GAS-PHASE FLASH REACTIONS OF DIBORANE, TRIBORANE CARBONYL AND TETRABORANE WITH ALKYNES

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Dedicated with affection and admiration to Dr Stanislav Heřmánek on the occasion of his 70th birthday, in recognition of his outstanding contributions to boron chemistry.

Several known volatile *closo*-carboranes (1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,10-$C_2B_8H_{10}$) and their alkyl derivatives and ten new alkyl derivatives of these carboranes were identified from the thermal gas-phase flash reactions of B_2H_6, B_3H_7CO and B_4H_{10} with ethyne, propyne and but-2-yne. In addition, *nido*-$C_4B_2H_6$ and its methyl derivatives were obtained from B_2H_6-alkyne flash reactions. All carboranes found in these high-energy reactions are the most thermally stable isomers of their class. The non-isolable borane $\{B_3H_7\}$ is suggested as the initiator in all thermal flash reactions reported here.

Key words: Boranes; Carboranes; Alkynes; Gas-phase reactions; Flash reactions.

During the early 1960s, the first small carboranes, 1,5-$C_2B_3H_5$ (**1**), 1,2-$C_2B_4H_6$ (**2**), 1,6-$C_2B_4H_6$ (**3**) and 2,4-$C_2B_5H_7$ (**4**), were reported as low-yield products from electric discharge reactions of pentaborane(9), B_5H_9, and ethyne[1–3]. Grimes later identified several more *closo*-carboranes from flash and electric discharge reactions of diborane and ethyne in the presence of helium[4,5]. They include various monomethyl derivatives of 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ but a claimed dimethyl derivative **5** of the unknown parent *closo*-carborane, 1,2-$C_2B_3H_5$, was later discounted (see below).

$$\begin{aligned} B_2H_6 + HC{\equiv}CH \rightarrow\ & 1,5\text{-}C_2B_3H_5\ (\mathbf{1}),\ 1,6\text{-}C_2B_4H_6\ (\mathbf{3}),\ 2,4\text{-}C_2B_5H_7\ (\mathbf{4}), \\ & C,3\text{-}Me_2\text{-}1,2\text{-}C_2B_3H_3\ (\mathbf{5}),\ 2\text{-}Me\text{-}1,5\text{-}C_2B_3H_4\ (\mathbf{6}), \\ & 2\text{-}Me\text{-}1,6\text{-}C_2B_4H_5\ (\mathbf{7}),\ 1\text{-}Me\text{-}2,4\text{-}C_2B_5H_6\ (\mathbf{8}), \\ & 3\text{-}Me\text{-}2,4\text{-}C_2B_5H_6\ (\mathbf{9}),\ 5\text{-}Me\text{-}2,4\text{-}C_2B_5H_6\ (\mathbf{10}) \end{aligned}$$

More small *closo*-carboranes were obtained from the thermal flash gas-phase reactions of tetraborane(10), B_4H_{10}, with alkynes at 100 °C as summarised below[6,7]. In addition, the larger *closo*-carboranes 1,6-$C_2B_8H_{10}$

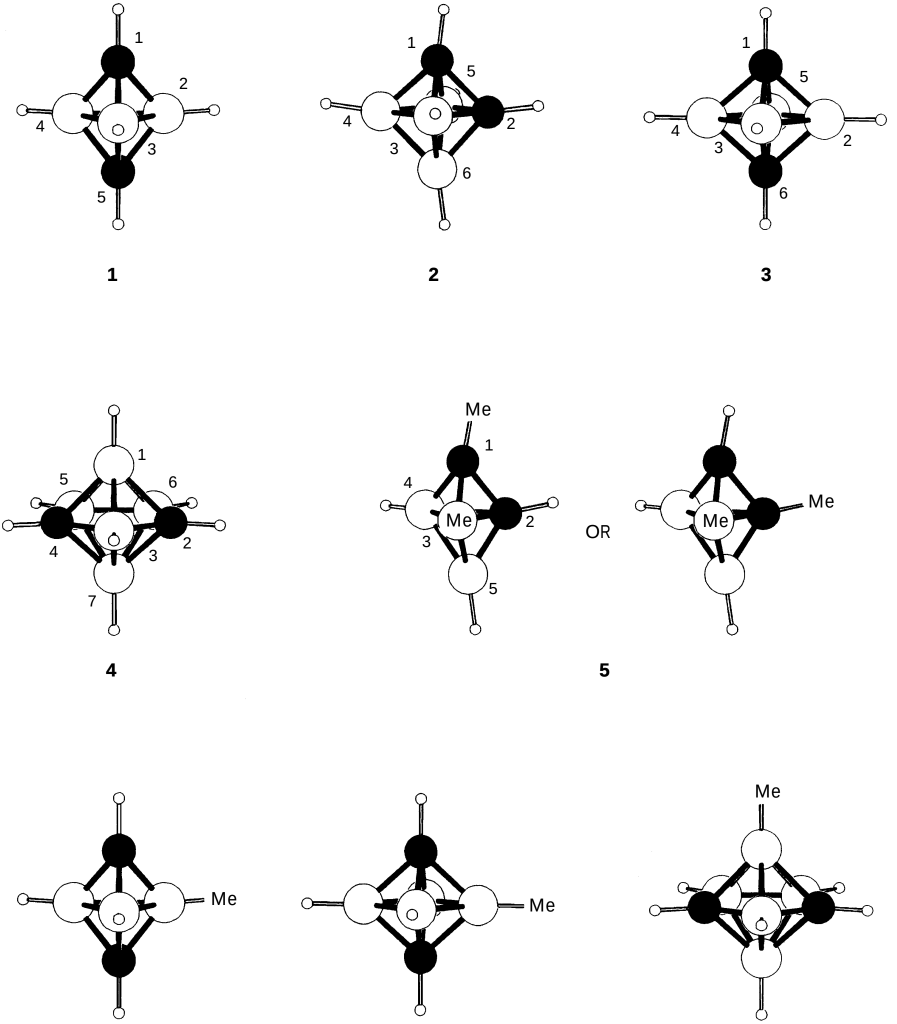
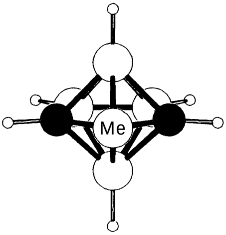


FIG. 1
Carboranes identified from reported high-energy borane–alkyne reactions

(**11**) and presumably one of six isomers of *B*-Me-1,6-$C_2B_8H_9$ (**12**) were obtained with ethyne. Thermal flash reactions of pentaborane(11), B_5H_{11}, with ethyne and propyne gave the same carboranes as flash reactions of B_4H_{10} with ethyne and propyne, respectively.



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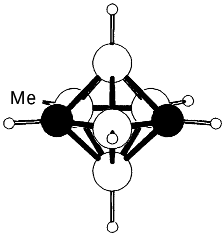

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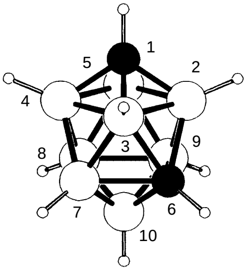

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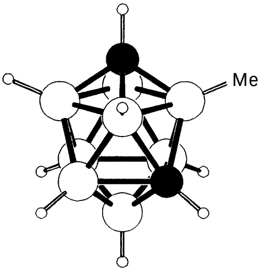

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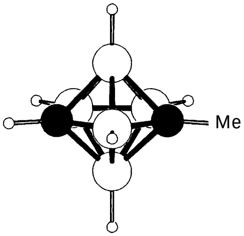

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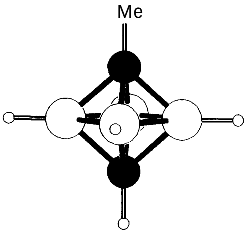

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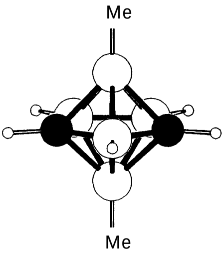

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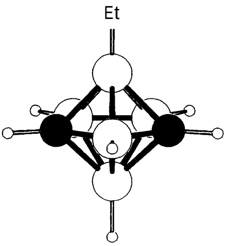

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FIG. 1
(*Continued*)

B_4H_{10} + HC≡CH → **3**, **4**, **6**, **8**, **9**, **10**, 1,6-$C_2B_8H_{10}$ (**11**), *B*-Me-1,6-$C_2B_8H_9$ (**12**), 2-Me-2,4-$C_2B_5H_6$ (**13**)

B_4H_{10} + MeC≡CH → **1**, **4**, **5**, **6**, **13**, 1-Me-1,6-$C_2B_4H_5$ (**14**), 1,7-Me_2-2,4-$C_2B_5H_5$ (**15**)

B_4H_{10} + MeC≡CMe → **1**, **4**, **5**, **6**, **13**, **14**, **15**, 1-Et-2,4-$C_2B_5H_6$ (**16**)

The compound originally thought to be C,3-Me_2-1,2-$C_2B_3H_3$ (**5**), has been shown by a recent detailed theoretical and experimental investigation, to be unlikely to have a stable existence under the reported conditions of synthesis, and has properties more consistent with its formulation as 2,3-Me_2-1,5-$C_2B_3H_3$ (**18**) (ref.[8]). Here we report the many known and new carboranes identified from the thermal flash reactions of B_2H_6, B_3H_7CO and B_4H_{10} with the alkynes, HC≡CH, MeC≡CH and MeC≡CMe.

EXPERIMENTAL

Standard high-vacuum systems fitted with greaseless O-ring taps and spherical joints (J. Young (Scientific Glassware) Ltd.) were used throughout. ^{11}B, $^{11}B\{^1H\}$, 2D ^{11}B-^{11}B COSY, ^1H and $^1H\{^{11}B$ selective$\}$-^1H subtraction spectra were obtained on a Bruker AM-400 NMR instrument with $CDCl_3$ as lock solvent at 298 K (ref.[9]). Chemical shifts reported here are referenced to $BF_3\cdot Et_2O$ 0.0 ppm for ^{11}B and TMS 0.00 ppm for ^1H. The boranes B_2H_6, B_3H_7CO and B_4H_{10} were all obtained as described in the literature[10–12]. The alkynes, HC≡CH (BOC), MeC≡CH (Cambrian Gases) and MeC≡CMe (Lancaster Synthesis) were purchased commercially.

General Procedure for Gas-Phase Thermal Flash Reactions of Diborane and Tetraborane with Ethyne, Propyne and But-2-yne

Typically, 6 mmol of borane and 6 mmol of alkyne were condensed at –196 °C (liquid nitrogen) into a 650 ml round-bottomed flask and then warmed quickly to 100 °C by means of a heated oil bath. As the temperature approached 100 °C, the gas mixture became cloudy and then flashed, giving tan solids which covered the inner flask walls. The flask was then cooled to –196 °C and hydrogen was removed by pumping. A representative sample of the volatiles was then transferred to a resealable Young's tube together with $CDCl_3$, and the remainder subjected to a cold-column fractionation[13]. Species leaving the column were sampled continuously *via* a glass capillary of length 200 mm and internal diameter 0.1 mm (Jencons Scientific Ltd.) and monitored by means of a Kratos MS30 mass spectrometer fitted with an MSS data system. Volatile carborane fractions with different mass cut-offs were collected and transferred to resealable Young's NMR tubes. These fractions were characterized by detailed ^{11}B and ^1H NMR spectroscopy (Table I).

TABLE I
128 MHz ^{11}B and 400 MHz ^{1}H NMR data for volatile carboranes identified from borane–alkyne flask reactions

	Ref.[a]	$\delta(^{11}B)$(*J*, Hz; assignment)	$\delta(^{1}H\{^{11}B\})$
		$C_2B_3H_5$ and derivatives	
1	33,34	3.5 (189; B2, B3, B4)	5.59 (CH), 3.90 (BH)
6	29	9.3 (s; B2), 7.4 (185; B3, B4)	5.23 (CH), 4.06 (BH), 0.38 (CH_3)
17		3.0 (186; B2, B3, B4)	5.29 (CH), 3.76 (BH), 2.28 (CH_3)
18	8,29	13.1 (s; B2, B3), 11.2 (180; B4)	4.86 (CH), 4.20 (BH), 0.40 (CH_3)
19	8	8.3 (s; B2), 6.3 (182; B3, B4)	4.94 (CH), 3.88 (BH), 2.12 (CCH_3), 0.31 (BCH_3)
20	8	2.5 (186; B2, B3, B4)	3.80 (BH), 2.21 (CH_3)
21	29	16.9 (s; B2, B3, B4)	4.49 (CH), 0.43 (CH_3)
		$C_2B_4H_6$ and derivatives	
3	35	–17.5 (191; B2, B3, B4, B5)	3.10 (CH), 1.94 (BH)
7		–8.4 (s; B2), –16.8 (188; B3, B5), –23.3 (188; B3, B5)	3.07 (CH), 1.86 (B3H, B5H), 1.72 (B4H), 0.37 (CH_3)
14		–16.3 (190; B2, B3, B4, B5)	2.80 (CH), 1.94 (BH), 1.50 (CH_3)
22		–8.1 (s; B2, B3), –22.5 (186; B4, B5)	2.98 (CH), 1.70 (BH), 0.31 (CH_3)
23		–14.4 (s; B2, B4), –16.1 (183; B3, B5)	2.98 (CH), 1.85 (BH), 0.31 (CH_3)
24		–7.6 (s; B2), –15.6 (186; B3, B5), –21.7 (186; B4)	2.80 (CH), 1.84 (B3H, B5H), 1.72 (B4H) 1.49 (CCH_3), 0.33 (BCH_3)
25	36	–15.0 (192; B2, B3, B4, B5)	1.96 (BH), 1.44 (CH_3)
26		–16.9 (189; B2, B3, B4, B5)	[b]
		$C_2B_5H_7$ and derivatives	
4	37	7.2 (179; B3), 3.9 (169; B5, B6) –21.5 (181; B1, B7)	5.66 (CH), 4.98 (B3H), 4.09 (B5H, B6H), 0.08 (B1H, B7H)
8	21,22	8.3 (178; B3), 4.0 (169[c]; B5, B6) –11.6 (s; B1), –27.4 (180; B7)	5.66(CH), 4.91 (B3H), 4.05 (B5H, B6H), –0.11 (B7H), –0.47 (CH_3)
9	21,22	14.2 (s; B3), 3.4 (169; B5, B6) –20.2 (177; B1, B7)	5.30 (CH), 3.97 (B5H, B6H), 1.02 (CH_3), 0.17 (B1H, B7H)
10	21,22	11.5 (s; B5), 6.7 (181; B3), 2.3 (170; B6), –20.9 (176; B1, B7)	5.49 (C2H), 5.26 (C4H), 4.85 (B3H), 3.86 (B6H), 0.72 (CH_3), 0.16 (B1H, B7H)

TABLE I
(*Continued*)

	Ref.[a]	$\delta(^{11}B)$(*J*, Hz; assignment)	$\delta(^{1}H\{^{11}B\})$
13		7.7 (182; B3), 6.1 (172[c], B6), 3.8 (169; B5), –19.5 (179; B1, B7)	5.52 (CH), 4.75 (B3H), 3.91 (B5H), 3.97 (B6H), 2.18 (CH_3), 0.22 (B1H, B7H)
27	21	14.9 (s; B3), 3.8 (171; B5, B6), –11.0 (s; B1), –25.9 (179; B7)	5.26 (CH), 3.93 (B5H, B6H), 0.98 ($B3CH_3$), 0.02 (B7H), –0.47 ($B1CH_3$)
28	21	13.6 (s; B3), 11.3 (s; B5), 1.9[c] (168[c]; B6), –19.5 (177; B1, B7)	5.12 (C2H), 4.93 (C4H), 3.82 (B6H), 0.92 ($B3CH_3$), 0.68 ($B5CH_3$), 0.23 (B1H, B7H)
29	21	11.3 (s; B5), 7.8 (181; B3), 1.9[c] (168[c]; B6), –10.5 (s; B1), –26.6 (180; B7)	5.48 (C2H), 5.26 (C4H), 4.71 (B3H), 3.82 (B6H), 0.68 ($B5CH_3$), –0.03 (B7H), –0.47 ($B1CH_3$)
30		7.2 (182; B3), 5.4 (171; B6), 3.5 (169; B5), –20.0 (180; B1, B7)	5.48 (CH), 4.71 (B3H), 4.02 (B6H), 3.93 (B5H), 2.47 (q, $^{3}J_{HH}$ = 7 Hz; $C\mathbf{H}_2$–CH_3), 1.18 (t, $^{3}J_{HH}$ = 7 Hz; CH_2–$C\mathbf{H}_3$), 0.20 (B1H, B7H)
		$C_2B_8H_{10}$ and derivatives	
31	17,38	–12.7 (161; B2–B9)	7.00 (CH), 2.00 (BH)
32		–3.5 (s; B2), –10.7 (163; B3, B5), –11.2 (162; B7, B8), –12.2 (164; B6, B9), –15.3 (161; B4)	6.83 (C10H), 6.62 (C1H), 2.15 (B3H, B5H), 2.04 (B7H, B8H), 1.94 (B6H, B9H), 1.80 (B4H), 0.18 (CH_3)
		$C_4B_2H_6$ and derivatives	
33	31	10.8 (145; B6), –60.6 (206; B1)	5.96 (C3H, C4H), 4.72 (C2H, C5H), 3.76 (B6H), –0.81 (B1H)
34		12.4 (148; B6), –50.9 (s; B1)	5.83 (C3H, C4H), 4.37 (C2H, C5H), 0.47 ($B6CH_3$), –0.74 (B1H)
35		19.8 (s; B1), –59.4 (204; B1)	5.99 (C3H, C4H), 4.49 (C2H, C5H), 3.82 (B6H), –0.31 ($B1CH_3$)
36		10.8[c] (B6), –58.5 (206; B1)	[b]
37		10.8[c] (B6), –57.0 (205; B1)	[b]
38		20.6 (s; B1), –50.0 (s; B1)	[b]

[a] Data reported here are in agreement with boron and/or proton NMR data in the literature. Where no reference is given, data are reported for the first time. [b] Not recorded. [c] Value uncertain due to peak overlap or poorly resolved peaks.

Flash Reaction of B_3H_7CO and Propyne

In a typical reaction, B_3H_7CO (0.35 mmol) was measured at –34 °C in a 196 ml flask and then MeC≡CH (0.35 mmol) was condensed into the reaction vessel. The mixture was warmed to –20 °C using an acetone–CO_2 slush and suddenly flashed. The tan-coated flask was then cooled to –196 °C and non-condensable gases (presumably CO and H_2) were pumped away. This process was repeated several times and the combined volatile products were subjected to cold-column fractionation and NMR spectroscopy as described in the previous method.

RESULTS AND DISCUSSION

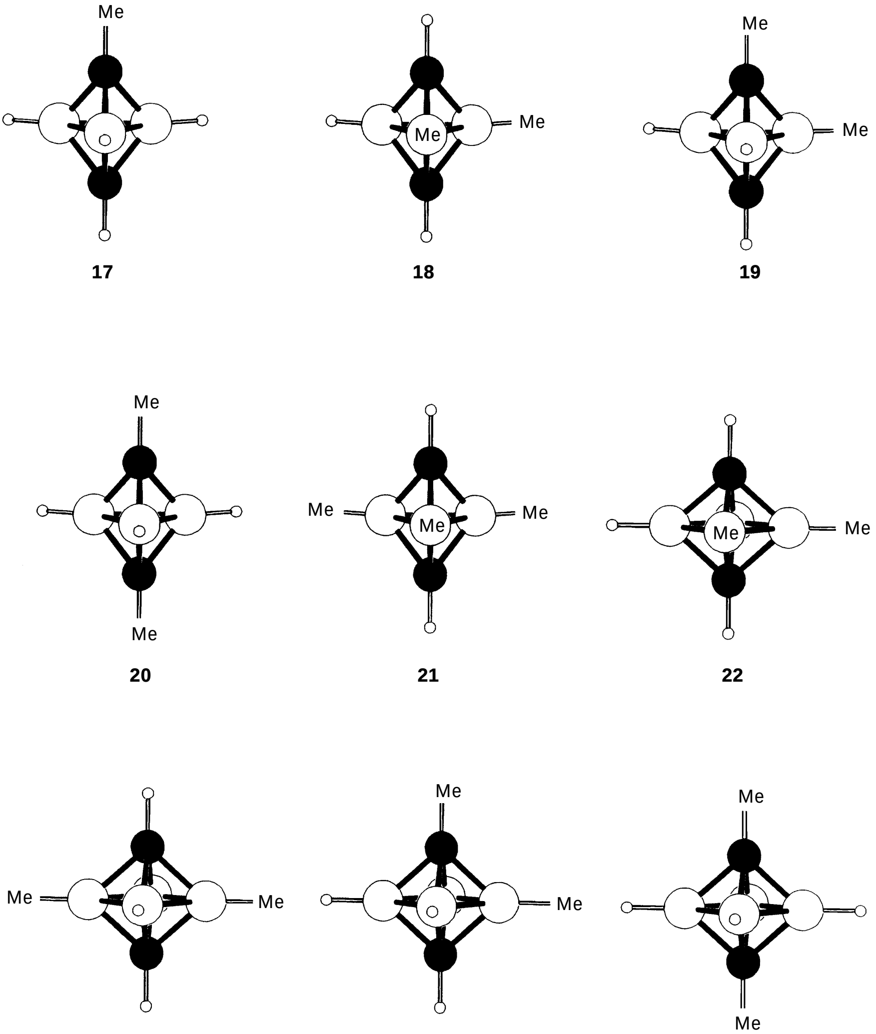
The volatile carboranes produced in the thermal flash reactions of B_2H_6 with the alkynes HC≡CH, MeC≡CH and MeC≡CMe are listed in Table II, together with their yields. Total yields of volatile carboranes from these reactions were only 2–3% with respect to the amount of boron consumed from B_2H_6. The major products were tan solids of polymeric nature and were not characterised. Thirty-two known or new compounds were identified from ^{11}B and ^{1}H NMR data (shown in Table I) as 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,10-$C_2B_8H_{10}$, 2,3,4,5-$C_4B_2H_6$ or their derivatives. Further information on these compounds is in Table II.

The *closo*-carboranes reported here are theoretically and experimentally the most thermodynamically stable isomers[14–19]. Ratios of the *B*-monomethyl and *B*-dimethyl substituted derivatives of 2,4-$C_2B_5H_7$ observed in our flash reactions fit well with the final products of the reported thermal rearrangements of *B*-monomethyl and *B*-dimethyl derivatives of 2,4-$C_2B_5H_7$, **8**–**10** and **27**–**29** (refs[20–24]). The *nido*-tetracarbaboranes **33**–**38** observed here must also be thermally robust to survive such high-energy reactions.

Thermal flash reactions of B_4H_{10} with the three alkynes gave nearly identical products and yields as the B_2H_6-alkyne reactions. Exceptions are the *nido*-$C_4B_2H_6$ derivatives, which are not observed among the products in the tetraborane–alkyne reactions. We believe that the *nido*-carboranes **33**–**38** were derived from compounds generated by B_2H_6 hydroboration of the alkyne[25] in the rapid warm-up period prior to the flash point in B_2H_6–alkyne reactions.

The *closo*-carboranes, 1,6-$C_2B_8H_{10}$ (**11**) and *B*-Me-1,6-$C_2B_8H_9$ (**12**) reported[6,7] from the thermal flash reactions of B_4H_{10} and HC≡CH are re-identified here as 1,10-$C_2B_8H_{10}$ (**31**) and 2-Me-1,10-$C_2B_8H_9$ (**32**), respectively. In addition, the carborane C,3-Me_2-1,2-$C_2B_3H_3$ (**5**) reported[7] from the flash reactions of B_4H_{10} with MeC≡CH and MeC≡CMe is re-identified here as 2,3-Me_2-1,5-$C_2B_3H_3$ (**18**) (ref.[8]). The derivatives 1,7-Me_2-2,4-$C_2B_5H_5$

(**15**) and 1-Et-2,4-$C_2B_5H_6$ (**16**) reported[7] as products of the reaction between B_4H_{10} and MeC≡CMe were not observed here and, based on their yields, we believe that these compounds are actually two of the isomers of Me_2-2,4-$C_2B_5H_5$, reported here as **27**–**29**.

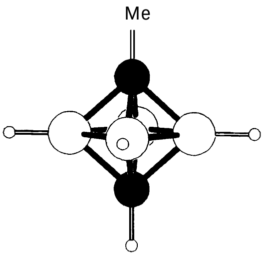


17 **18** **19**

20 **21** **22**

23 **24** **25**

FIG. 2
Carboranes identified from borane–alkyne flash reactions in this study



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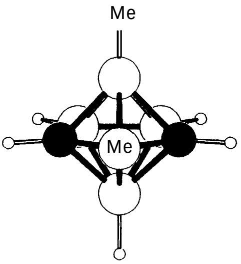

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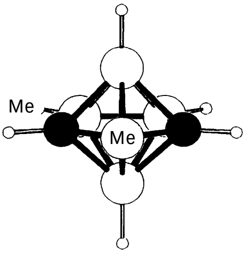

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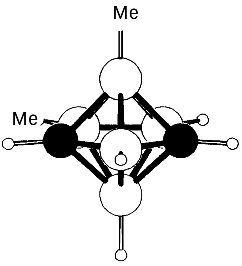

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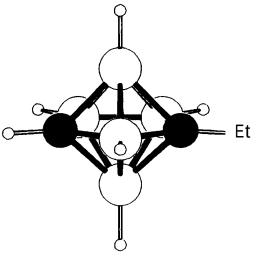

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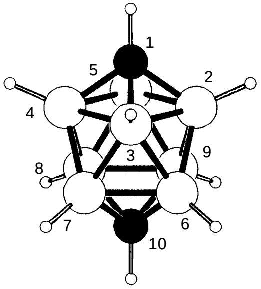

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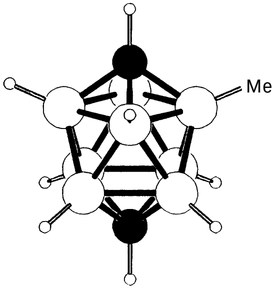

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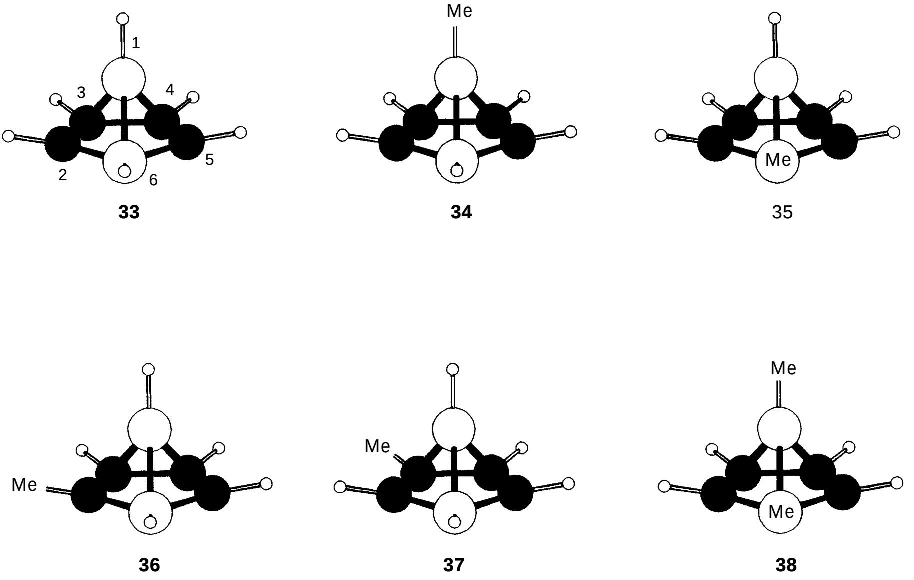
Fig. 2
(*Continued*)

The unstable compound B_3H_7CO was found to undergo a flash reaction at –20 °C with propyne, MeC≡CH, to give *closo*-carboranes identical to those obtained from the B_4H_{10}–MeC≡CH thermal flash reaction. The similarity in the products of the B_2H_6–alkyne, B_3H_7CO–alkyne and B_4H_{10}–alkyne flash reactions suggests that they are initiated by a common borane intermediate, and there is good reason to believe that this is the non-isolable species $\{B_3H_7\}$. This intermediate plays an important role in the early stages of thermal decomposition of B_2H_6 at *ca* 100 °C (ref.[26]) and the latter is known to be formed in the thermolysis of B_4H_{10} at 100 °C (ref.[27]). The intermediate $\{B_3H_7\}$ is also likely to be formed in the initial dissociation step of B_3H_7CO, and this is known to occur at the much lower temperature of –30 °C (ref.[11]). Significantly, the flash reactions involving B_2H_6 and B_4H_{10} occur at *ca* 100 °C, whereas that involving B_3H_7CO is initiated at *ca* –20 °C. The non-isolable borane $\{B_3H_7\}$ is therefore a good candidate as the initiator for the flash reactions described here. Interestingly, a recent computational study[28] on borane–ethyne reactions includes an addition (not hydroborated) product from $\{B_3H_7\}$ and HC≡CH, which is formed with little or no barrier, as an initial step to carborane formation.



33 **34** 35

36 **37** **38**

FIG. 2
(*Continued*)

TABLE II
Volatile carboranes identified from diborane–alkyne flash reactions. Yields are percentages of the total volatile carborane fraction and are rounded to the nearest integer (tr, trace)

Compound		Ref.	HC≡CH	MeC≡CH	MeC≡CMe
		$1,5\text{-}C_2B_3H_5$ and derivatives			
1	Parent	1	11	4	
6	2-Me	5	4	11	4
17	1-Me	new		3	4
18	$2,3\text{-}Me_2\text{-}$	29	1	6	9
19	$1,2\text{-}Me_2\text{-}$	8		3	6
20	$1,5\text{-}Me_2\text{-}$	8		1	3
21	$2,3,4\text{-}Me_3\text{-}$	29		3	3
	Total		*16*	*31*	*29*
		$1,6\text{-}C_2B_4H_6$ and derivatives			
3	Parent	2	7	3	
7	2-Me-	5	1	2	1
14	1-Me-	7	tr	5	4
22	$2,3\text{-}Me_2\text{-}$	new		1	3
23	$2,4\text{-}Me_2\text{-}$	new		tr	1
24	$1,2\text{-}Me_2\text{-}$	new		tr	3
25	$1,6\text{-}Me_2\text{-}$	30		tr	1
26	1-Et-	new			1
	Total		*8*	*11*	*13*
		$2,4\text{-}C_2B_5H_7$ and derivatives			
4	Parent	3	32	7	6
8	1-Me-	5	6	6	5
9	3-Me-	5	6	6	5
10	5-Me-	5	5	4	3
13	2-Me	6	9	10	7
27	$1,3\text{-}Me_2\text{-}$	21	2	6	6
28	$3,5\text{-}Me_2\text{-}$	21	1	3	3
29	$1,5\text{-}Me_2\text{-}$	21	1	3	3
30	2-Et-	new		1	2
	Total		*62*	*46*	*40*

TABLE II
(*Continued*)

	Compound	Ref.	HC≡CH	MeC≡CH	MeC≡CMe
	$1,10\text{-}C_2B_8H_{10}$ and derivatives				
31	Parent	7	6	3	1
32	2-Me-	new	3	2	2
	Total		*9*	*5*	*3*
	$2,3,4,5\text{-}C_4B_2H_6$ and derivatives				
33	Parent	31	1	2	3
34	1-Me-	new		1	2
35	6-Me-	new		1	2
36	2-Me-	32		tr	tr
37	3-Me-	32		tr	tr
38	$1,6\text{-}Me_2\text{-}$	new		tr	tr
	Total		*1*	*4*	*7*

CONCLUSIONS

Ten new alkyl derivatives of the volatile *closo*-carboranes $1,5\text{-}C_2B_3H_5$, $1,6\text{-}C_2B_4H_6$, $2,4\text{-}C_2B_5H_7$, $1,10\text{-}C_2B_8H_{10}$ have been identified among the products of thermal gas-phase flash reactions of B_2H_6, B_3H_7CO and B_4H_{10} with ethyne, propyne and but-2-yne. The parent carboranes and many derivatives reported previously were also present, but five of these products have been re-identified. In addition, *nido*-$C_4B_2H_6$ and its methyl derivatives were obtained from the B_2H_6–alkyne flash reactions. All carboranes found in these high-energy reactions are the most thermally stable isomers of their class. It is suggested that the non-isolable borane $\{B_3H_7\}$ is the initiator in all thermal flash reactions reported here.

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