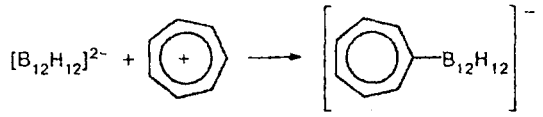
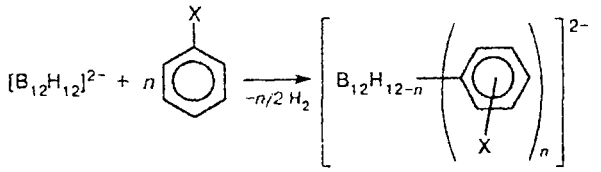
The sodium salt of $[B_{12}H_{12}]^{2-}$ dianion reacts with carboxylic acid halides to give a mixture of B-acylated product $[B_{12}H_{11}COR]^{2-}$ and an unstable intermediate, the latter undergoing hydrolysis to form $[B_{12}H_{11}OH]^{2-}$. The ratio of the products formed depends on the nature of the radical R. The reaction mechanism was studied by NMR spectroscopy. A number of novel $[B_{12}H_{11}COR]^{2-}$ compounds were synthesized; their structures were confirmed by NMR and IR spectral data.

Key words: dodecahydro-*closo*-dodecaborate, dianion, acylation by carboxylic acid halides; acylundecahydro-*closo*-dodecaborates, ^1H, ^{13}C, and ^{11}B NMR spectra.

At present, the possibility of using boron compounds in neutron capture therapy of cancer is being intensively studied. The most suitable compounds for these studies are those which contain a great number of B atoms, on one hand (for example, carboranes $C_2B_{10}H_{12}$ or dodecaborate$[B_{12}H_{12}]^{2-}$), and, on the other hand, are soluble in aqueous media. However, the pathways for the synthesis of $[B_{12}H_{12}]^{2-}$ derivatives containing B—C bond are rather complicated, and the known syntheses are limited to only several examples. One of them is the reaction with tropylium cation.[1]



Interaction of the boron cage with different halobenzenes, occurring with liberation of molecular oxygen, has also been performed.[2]



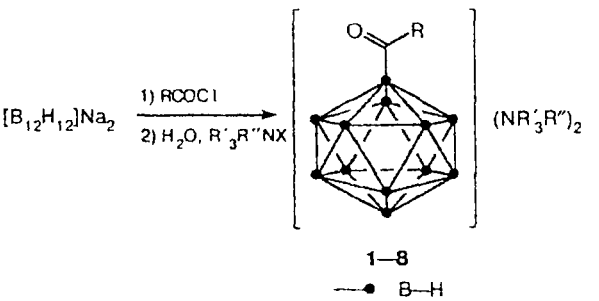
In this study, we synthesize boron cages containing B—C bond by direct B-acylation of $[B_{12}H_{12}]^{2-}$ using carboxylic acid halides.

Results and Discussion

Dodecaborate cages with COAr substituents were not reported earlier. Acylation of $[B_{10}H_{10}]^{2-}$ systems with $PhCOOSO_2R$ was carried out, but the structure of the compounds obtained was not strictly established.[3]

Acylation of $[B_{12}H_{12}]^{2-}$ does not occur under the same conditions; however, the sodium salt of $[B_{12}H_{12}]^{2-}$ in acetone readily reacts with chlorides of both aromatic and aliphatic carboxylic acids. Hydrolysis of the reaction mixture and the subsequent treatment with tetraalkylammonium salts gave acylated derivatives $[B_{12}H_{11}COR]^{2-}$ (Scheme 1, Table 1).

Scheme 1



1—8

—● B—H

1: R = R′ = R″ = Me
2: R = CH_2Ph, R′ = R″ = Me
3: R = CH_2CH_2Ph, R′ = R″ = Me
4: R = Ph, R′ = R″ = Me
5: R = α-naphthyl, R′ = R″ = Me
6: R = 4-$NO_2C_6H_4$, R′ = R″ = Me (**a**); R′ = Me, R″ = Ph (**b**)
7: R = 4-ClC_6H_4, R′ = R″ = Et
8: R = 4-BrC_6H_4, R′ = R″ = Et

Dianion $[B_{12}H_{11}OH]^{2-}$ is formed as a by-product. Separation of the reaction products is based on the fact that $[B_{12}H_{11}COR]^{2-}$ can be precipitated from its aque-

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Table 1. Yields of compounds $[B_{12}H_{11}COR]^{2-}$ (**1—8**) and conditions of their syntheses

R	Compound	T_{exp}/°C	Yield (%)	
			$[B_{12}H_{11}COR]^{2-}$	$[B_{12}H_{11}OH]^{2-}$
Me	**1**	20	10*	76
$PhCH_2$	**2**	20	24	75
$PhCH_2CH_2$	**3**	20	27	69
Ph	**4**	20	42	36
α-Naphthyl	**5**	20	29	44*
4-$NO_2C_6H_4$	**6a,b**	−20	17 (**6a**), 58 (**6b**)	Traces*
4-ClC_6H_4	**7**	20	52	25*
4-BrC_6H_4	**8**	20	59	17
4-$MeOC_6H_4$		20	Traces*	78

* Found from ^{11}B NMR spectrum of the reaction mixture.

ous solution by light tetraalkylammonium cations (Me_4N^+, Et_4N^+, *etc.*), and $[B_{12}H_{11}OH]^{2-}$ can be isolated only in the form of its tetrabutylammonium salt.

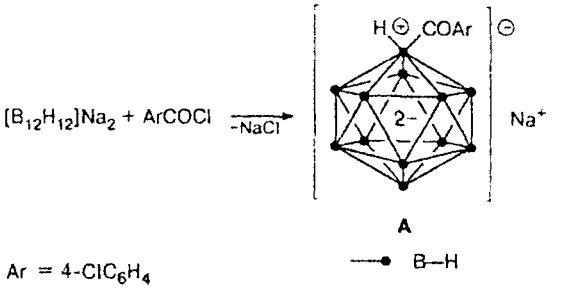
In the case of aromatic acid halides, the yields of acylation products increase when the aromatic ring contains electron-withdrawing substituents. In such cases, the rate of the process also increases; therefore, the reaction of $[B_{12}H_{12}]Na_2$ with 4-nitrobenzoyl chloride should be carried out at reduced temperatures to avoid the formation of by-products.

The fact that interaction of $[B_{12}H_{12}]Na_2$ with RCOCl is a two-step process was the starting point in studying its mechanism. In the initial step (in acetone), liberation of NaCl (1 mol-equiv. per 1 mol of $[B_{12}H_{12}]Na_2$) occurs in 100% yield. In the second step, when the reaction mixture is treated either with water or ethanol, $[B_{12}H_{11}OH]^{2-}$ is always formed as a by-product (at 20 °C) regardless of the agent used (water or ethanol).

The first step of the reaction was studied in an NMR tube using equimolar amounts of $[B_{12}H_{12}]Na_2$ and 4-chlorobenzoyl chloride in acetone-d_6; the ^{11}B and ^1H NMR, ^1H-{^{11}B}NMR, and ^{13}C NMR spectra were recorded every 15, 30, and 60 min, respectively. At 20 °C, the reaction in the NMR tube proceeds rather quickly. In 2.5 h after starting the experiment, there were no signals of $[B_{12}H_{12}]^{2-}$ (δ −13.9) in the ^{11}B NMR spectra and of *p*-ClC_6H_4COCl in the ^1H NMR spectra. The spectral data indicate that stable intermediate **A** is formed in the initial step of the reaction (Scheme 2).

The structure of the intermediate **A** was established by NMR spectroscopy. There are signals of aromatic AX-system at δ 7.91 and 7.38 in the ^1H NMR spectrum. The ^{13}C NMR spectrum contains the signals of the carbonyl group (δ 167.0) and the aromatic ring carbons at δ 137.0 (C_{ipso}), 132.7 (C_p), 131.7 (C_o), and 128.6 (C_m). These data are consistent with those obtained for $[B_{12}H_{11}COC_6H_4Cl]^{2-}$ (**7**). Hence it follows that the COAr substituent is present at the boron atom in molecule **A**. However, the ^{11}B NMR spectrum of the intermediate **A** differs from the spectrum of compound **7**. The signal of the substituted boron atom is shifted by

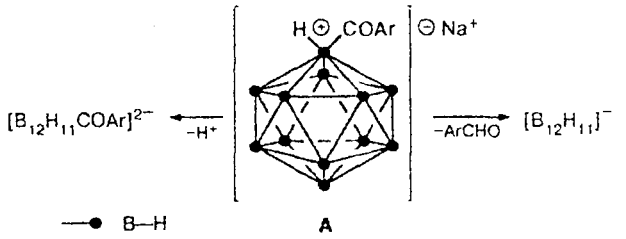
Scheme 2



2 ppm to lower field as compared to the similar signal in the spectrum of compound **7**, and in the ^{11}B-{^1H} NMR spectrum, this signal is observed as a doublet (J_{B-H} = 102.3 Hz). In addition, there are five signals at δ 2.22, 1.44, 1.38, 1.30, and 1.10 (in the ratio of 1 : 2 : 3 : 1 : 5) in the ^1H-{^{11}B} NMR decoupling spectrum of intermediate **A**, unlike the spectra of compounds **2—8** which consist of three signals in 5 : 5 : 1 ratio. The signal at δ 2.22 is shifted downfield as compared to the others and can be assigned to the proton in position 1.

Intermediate **A** is relatively stable and it starts to decompose only 4 h after the beginning of the NMR spectra recording. In this case, the signals assigned to compound **7** appear in the ^1H, ^{11}B, and ^{13}C NMR spectra. In addition, in the ^{13}C NMR spectra we observed the signals at δ 191.7, 140.9, 137.3, and 129.3, which coincide with the published data for 4-chlorobenzaldehyde.[5] Thus, decomposition of the intermediate **A** occurs by two pathways: by elimination of a proton leading to the acylation product or by elimination of the aldehyde resulting in the formation of $[B_{12}H_{11}]^-$ anion (Scheme 3).

Scheme 3



Scheme 3 makes clear the appearance of $[B_{12}H_{11}COR]^{2-}$, but it is necessary to explain the formation of $[B_{12}H_{11}OH]^{2-}$. If the reaction mixture is treated with water, $[B_{12}H_{11}OH]^{2-}$ is actually formed from $[B_{12}H_{11}]^-$. However, in some cases, (reactions with $PhCH_2CH_2COCl$ and α-$C_{10}H_7COCl$) the reaction mixture was treated with anhydrous methanol (and only then with water), but nevertheless the reaction product was $[B_{12}H_{11}OH]^{2-}$, not $[B_{12}H_{11}OMe]^{2-}$.

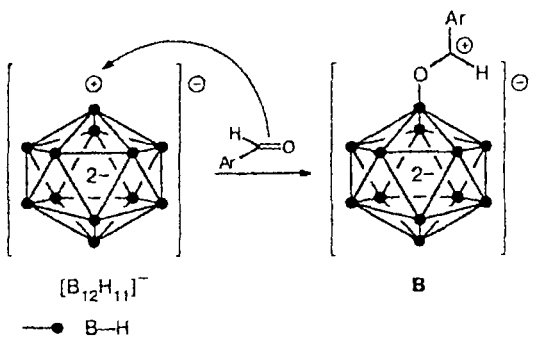
Note that the aldehyde detected in the reaction mixture at the initial steps of the reaction carried out in

an NMR tube disappeared in 3 h (according to NMR data), and in addition to intermediate **A**, there is another intermediate **B** in the reaction mixture in the ratio: **B** : 7 ≈ 4 : 5.

The signal at δ 6.7 in the ^{11}B NMR spectrum is assigned to the substituted boron atom of intermediate **B**. The fact that this signal is in low field indicates the strong electron-withdrawing character of the substituent at the boron atom. In the ^{1}H NMR spectrum, the signals of the AX-system at δ 8.22 and 7.72 are assigned to intermediate **B**. In the ^{13}C NMR spectrum, the signals of the aromatic ring of the intermediate **B** are observed at δ 133.5, 129.9, 137.3, and 143.2. This indicates that the aromatic ring is bonded to the carbocation center.[5] The signal at δ 202.9 can be assigned to C^+.

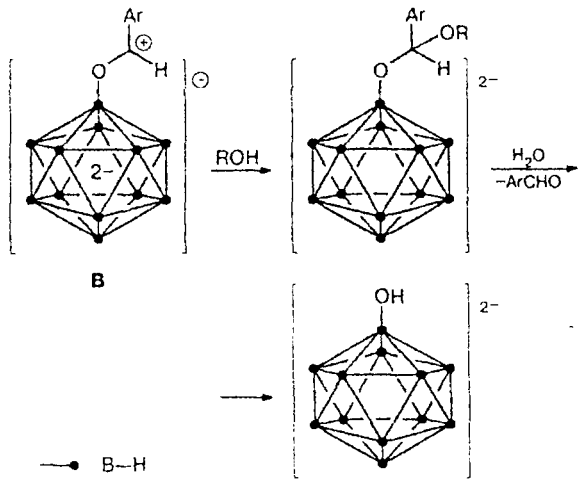
Hence it follows that the aldehyde that formed in the early steps of the reaction immediately reacts with anion $[B_{12}H_{11}]^-$ to give carbocation **B** (Scheme 4).

Scheme 4



Indeed, hydrolysis or alcoholysis of intermediate **B** always leads to $[B_{12}H_{11}OH]^{2-}$ (Scheme 5).

Scheme 5



One more evidence of the proposed mechanism may be liberation of pure *p*-methoxybenzaldehyde in the reaction of $Na_2[B_{12}H_{12}]$ with *p*-methoxybenzoyl chloride (in which $[B_{12}H_{11}OH]^{2-}$ is the major product).

The structure of the synthesized acylated derivatives of cage B_{12} was established using IR and NMR (^{11}B, ^{1}H, proton decoupled ^{1}H-{^{11}B}, and ^{13}C) spectra. Study of the ^{1}H and ^{13}C NMR spectra of compounds **4**—**8** (R = Ar) was primary interest to us. Since the aromaticity of the three-dimensional cage B_{12} has been established,[6] the electron structure of substituent ArCO in compounds of the $[B_{12}H_{11}COAr]^{2-}$ type should be similar to that in benzophenones PhCOAr, and therefore, the parameters of the ^{1}H and ^{13}C spectra for the substituent Ar should coincide.

As expected, there are the absorption bands of B—H and C=O groups in the IR spectra of compounds **2**—**8** (Table 2). The absorption of the carbonyl groups appears in the 1650—1690 cm^{-1} region. These values differ from those reported earlier for ArCOPh (1680—1700 cm^{-1}).[4] This means that in the case of "ketones" of both types ($[B_{12}H_{11}COAr]^{2-}$ and PhCOAr), the carbonyl groups are conjugated with the B_{12} and the aryl substituent, and the difference in the wave number values is most likely due to the $-I$-effect of the boron cage.

In the ^{11}B NMR spectra of compounds **2**—**8** (Table 3), there are four signals in 1 : 5 : 5 : 1 ratio,

Table 2. Parameters of IR spectra of compounds **2**—**8**

Compound	Medium	ν/cm^{-1}	
		C=O	B—H
2	Nujol	1662.3	2499
3	The same	1688.5	2487
4	The same	1688.8	2484
5	KBr	1676.7	2488
6b	KBr	1652.7	2477
7	Nujol	1674.9	2498
8	The same	1676.4	2479

Table 3. Parameters of ^{11}B NMR spectra (in CD_3CN) and coupling constants of compounds **2**—**8** and $[B_{12}H_{11}OH]^{2-}$

Compound	δ (J_{B-H}/Hz)			
	B(1)	B(2)—B(6)	B(7)—B(11)	B(12)
2	3.0	−15.4 (106.6)	−16.7 (104.2)	−21.1*
3	3.0	−15.6 (105.3)	17.0 (107.9)	−20.2*
4	3.2	−15.8 (118.5)	−17.0 (119.4)	−20.4 (120.3)
5	3.3	−15.6 (109.8)	−17.0 (109.2)	−20.2*
6b	2.7	−16.2*	−17.4*	−21.5*
7	3.1	−15.6 (102.7)	−17.2 (101.4)	−20.4*
8	3.0	−15.7 (109.2)	−17.1 (108.5)	−21.2*
$[B_{12}H_{11}OH]^{2-}$	5.1	−15.8 (116.5)	−18.0 (121.6)	−24.0 (126.1)

* The constant is not resolved.

Table 4. Chemical shifts of B—H protons in ^1H-{^{11}B} NMR spectra (in CD_3CN) of compounds **2—8** and $[B_{12}H_{11}OH]^{2-}$

Compound	δ		
	H(2)—H(6)	H(7)—H(11)	H(12)
2	1.44	0.97	0.76
3	1.45	0.96	0.77
4	1.45	0.95	0.77
5	1.45	0.96	0.78
6b	1.23	0.96	0.78
7	1.24	0.83	0.68
8	1.23	0.82	0.66
$[B_{12}H_{11}OH]^{2-}$	0.50	0.23	0.02

which indicate that monosubstitution in the cage occurs. In the ^{11}B-{H^1} coupled spectrum, the most low-field signal remains a singlet, which proves its assignment to the substituted boron atom.

It is interesting to note that the signals of the substituted boron atoms in the spectra of $[B_{12}H_{11}COAr]^{2-}$ (**2—8**) are shifted to higher field as compared to $[B_{12}H_{11}OR]^{2-}$ (R = H, COR),[7] and the signals of antipodal boron atoms are shifted downfield, although COR is the stronger electron-withdrawing substituent than OH^-. Obviously, this is explained by the conjugation that occurs between the boron cage and the aromatic ring *via* the carbonyl group.

Chemical shifts of B—H protons were obtained from the ^1H-{^{11}B} NMR spectra recorded with CH decoupling. In the spectra of compounds **2—8**, there are three signals with integral intensity ratio 5 : 5 : 1 (Table 4). These data additionally confirm that the monosubstitution products were isolated. We should note that the signals of protons of B—H of $[B_{12}H_{11}COAr]^{2-}$ are in the lower field as compared with those of $[B_{12}H_{11}OH]^{2-}$. This is explained, on the one hand, by the strong +*M*-effect of the OH group with respect to the polyhedron (cage) and, on the other hand, by the exclusive electron-withdrawing effect of COR group on the cage.

The signals from cations and protons of radicals R were detected in the ^1H NMR spectra of compounds **2—8**. The chemical shifts of the aromatic ring protons of anion $[B_{12}H_{11}COPh]^{2-}$ (**4**) and protons of its organic analog, benzophenone, are almost identical (Table 5). This proves directly that both compounds have very similar electron structures.

Table 5. Chemical shifts of aromatic ring protons in ^1H NMR spectra of $[B_{12}H_{11}COPh]^{2-}$ (**4**) and PhCOPh and their increments with respect to benzene ($\Delta = \delta_H - \delta_{PhH}$)

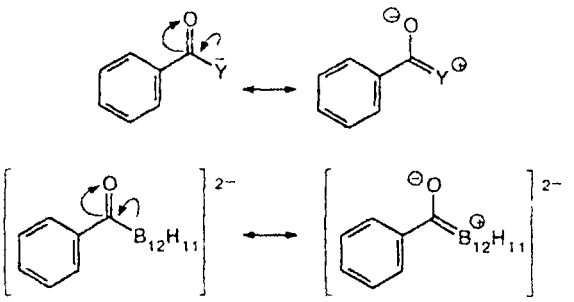
Compound	H_o		H_m		H_p	
	δ	Δ	δ	Δ	δ	Δ
$[B_{12}H_{11}COPh]^{2-}$	7.90	0.64	7.38	0.12	7.46	0.20
PhCOPh	7.78	0.47	7.39	0.18	7.48	0.22

In addition to the cation signals, there are signals of the carbons of the carbonyl group and radical R in the ^{13}C NMR spectra of compounds **2—8.**

Compound	**2**	**3**	**4**	**5**	**6a**	**7**	**8**
δ ^{13}C	174.1	174.2	166.8	168.6	169.0	165.8	165.5

The signals of the carbonyl carbons of compounds **2—8** are in the higher field as compared to those of benzophenone (for PhCOPh — δ 192.5).[5] This may be due to the electron-donor effect of the boron cage. Chemical shifts of the carbonyl groups are very close to the corresponding chemical shifts in the spectra of compounds of the ArCOY type (Y = OR, NR [5]), and the boron substituent may affect similarly the carbonyl group (Scheme 6).

Scheme 6

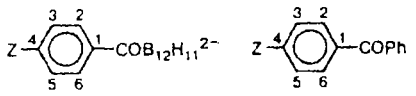


However, ^{13}C NMR chemical shifts of the signals of the aromatic ring carbons of compounds $[B_{12}H_{11}COAr]^{2-}$ **2—8** are almost equal to those of the corresponding carbons of benzophenone PhCOAr (Table 6). The most pronounced difference in chemical shift values between $[B_{12}H_{11}COAr]^{2-}$ and PhCOAr is observed in the case of carbons bonded to the carbonyl group (C_{ipso}), namely, the signal of C_{ipso} of $[B_{12}H_{11}COAr]^{2-}$ is always in the higher field as compared to the corresponding signal of PhCOAr. This may be due to the electronegative effect of the dodecaborate cage. The values of δ (^{13}C NMR) of C_o, C_m, and C_p are almost identical. These data show that substituents $[B_{12}H_{11}CO]^{2-}$ and PhCO affect very similarly the aromatic ring bonded to them.

Increments of chemical shifts presented in Table 6 were calculated using the formula $\Delta = \delta_C - \delta_{PhH}$. The values of the increments for the $[B_{12}H_{11}CO]^{2-}$ substituent were taken from the ^{13}C NMR spectrum of the aromatic ring of compound **4** $[B_{12}H_{11}COPh]^{2-}$ (C_{ipso}, +7.7; C_o, +1.6; C_m, +0.4; C_p, +3.5 ppm), and the corresponding values for substituted benzophenones were taken from the literature.[5] The calculated and measured values of chemical shifts match perfectly.

Analysis of the NMR spectra of $[B_{12}H_{11}COAr]^{2-}$ indicates the similarity of their parameters assigned to the COAr moiety to those of the corresponding benzophenones. This means that the conjugation observed

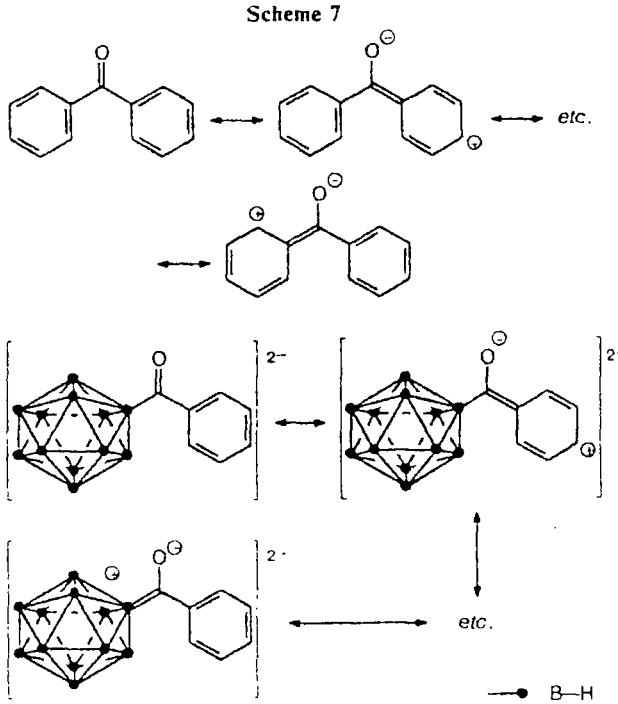
Table 6. Chemical shifts of aromatic carbon atoms in ^{13}C NMR spectra of compounds $[B_{12}H_{11}COAr]^{2-}$ compared to those in spectra of *p*-substituted benzophenones PhCOAr ($\Delta = \delta_C - \delta_{PhH}$)



Z	Atom	$\delta[B_{12}H_{11}COAr]^{2-}$		Δ		PhCOAr	
		found	calculated	found	calculated	δ	Δ
H	C(1)	136.2		7.7		137.8	9.3
	C(2), C(6)	130.1		1.6		130.1	1.6
	C(3), C(5)	128.9		0.4		128.1	−0.4
	C(4)	132.0		3.5		132.2	3.7
NO_2	C(1)	138.9	142.3	10.4	13.8	144.3	15.8
	C(2), C(6)	131.6	131.0	3.1	2.5	131.4	2.9
	C(3), C(5)	1214.2	124.0	−4.3	−4.5	125.0	−3.5
	C(4)	151.3	151.9	22.9	23.4	151.2	22.8
Cl	C(1)	134.0	134.3	5.5	5.8	135.7	6.2
	C(2), C(6)	131.4	131.5	2.9	3.0	131.5	3.0
	C(3), C(5)	128.6	129.3	0.1	0.8	128.5	0.0
	C(4)	137.7	138.3	8.8	9.8	136.1	9.7
Br	C(1)	135.2	135.1	6.7	6.6	No data	
	C(2), C(6)	131.9	131.7	3.4	3.2		
	C(3), C(5)	126.0	126.6	−2.5	−1.9		
	C(4)	137.6	137.8	9.1	9.3		

in benzophenones may also take place in the cages we synthesize; this fact suggests that their structures are of the same type as the Lewis structures for benzophenones (Scheme 7).

Scheme 7



Experimental

The reagents used were commercial samples (Bayer AG, Aldrich). Acetone was distilled over calcined K_2CO_3 immediately prior to use. Carboxylic acid chlorides were vacuum distilled over PCl_5. Methanol was distilled over magnesium. The ^1H, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer (at 200.13, 64.21, and 50.61 MHz, respectively). Me_4Si, $BF_3 \cdot Et_2O$, and D_2O were used as internal standards. IR spectra were recorded on a Nicolet-520-IR/FT instrument in Nujol or in KBr pellets. Melting points were measured in open capillary tubes.

Synthesis of tetraalkylammonium acylundecahydro-*closo*-dodecaborates (1—5, 7, 8) (general procedure). A carboxylic acid chloride (11 mmol) was added to a solution of $[B_{12}H_{12}]Na_2$ (1.9 g, 10 mmol) in acetone (50 mL) and the resulting mixture was stirred for 10 h. The precipitate (NaCl) that formed was filtered off, and the acetone was evaporated *in vacuo*. The pale-yellow residue was dissolved in water (50 mL), and R_4NBr (20 mmol) in water (10 mL) was added. The acylation product $[B_{12}H_{11}COR](NR'_4)_2$ precipitated as a pure compound, which was filtered off, washed with water (2×10 mL) and diethyl ether (2×10 mL), and dried *in vacuo*. The addition of Bu_4NBr (6.5 g, 20 mmol) to the mother liquor caused the precipitation of $[B_{12}H_{11}OH](NBu_4)_2$, which was filtered off and dried *in vacuo*.

In the case of compounds **3** and **5**, the precipitate (NaCl, 0.54 g, 4.8 mmol) was filtered off, and CsF (3.02 g, 20 mmol) in methanol (50 mL) was added to the resulting solution to cause the precipitation of a mixture of the acylation product and $[B_{12}H_{11}OH]^{2-}$ as cesium salts. The precipitate was filtered off, washed with methanol (2×10 mL), air-dried, and dissolved in water (50 mL); Me_4NBr (20 mmol) in 10 mL of water was added to the resulting solution to cause the precipitation of the acylation product as a pure compound, which was filtered off, washed with water (2×10 mL), and dried *in vacuo*.

Tetramethylammonium phenylacetylundecahydro-*closo*-dodecaborate (2). Yield 1.2 g (29%), m.p. 329 °C. Found (%): C, 46.83; H, 10.69; N, 6.89. $C_{16}H_{42}B_{12}N_2O$. Calculated (%): C, 47.07; H, 10.37; N, 6.86. ^1H NMR (CD_3CN), δ: 7.22—7.32 (m, 5 H, Ph); 3.50 (s, 2 H, CH_2); 3.06 (s, 24 H, Me—N); 3.60 to −0.25 (m, 11 H, BH).

Tetramethylammonium benzylacetylundecahydro-*closo*-dodecaborate (3). Yield 1.17 g (27%), m.p. 308—310 °C. Found (%): C, 47.51; H, 10.41; N, 6.54. $C_{17}H_{44}B_{12}N_2O$. Calculated (%): C, 48.35; H, 10.50; N, 6.63. ^1H NMR (CD_3CN), δ: 7.20 (m, 5 H, Ph); 3.05 (s, 24 H, Me—N); 2.76 (t, 2 H, CH_2CO); 2.47 (t, 2 H, CH_2Ph); 3.60 to −0.25 (m, 11 H, BH).

Tetramethylammonium benzoylundecahydro-*closo*-dodecaborate (4). Yield 1.66 g (42%), m.p. 317 °C. Found (%): C, 44.97; H, 10.65; N, 6.93. $C_{15}H_{40}B_{12}N_2O$. Calculated (%): C, 45.66; H, 10.73; N, 7.10. ^1H NMR (CD_3CN), δ: 7.90, 7.41, 7.38 (m, 2 H + 1 H + 2 H, Ph); 3.09 (s, 24 H, Me—N); 3.60 to −0.25 (m, 11 H, BH).

Tetramethylammonium α-naphthaloylundecahydro-*closo*-dodecaborate (5). Yield 1.3 g (29%), m.p. 310—312 °C. Found (%): C, 50.60; H, 9.38; N, 6.13. $C_{19}H_{42}B_{12}ON_2$. Calculated (%): C, 51.32; H, 9.53; N, 6.30. ^1H NMR (CD_3CN), δ: 8.83 (d, 1 H) + 7.89 (m, 3 H) + 7.52 (m, 3 H) (α-naphthyl); 3.06 (s, 24 H, Me—N); 3.60 to −0.25 (m, 11 H, BH).

Tetraethylammonium 4-chlorobenzoylundecahydro-*closo*-dodecaborate (7). Yield 2.84 g (52%), m.p. 280—282 °C. Found (%): C, 49.70; H, 9.73; N, 4.99; Cl, 6.41. $C_{23}H_{55}B_{12}ClN_2O$ Calculated (%): C, 51.03; H, 10.25; N, 5.18; Cl, 6.55 ^1H NMR (CD_3CN), δ. 7.98, 7.40 (dd, 4 H, Ar); 3.11 (q,

16 H, CH_2—N); 1.33 (t, 24 H, N—CH_2—CH_3); 3.60 to −0.25 (m, 11 H, BH).

Tetraethylammonium 4-bromobenzoylundecahydro-*closo*-dodecaborate (8). Yield 3.42 g (59%), m.p. 275—277 °C. Found (%): C, 46.73; H, 9.23; N, 4.33; Br, 13.59. $C_{23}H_{55}B_{12}BrN_2O$. Calculated (%): C, 47.20; H, 9.47; N, 4.79; Br, 13.65. ^{1}H NMR (CD_3CN), δ: 7.79, 7.54 (dd, 4 H, Ar); 3.14 (q, 16 H, CH_2); 1.20 (t, 24 H, N—CH_2—CH_3); 3.60 to −0.25 (m, 11 H, BH).

Tetramethylammonium 4-nitrobenzoylundecahydro-*closo*-dodecaborate (6a) and trimethylphenylammonium 4-nitrobenzoylundecahydro-*closo*-dodecaborate (6b). A solution of nitrobenzoyl chloride in 20 mL of acetone was added dropwise to a solution of $[B_{12}H_{12}]Na_2$ (1.9 g, 10 mmol) in acetone (20 mL) for 30 min at −20 °C. The reaction mixture was stirred for 1 h at −20 °C and for 2 h at 20 °C. Then the precipitate of NaCl (0.55 g, 4.8 mmol) that formed was filtered off and the acetone was evaporated *in vacuo*. The pale yellow residue was dissolved in water (50 mL), and Me_4NBr (3.2 g, 20 mmol) in 10 mL of water was added to the resulting solution. The precipitate that formed was filtered off, washed with water (2×10 mL) and diethyl ether (2×10 mL), and dried *in vacuo* to give compound **6a** (0.75 g, 17%), m.p. 359 °C. The addition of Me_3NPhCl (34 g, 20 mmol) instead of Me_4NBr resulted in compound **6b** (2.28 g, 58%).

Compound 6a. Found (%): C, 40.12; H, 8.72; N, 9.44. $C_{15}H_{39}B_{12}N_3O_3$. Calculated (%): C, 40.98; H, 8.95; N, 9.56. ^{1}H NMR (CD_3CN), δ: 8.17 (dd, 4 H, Ar); 3.04 (s, 24 H, N—CH_3); 3.60 to −0.25 (m, 11 H, BH).

Compound 6b. Found (%): C, 52.72; H, 7.53; N, 7.48. $C_{25}H_{43}B_{12}N_3O_3$. Calculated (%): C, 53.25; H, 7.69; N, 7.46.

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