

FACTORS RELATING TO THE FORMATION OF B-PHENYL-N-ALKYLBORAZINES

B. R. CURRELL, W. GERRARD AND M. KHODABOCUS

Chemistry Department, Northern Polytechnic, Holloway Road, London, N. 7. (Great Britain)

(Received September 21st, 1966)

The propensity of boron to form six-membered "trimer" rings, $(\text{XBNY})_3$, with alternating boron atoms, to the considerable exclusion of chains or rings of other sizes, has attracted considerable attention. Hopes of effecting a catenation of borazine or some related ring structures, or of forming long chains by avoiding ring formation have been entertained in connection with the attempts to produce "boron polymers" having industrial applicability for special service at temperatures around 500° . The first report¹ from this aspect was mainly on the formation of hexaphenylborazine and on the technical difficulty in the preparation of one of the starting materials, dichlorophenylborane, a difficulty since resolved².

In attempts to trace the steps by which the borazine ring is developed in the phenyl-boron systems we have prepared (Table 1) a selection of primary alkylammo-

TABLE 1

PREPARATION OF $\text{RNH}_3^+(\text{PhBCl}_3)^-$

R	RNH_3Cl (g)	PhBCl_2 (g)	Yield [g (%)]	Analysis found (calcd.)		
				B %	Cl %	N %
Pr	75.0	127.1	93.5	4.3 (4.25)	41.7 (41.8)	5.45 (5.5)
iso-Bu	44.5	67.2	70.6 ^a (25.7) ^a	4.3	38.7	5.0
sec-Bu	53.1	78.1	73.6 ^a (25.0) ^a	4.1	39.3	4.95
tert-Bu	75.4	109.6	86.6 ^a (13.0) ^a	4.1 (4.0)	39.2 (39.6)	5.3 (5.2)

^a From the filtrate

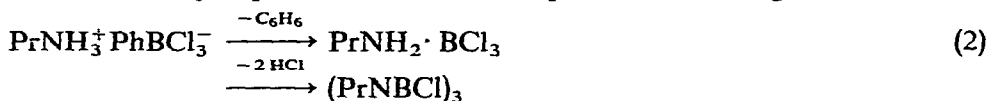
nium trichlorophenylborates, $\text{RNH}_3^+\text{PhBCl}_3^-$, by procedure (1), and have studied the condensation of these under certain conditions (see Tables).



R = Pr, iso-Bu, sec-Bu, tert-Bu

At temperatures of $106\text{--}109^\circ$ (see Table 2), n-propylammonium trichlorophenylborate evolved hydrogen chloride (0.113 mol.) and benzene (0.8 mol.); but at

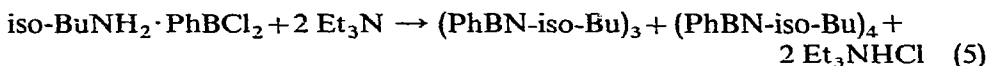
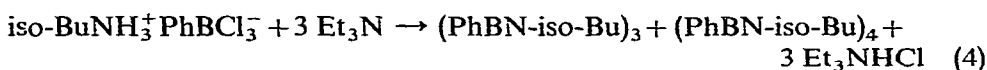
180–220° only hydrogen chloride (1.85 mol.) was evolved, giving the dephenylated borazine, (CIBNPr)₃ in 82% yield, presumably by the sequence shown in (2). Differential thermal analysis pointed to a similar sequence³. In boiling chlorobenzene,



with a stream of nitrogen, there was an evolution of hydrogen chloride (2.75 mols.); the phenylated borazine, (PrNBPh)₃ (64% yield), was accompanied by a much smaller yield of the B-chloroborazine (PrNBCl)₃. In boiling toluene, however, there was but a small amount of dephenylation, and condensation proceeded no further than the complex, PrNH₂·PhBCl₂, only 1 mol. of hydrogen chloride being evolved. In boiling xylene, hydrogen chloride (2 mol.) was evolved; but characterisation of the other products was not achieved, although when heated at 170–190° the dried residue gave benzene (0.64 mol.) and the B-chloroborazine, (PrNBCl)₃. In toluene at room temperature, treatment with triethylamine gave the phenylated borazine (3).



The isobutyl system tended to respond similarly, except that the factor due to branching in the alkyl group began to show; for, in the presence of triethylamine, the trimer (PhBN-iso-Bu)₃ (21% yield) and the tetramer (PhBN-iso-Bu)₄ (4% yield) were obtained, these products also being formed from the complex, iso-BuNH₂·PhBCl₂.



Effect of branching in the alkyl group is again seen in the sec-butyl and tert-butyl systems; for, although there are indications of predominant dephenylation in the absence of solvent, and dehydrochlorination in solvents, a certain lack of ring products was evident. Pyrolysis of sec-butylammonium trichlorophenylborate gave products such as the sec-BuNH₂·BCl₃ complex and sec-BuNH₃Cl; in the presence of triethylamine at room temperature, dehydrochlorination proceeded only to the 2 mol. stage, and gave the (alkylamino)chlorophenylborane, RNHPhCl, and in this respect the tert-butyl system behaved similarly. Pyrolysis of the tert-butylammonium trichlorophenylborate gave nearly 1 mol. of tert-butyl chloride.

TYPES OF RING

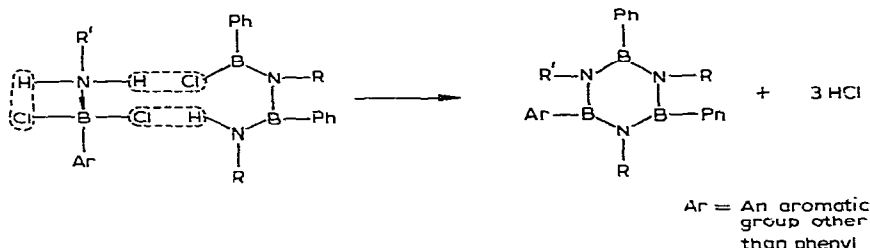
Cyclic dimers⁴, trimers (*cf.* ref. 5), and tetramers⁶ have been described; and certain linear polyborazines^{7,8} have been indicated, although for these the definition of conditions would appear to require more attention⁹.

The trimer, (PhBN-iso-Bu)₃, and the tetramer, (PhBN-iso-Bu)₄¹⁰, prepared as described herein, have been fully characterised by full elemental analysis and molecular weight (both by vapour pressure osmometer and by mass spectroscopy).

Differential thermal analysis has also been reported¹⁰, and the change tetramer \rightarrow trimer at 250° revealed.

We find that (sec-butylamino)chlorophenylborane dimerises slowly (a period of months) at room temperature, but the tert-butyl compound does not.

An outstanding feature of the work now reported, as well as that relating to the alkylammonium tetrachloroborate systems is the elusiveness of any intermediate on the route from the 1 : 1 complex to the borazine. One of the aims of the projects referred to herein and in the other paper cited, has been to isolate such intermediates so that it could be heated with a different 1 : 1 complex in order to produce a mixed borazine, *e.g.*



PYROLYSIS OF ALKYLAMMONIUM TETRAPHENYLBORATES

An approach was made from the fully phenylated boron end. The pyrolysis of the chosen alkylammonium tetraphenylborates, $\text{RNH}_3^+(\text{BPh}_4)^-$ ($\text{R} = \text{Pr}$, iso-Bu, sec-Bu) at 110–150° in an inert atmosphere gave amine, and the amine–triphenylborane complex, $\text{RNH}_2 \cdot \text{BPh}_3$, which at about 200° gave benzene (1 mol.) and the (alkylamino)diphenylborane, distillable at atmosphere pressure at about 300°. Differential thermal analysis³ supports these observations.



The formation of amine and triphenylborane occurred to the extent of 4%. tert-Butylammonium tetraphenylborate at 120–150° gave tert-butylamine (0.6 mol.) and benzene (2 mol.), and up to 300°, more benzene (0.22 mol.) was evolved, and the residue afforded triphenylborane (0.07 mol.) and (tert-butylamino)diphenylborane (0.27 mol.) on distillation. The formation of a dimer, trimer or tetramer ring was not observed.

EXPERIMENTAL

Preparation of primary alkylammonium trichlorophenylborates

Dichlorophenylborane (1.1 mol.) was added dropwise to anhydrous alkylammonium chloride (1 mol.) suspended in dichloromethane at 5°. The crystalline white powder was immediately filtered off, washed with solvent and dried in a vacuum. More product was obtained by evaporating the solvent from the mother liquor (see Table I.)

Decomposition of the trichlorophenylborates. These systems were heated at

TABLE 2
PYROLYSIS OF ALKYLAMMONIUM TRICHLOROPHENYLBORATES (1 MOL.)

R	RNH ₃ ⁺ (PhBCl ₃) (g)	Temp. (°C)	Time (h)	Volatile compounds (mols.)			Distillation of residue
				HCl	C ₆ H ₆	C ₆ H ₅ BCl ₂	
Pr	18.0	106-109°	2	0.113	0.80	nil	(CIBNPr ₃) ₃ (82%), b.p. 163-164°/14 mm, m.p. 76°. (Found: B, 10.15; Cl, 34.15; N, 13.3; mol.wt., 302. C ₉ H ₂₁ B ₃ calcd.: B, 10.45; Cl, 34.3; N, 13.55%; mol.wt., 310)
		120-180°	1	nil	0.05	0.03	
		220°	2	1.85	nil	nil	
iso-Bu	25.6	220-330°		nil	nil	nil	Liquid (2.23 g), b.p. 88-89°/0.1 mm. (Found: B, 8.8; Cl, 35.4; N, 11.1%; B/Cl/N, 0.81/1.0/0.79.)
		115-125°	1	0.16	0.73	nil	
		200-210°	2	0.37	0.17	0.07	
sec-Bu	44.3	245-255°	3	1.1	nil	nil	(CIBN-iso-Bu) ₃ (5.7 g, 51% yield), b.p. 125-127°/0.1 mm, m.p. 37° (Found: B, 9.15; Cl, 30.05; N, 11.8; mol.wt., 346. C ₁₂ H ₂₇ B ₃ Cl ₃ N ₃ calcd.: B, 9.2; Cl, 30.2; N, 11.9%; mol.wt., 352.)
		120-125°	1.5	0.18	0.69	nil	
tert-Bu	46.5	140 ^{oa}	2	0.35	0.95	0.04	PhBCl ₂ (4.0 g). sec-BuNH ₂ ·BCl ₃ (21.4 g), b.p. 192°. (Found: B, 5.7; Cl, 55.7; N, 7.1. C ₄ H ₁₁ BCl ₃ N calcd.: B, 5.7; Cl, 55.9; N, 7.4%) Impure sec-BuNH ₂ ·PhBCl ₂ (3.4 g) and sec-BuNH ₃ Cl (4.05 g). tert-BuNH ₃ Cl (1.1 g) as sublimate at 200°/0.05 mm. Final residue (5.4 g). (Found: B, 31.4; Cl, 10.35; N, 42.7%; B/Cl/N, 10/1/10.5) approaching boron nitride.
		180-240 ^{ob}		0.70	nil	nil	

^a tert-BuCl (0.94 mol.) and BCl₃ (0.04 mol.), ^b Distillate (1.9 g), b.p. 220-230° (Found: B, 6.4; Cl, 41.2; N, 7.8%).

TABLE 3
DECOMPOSITION OF ALKYLAMMONIUM TRICHLOROPHENYLBORATE IN BOILING SOLVENTS

R	RNH ₃ - (PhBCl ₃) (g)	Solvent (ml)	Time (h)	HCl evolved (mols.)	Other products on removal of solvent
Pr	63.3	Toluene (200)	7.25	1.00	Benzene (0.08 mol.) PrNH ₂ ·PhBCl ₂ (55.8%) ^a plus impure complex (21.8 g)
Pr	51.05	Xylene (200)	20.5	1.90	Benzene (0.32 mol.) Residue heated at 170–190° (2.5 h) gave: benzene (9.74 g, 0.64 mol.); HCl (0.09 mol.); (CIBNPr) ₃ (14.0 g, 67.5%), m.p. 76 ^{ob}
Pr	28.3	Chlorobenzene (119)	95.5	2.75	(PhBNPr) ₃ (11.9 g, 64%), m.p. 170–172° Impure (CIBNPr) ₃ (2.05 g), b.p. 165/15 mm
iso-Bu	31.2	Toluene (200)	40	1.73	The several products could not be effectively isolated.
iso-Bu	24.5	Chlorobenzene (150)	56	2.42	Benzene (0.06 mol.) and a mixture of products
sec-Bu	36.6	Xylene (100) (N ₂ sweep)	48	1.95	Benzene (0.32 mol.), PhB(Cl)NH-sec-Bu ^d (9.96 g), b.p. 75–80°/0.3 mm, liquid (5.99 g), b.p. 80–87°/10.3 mm, liquid (2.76 g), b.p. 92–96°/0.1 mm, and other products
tert-Bu	50.2	Xylene (150)	22	0.32	[BCl ₃ (0.17 mol.); tert-BuCl (0.32 mol.)] Products not identified

^a Found: B, 5.0; Cl, 33.2; N, 6.4. C₉H₁₄BCl₂N calcd.: B, 5.0; Cl, 32.6; N, 6.4%.^b Found: B, 10.4; Cl, 34.3; N, 13.55%.^c Found: B, 7.4; Cl, nil, N, 9.6. C₂₇H₃₆B₃N₃ calcd.: B, 7.5; N, 9.7%.^d Found: B, 5.7; Cl, 18.7; N, 7.1. C₁₀H₁₃BCIN calcd.: B, 5.5; Cl, 18.15; N, 7.2%.

the temperatures stated in Table 2, until volatile matter ceased to be evolved. Finally the residue was distilled. The decomposition of these systems when heated in solvent under reflux was also studied, see Table 3.

The action of triethylamine (3 mol.) on alkylammonium trichlorophenylborates. The amine (47.8 g) was added dropwise to a stirred suspension of the trichloroborate, $\text{PrNH}_3^+(\text{PhBCl}_3)^-$ (40.05 g) in toluene (210 ml). After 7 h triethylammonium chloride (2.92 mol.) was filtered off, and the filtrate afforded B-triphenyl-N-tri-n-propylborazine, $(\text{PhBNPr})_3$ (14.1 g, 60%), giving large translucent crystals from chloroform m.p. 168°. (Found: B, 7.6; N, 9.4; mol.wt., 430. $\text{C}_{27}\text{H}_{36}\text{B}_3\text{N}_3$ calcd.: B, 7.6; N, 9.6%; mol.wt., 435.)

The isobutyl compound (11.85 g), by a similar procedure (stirring for 2 h) afforded triethylammonium chloride (100%), bis(isobutylamino)phenylborane (2.4 g), b.p. 90–92°/0.2 mm (Found: B, 4.5; N, 12.0. $\text{C}_{14}\text{H}_{25}\text{BN}_2$ calcd.: B, 4.6; N, 12.05%) and white crystals (3.8 g) (Found: B, 8.0; N, 7.95%). In petroleum (b.p. 30–40°) (150 ml) (stirring for 2 h) the isobutylammonium trichlorophenylborate afforded B-triphenyl-N-triisobutylborazine (5.5 g, 21.4%), m.p. 134° (Found: B, 6.9; N, 8.7. $\text{C}_{30}\text{H}_{42}\text{B}_3\text{N}_3$ calcd.: B, 6.8; N, 8.8%). The ebullioscopic method gave mol.wt. 339 in CHCl_3 , 440 in C_6H_6 ; the vapour pressure method (toluene at 37°) gave 460 (calcd.: 477). By washing the precipitated triethylammonium chloride with water, hot aqueous sodium hydroxide and hot water, B-tetraphenyl-N-tetraisobutylborazocine, $(\text{PhBN-iso-Bu})_4$, (1.03 g, 4%), m.p. 233° (Found: B, 6.6; N, 8.7%). Whereas the ebullioscopic methods gave mol.wt. 388 in CHCl_3 , the vapour pressure method in toluene 37° gave 640 (calcd.: 636). We have strong grounds for suspecting the ebullioscopic method for certain B-phenyl compounds related to borazine systems. The borazine $(\text{PhBN-iso-Bu})_3$ (44%) and the borazocine $(\text{PhBN-iso-Bu})_4$ (5%) were similarly obtained from the interaction of triethylamine and the complex, $\text{PhBCl}_2 \cdot \text{NH}_2\text{-iso-Bu}$. The molecular weights of this borazine and the borazocine were confirmed by mass spectrometry.

sec-Butylammonium trichlorophenylborate (33.7 g), in toluene (150 ml) gave, during 6 h, triethylammonium chloride (2.3 mol.) (unreacted amine, 0.7 mol.) and (sec-butylamino)chlorophenylborane, PhB(Cl)NH-sec-Bu (A) (18.5 g, 75%), b.p. 56°/0.005 mm (Found: B, 5.65; Cl, 17.65; N, 7.4%). After the original system had been shaken for 19 days, the yield of (A) was 51%, and triethylamine/dichlorophenylborane complex (4.3%) was isolated, m.p. 88–90°. (Found: C, 55.8; H, 8.0; B, 4.3; Cl, 26.4; N, 5.4. $\text{C}_{12}\text{H}_{20}\text{BCl}_2\text{N}$ calcd.: C, 55.4; H, 7.75; B, 4.2; Cl, 27.2; N, 5.4%)

TABLE 4

PREPARATION OF PRIMARY ALKYLAMMONIUM TETRAPHENYLBORATES, $\text{RNH}_3^+(\text{BPh}_4)$

RNH_3Cl	Yield	Found (%)		Calcd. (%)			
		weight (g)	(g)	(%)	B	N	
R				B	N	B	N
Pr	6.2	21.3	96.0	2.85	3.6	2.9	3.7
iso-Bu	7.0	22.0	96.5	2.8	3.5	2.8	3.6
sec-Bu	8.8	27.3	95.0	2.75	3.5		
tert-Bu	5.3	15.7	91.5	2.7	3.5		

TABLE 5

PYROLYSIS OF ALKYLAMMONIUM TETRAPHENYLBORAZES (1 MOL.)

R	RNH ₃ Ph ₄ B (g)	Temp. (°C)	Time (h)	C ₆ H ₆ (mols.)	Products separated by distillation of residue
Pr	3.8	150	2.0	0.85	Ph ₂ BNHPr (1.9 g), b.p. 175°/13 mm (Found: B, 4.95; N, 6.2; mol.wt., 228 ^b . C ₁₅ H ₁₉ BN calcd.: B, 4.85; N, 6.3%; mol.wt., 223.)
		180-200	3.0	1.10	
		up to 320 ^a	ca. 1	nil	
Pr	19.3	150-155	3.0	0.75	C ₆ H ₆ (0.25 mol.) removed at 60°/12 mm. PrNH ₂ ·BPh ₃ (1.5.1 g) (Found: B, 3.6; N, 4.5. C ₂₁ H ₂₄ BN calcd.: B, 3.6; N, 4.65%)
iso-Bu	15.5	120-130	1.5	0.36	[iso-BuNH ₂ (0.04 mol.) during pyrolysis at 160-245°] Ph ₂ BNH-iso-Bu (7.86 g), b.p. 310° (Found: B, 4.6; N, 5.8; mol.wt., 224 ^f . C ₁₆ H ₂₀ BN calcd.: B, 4.6; N, 5.9%; mol.wt., 237.), plus 1.0 g at 162°/10 mm.
		160-165	8.0	1.06	
		235-245	4.0	0.52	
		up to 340°	ca. 1	nil	
iso-Bu	4.1	125	5.0	nil	C ₆ H ₆ (0.98 mol.) and iso-BuNH ₂ (0.03 mol.) removed at 50°/12 mm. Impure iso-BuNH ₂ ·BPh ₃ complex (3.2 g) (Found: B, 3.5; N, 4.3. C ₂₂ H ₂₆ BN calcd.: B, 3.4; N, 4.4%)
tert-Bu	11.2	120-148	2.0	2.04	[tert-BuNH ₂ (0.60 mol.) evolved at 120-148°] BPh ₃ (0.07 mol.), m.p. 140°.
		up to 300°	3.0	0.22	
sec-Bu	20.6	135-150	1.5	0.81	[sec-BuNH ₂ (0.008 mol.) evolved at 135-200°] Ph ₂ BNH-sec-Bu (0.72 mol.), b.p. 175°/13 mm (Found: C, 81.1; H, 8.5; B, 4.5; N, 5.95. C ₁₆ H ₂₀ BN calcd.: C, 81.1; H, 8.45; B, 4.6; N, 5.9%), plus 0.23 mol. shown to be present in liquid having higher b.p. and from which Ph ₃ B (0.1 g), m.p. 142°, separated.
		190-200	4.0	1.18	
		up to 330 ^{ca}	ca. 1		

^a Residue refluxed. ^b Mol.wt. ebullioscopic (C₆H₆), 231; vapour pressure (CH₃C₆H₅, 37°), 228; cryoscopic in C₆H₆, 220. ^c Ebull. in C₆H₆.

The thermal transformation (PhBN-iso-Bu)₄ → (PhBN-iso-Bu)₃

The tetramer, (PhBN-iso-Bu)₄ (0.83 g) was heated to 250°, it melted to a pale red liquid. After ½ h it was allowed to cool, the resultant white solid analysed as the trimer, (PhBN-iso-Bu)₃ (0.81 g, 97.5%), m.p. 129°. (Found: B, 6.65; N, 8.9%; mol.wt. cryoscopic in benzene, 459, confirmed by mass spectrometry.)

Preparation of primary alkylammonium tetraphenylborates

Sodium tetraphenylborate (1 mol.) was mixed with alkylammonium chloride (1.1 mol.) in the minimum amount of water. The precipitate (Table 4) was dried in a vacuum for 7 days.

Pyrolysis of the tetraphenylborates. These systems were heated at the temperatures stated in Table 5, until volatile matter ceased to be evolved. Finally the residue was distilled.

Pyrolysis of n-propylamine/triphenylborane complex. The complex (13.6 g, 1 mol.) was heated at 200° for 3 h, when reaction appeared to have ceased. There was no apparent reaction whilst the system was heated to 320°. The distillate (3.59 g) comprised benzene (3.57 g, 1.02 mol.) and n-propylamine (0.5% yield). The residue afforded (n-propylamino)diphenylborane (9.1 g, 90.5% yield), b.p. 190°/22 mm. (Found: B, 4.9; N, 6.2%.)

Pyrolysis of (isobutylamino)diphenylborane. The borane, iso-BuNHBPh₂ (7.46 g, 1 mol.) was heated for 58 h under a short condenser held at 75–85° (Table 6). The

TABLE 6

PYROLYSIS OF (ISOBUTYLAMINO)DIPHENYLBORANE

Temp.	Time of heating (h)	C ₆ H ₆ evolved (mol.)	iso-BuNH ₂ evolved (mol.)
300–340°	19.5	0.224	0.021
340–370°	31.0	0.686	0.066
370–400°	7.5	0.165	0.001
Totals		1.075	0.088

gluey residue [4.07 g reduced to 3.99 g by extraction with petroleum (b.p. 30–40°)] (Found: B, 8.25; N, 8.4%; B/N, 1.27/1.) gave the amine on complete hydrolysis (0.5 h) with hot 2*N* NaOH.

ACKNOWLEDGEMENT

We wish to gratefully acknowledge the assistance give by Mr. G. GOUGH of the Distillers Co., Ltd., who provided the mass spectral data.

SUMMARY

The preparation and decomposition of alkylammonium trichlorophenylborates and tetraphenylborates is reported. The n-propylammonium trichlorophenyl-

borate decomposes on heating to give the B-trichloro-N-tri-n-propylborazine [(PrNBCl)₃] and the B-triphenyl-N-tri-n-propylborazine [(PrNBPh)₃], the relative amounts of each depending on the conditions. The isobutyl system in the presence of triethylamine gives a mixture of the trimer, (iso-BuNBPh)₃ and the tetramer, (iso-BuNBPh)₄. Alkylammonium tetraphenylborates on pyrolysis give the amine/triphenylborane complex and then the (alkylamino)diphenylborane.

REFERENCES

- 1 W. L. RUIGH, C. E. ERICKSON, F. C. GUNDERLAY, M. SEDLAK, P. A. VAN DER MEULEN, A. D. OLIN AND N. G. STEINBERG, *W.A.D.C. Tech. Rept.*, 55/26 Parts I to IV, 1955.
- 2 W. GERRARD, M. HOWARTH, E. F. MOONEY AND D. E. PRATT, *J. Chem. Soc.*, (1963) 1582.
- 3 B. R. CURRELL AND M. KHODABOCUS, *J. Inorg. Nucl. Chem.*, 28 (1966) 371.
- 4 M. F. LAPPERT AND M. K. MAJUMDAR, *Proc. Chem. Soc.*, (1962) 88; J. CASANOVA, JR., H. R. KIEFER, D. KUWADA, AND A. H. BOULTON, *Tetrahedron Letters*, (1965) 703; P. I. PAETZOLD, *Z. Anorg. Allgem. Chem.*, 326 (1963) 47.
- 5 K. NIEDENZU AND J. W. DAWSON, *Boron-Nitrogen Compounds*, Springer-Verlag, Berlin, 1965.
- 6 H. S. TURNER AND R. J. WARNE, *Proc. Chem. Soc.*, (1962) 69.
- 7 A. B. BURG AND J. BANUS, *J. Am. Chem. Soc.*, 76 (1954) 3903; T. C. BISSOT, D. H. CAMPBELL AND R. W. PARRY, *J. Am. Chem. Soc.*, 80 (1958) 1865.
- 8 J. E. BURCH, W. GERRARD AND E. F. MOONEY, *J. Chem. Soc.*, (1959) 2927.
- 9 J. A. SEMLYEN AND P. J. FLORY, *J. Chem. Soc.*, (A), (1966) 191.
- 10 B. R. CURRELL, W. GERRARD AND M. K. KHODABOCUS, *Chem. Commun.*, (1966) 77.

J. Organometal. Chem., 8 (1967) 411-419