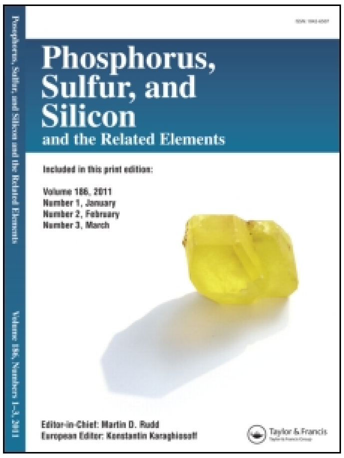


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

$(\mu_2)_2$-Dimercaptotetraborane(10), $H_2B(\mu_2\text{-SR})_2B_3H_6$

Herbert Binder[a]; Paraschos Melidis[a]; Serdar Söylemez[a]; Gernot Heckmann[a]
[a] Institut für Anorganische Chemie der Universität Stuttgart, Stuttgart 80

To cite this Article Binder, Herbert , Melidis, Paraschos , Söylemez, Serdar and Heckmann, Gernot(1992) '$(\mu_2)_2$-Dimercaptotetraborane(10), $H_2B(\mu_2\text{-SR})_2B_3H_6$', Phosphorus, Sulfur, and Silicon and the Related Elements, 64: 1, 1 — 6
To link to this Article: DOI: 10.1080/10426509208041121
URL: http://dx.doi.org/10.1080/10426509208041121

Phosphorus, Sulfur, and Silicon, 1992, Vol. 64, pp. 1–6
Reprints available directly from the publisher
Photocopying permitted by license only

$(\mu_2)_2$-DIMERCAPTOTETRABORANE(10), $H_2B(\mu_2\text{-}SR)_2B_3H_6$

HERBERT BINDER, PARASCHOS MELIDIS, SERDAR SÖYLEMEZ AND GERNOT HECKMANN
Institut für Anorganische Chemie der Universität Stuttgart,
Pfaffenwaldring 55, D-7000 Stuttgart 80

Abstract B_4H_{10} reacts with mercaptans by splitting off H_2 to form $H_2B(\mu_2\text{-}SR)_2B_3H_6$ **III**. An unstable adduct $B_4H_{10}\cdot RSH$ **I** was identified as a precursor of **III**. The ^{11}B NMR spectra of **III** showed that the B1,3 signals coalesce at 70°C indicating a rapid inversion. On cooling however, the exo-exo, endo-endo and exo-endo invertomers were detected.

Introduction

Like diborane, tetraborane(10) has a structure in which there are two BH_2 units, each of which is linked to the rest of the molecule by two BHB bridges. This structural similarity is reflected in the types of reaction it undergoes. For example, it is susceptible to attack by nucleophiles; Lewis bases cleave the BHB bridging units in a manner reminiscent of their effect on diborane. A general reaction for preparing adducts of the B_3H_7 group involves bridge cleavage of B_4H_{10} [1].

$$B_4H_{10} + 2\,L \longrightarrow B_3H_7L + BH_3L \qquad (1)$$

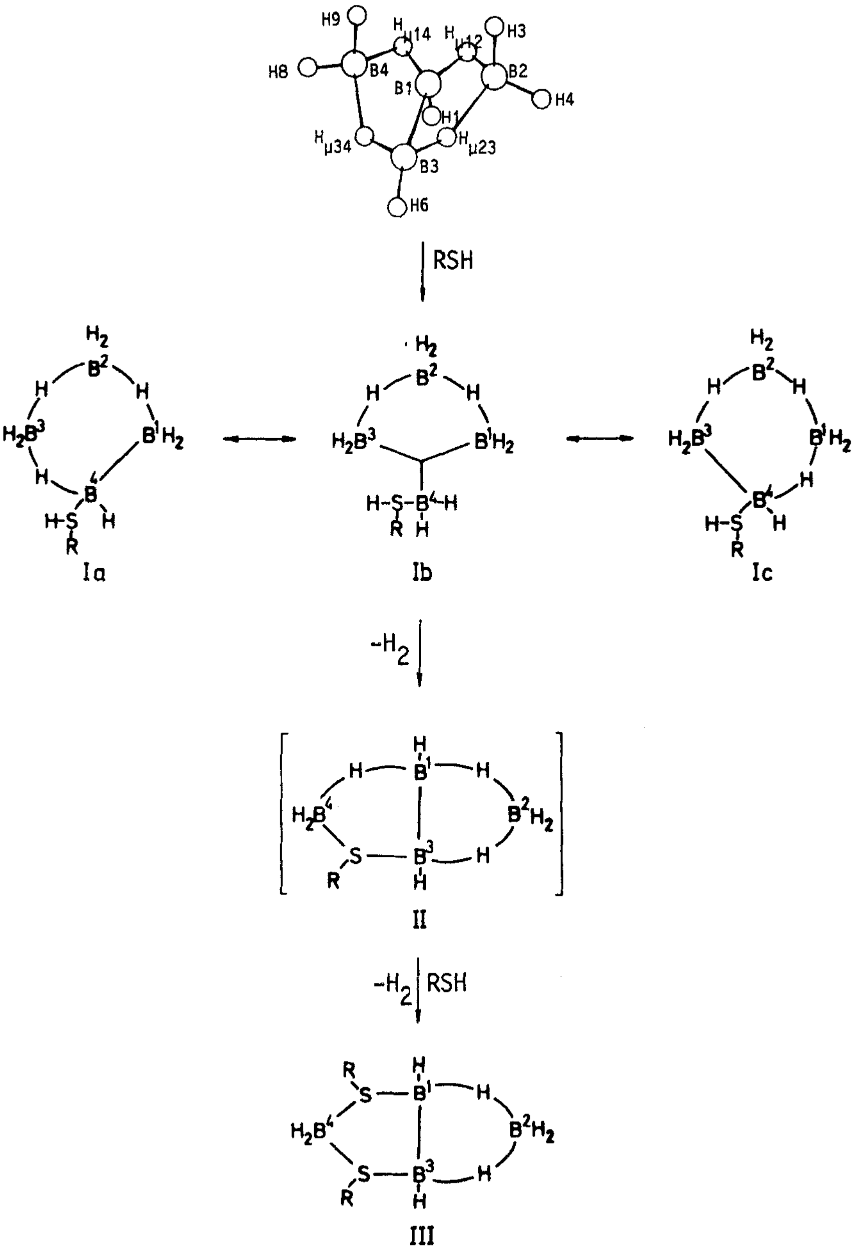
These reactions are believed to proceed via initial attack on boron-2 or -4 (the borons of the BH_2 groups), which are slightly more positively charged than the other borons, the important difference being that they have a terminal $B(\delta+)\text{-}H(\delta-)$ group whereas borons-1 and 3 have a B-B link.

Results and Discussion

When B_4H_{10} was treated with mercaptan B_4H_{10}•RSH formed immediately according to (2).

$$B_4H_{10} + RSH \longrightarrow \underset{\textbf{I}}{B_4H_{10}\cdot RSH} \qquad (2)$$

The BH_2 group is the most susceptible to nucleophilic attack. The adducts thereby formed are unstable intermediates in the preparation of the title compound. The adduct **I** was characterized by its ^{11}B NMR spectrum which showed signals at -7.2, and -35.8 ppm with an intensity ratio of 3:1. In the $^{11}B\{^1H\}$ NMR spectrum, the half width of the two signals are reduced; this indicates $^{11}B^1H$ coupling and rapid exchange of bridging and terminal hydrogen atoms, apparently because alternative structures (**Ia-c**) are possible, Scheme 1. Reaction of B_4H_{10} with the Lewis base RSH is facilitated by rearrangements involving a reduction in the number of bridging hydrogen atoms; such rearrangements are a consequence of the fact that an extra pair of bonding electrons cannot be accomodated without structural modification of the tetraborane(10). The adducts **I** represent only the first stage in the interaction of the donor molecules RSH with B_4H_{10}. Evidently **I** loses hydrogen readily whereby a bridging hydrogen atom is substituted by a RS group with formation of the intermediate **II**. The reaction may well occur between the acidic SH hydrogen and a hydridic hydrogen atom of a BH_2 group. The new intermediate **II** reacts even more readily with a second RSH thus leading to the formation of **III** in which two bridging H atoms ($H_{\mu14}$, $H_{\mu34}$) are replaced by two RS groups, Scheme 1. That the terminal hydrogen atom positions as well as the other bridging H positions remain unaffected is shown by the ^{11}B NMR spectrum. There was no evidence for the formation of either of the isomers in which $H_{\mu14}$, $H_{\mu12}$ or $H_{\mu14}$, $H_{\mu23}$ was replaced by RS groups. The ^{11}B NMR spectrum of bis (μ_2-methylmercapto)tetraborane(10) **IIIa** at room temperature consists of several overlapping multiplets. On warming the sample to 70°C a NMR spectrum is obtained (Fig.1) whose peaks have areas which point to an unambiguous assignment of a static and dynamic part of the molecule.



SCHEME 1. Proposed reaction sequence leading to the formation of $(\mu_2)_2$-dimercaptotetraborane(10) **III.**

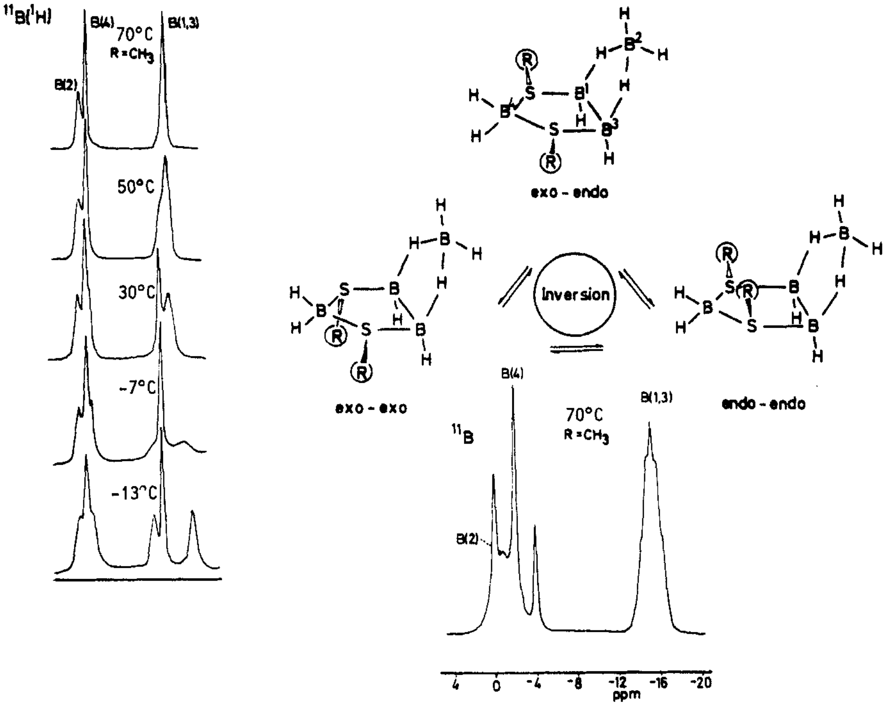


FIGURE 1. ^{11}B and $^{11}B\{^1H\}$ NMR spectra (64.21 MHz, toluene-d_8) of $H_2B(\mu_2\text{-}SCH_3)_2B_3H_6$ **IIIa** for a range of temperature.

The ^1H decoupled spectrum shows the intensity ratio 1:1:2, the triplet of intensity 1 being assigned to B4 and the septet of intensity 2 with the smaller $^{11}B^1H$ coupling constant to B1B3; the $B1B2B3H_6$ part of the molecule is fluxional and, moreover, the expected septet for B2 (intensity 1) is not resolved and being overlapped by the triplet of B4. The change in the ^{11}B NMR spectrum on warming clearly shows the existence of invertomers. Variable temperature ^{11}B NMR studies have shown considerable barriers to inversion of the RS group between two adjacent boron atoms. For this reason we only consider the ^1H decoupled B1B3 resonance signal which is well separated from those of B2 and B4. The broadened singlet at 30°C (Fig.1) begins to split into two signals at -7°C, which are finally resharpened at -13°C. The two new signals are assigned to the exo-exo and endo-endo invertomers whereas the unchanged sharp signal represents the exo-endo invertomer which is equal to the average of the chemical shifts of B1 and B3. The unsplit broadened singlet at 30°C further demonstrates a fast equilibrium between the exo-exo and endo-endo invertomers. The collapse of the three signals on warming the sample from -13°C to 70°C is due to this fast inversion process. When R = Bu^t no inversion is observed which is obviously because steric hindrance only allows formation of the exo-exo isomer. With the ^{11}B spectral data it is possible to calculate the activation energy for inversion in **III**, Table 2. The ^{11}B NMR data for a series of compounds of type **III** are summarized in Table 1.

TABLE 1 ^{11}B NMR data for $H_2B(\mu_2\text{-}SR)_2B_3H_6$ (64.21 MHz, toluene-d_8)

R		$\delta^{11}B(B4)$ [ppm]	$^1J(^{11}B^1H)$ [Hz]	$\delta^{11}B(B2)$ [ppm]	$\delta^{11}B(B1B3)$ [ppm]	$^1J(^{11}B^1H)(B1B3)$ [Hz]
CH_3	**IIIa**	-2.0 (t) 70°C	125	-0.9 unres.	-14.7 (sept)	32
C_2H_5	**IIIb**	-4.5 (t) 70°C	125	-1.1 unres.	-16.0 (sept)	30
Pr^i	**IIIc**	-6.6 (t) 70°C	120	-1.0 unres.	-18.4 (sept)	30
Bu^t	**IIId**	-11.5 (t) 25°C	125	-1.8 unres.	-22.2 (sept)	30
C_6H_5	**IIIe**	-7.0 (t) 25°C	120	-5.0 unres.	-19.5 (unres.)	-

t = triplet; sept = septet

TABLE 2 Activation energies E_a of the exo-exo/endo-endo inversion of $H_2B(\mu_2\text{-}SR)_2B_3H_6$

Compound R		T_c [K]	$\Delta\nu$ [Hz]	E_a [$Kcal\cdot mol^{-1}$]
CH_3	**IIIa**	290	420	12.8
C_2H_5	**IIIb**	290	402	12.8
Pr^i	**IIIc**	290	308	13.0
Bu^t	**IIId**	-	-	-
C_6H_5	**IIIe**	290	190	13.3

T_c = coalescence temperature; $\Delta\nu$ = chemical shift difference of B1B3 of the exo-exo/endo-endo invertomers

The compounds **IIIa, c, d, e** exhibit an electron-impact mass spectrum containing cut offs at m/e 146 $\{M\}^+$ **IIIa**; 199 $\{M-2H\}^+$ **IIIc**; 228 $\{M-2H\}^+$ **IIId**; 270 $\{M\}^+$ **IIIe**; the parent envelopes are consistent with the presence of 4 boron atoms. The compound **IIIb** polymerizes in the solvent free state and does not give a mass spectrum at 70 eV/330 K.

As part of this investigation we have recently studied the reactions of B_4H_{10} with a variety of bifunctional mercaptans which lead to transannularly bridged $(\mu_2)_2$-dimercaptotetraborane(10) derivatives [2]; these are structurally related to **III**. The new compounds reported here together with the recently synthesized compound $(\mu\text{-}Me_2N)_2B_4H_8$ [3] are the first examples of bridge substituted B_4H_{10} derivatives.

Experimental

In a typical reaction 4 mmol of the respective mercaptan are added tropwise at room temperature to a solution of 2.0 mmol of B_4H_{10} in CH_2Cl_2 [4]. Hydrogen is evolved in this reaction. After stirring for 30-45 min the reaction is complete. The remaining reaction mixture is examined ^{11}B NMR spectroscopically. Side products can be $(RSBH_2)_n$.

This work was supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie, and by Bayer AG.

REFERENCES

[1] S.G.Shore, in "Boron Hydride Chemistry" (E.L.Muetterties, ed.), Chapter 3, p.132, Academic Press, New York, San Francisco, London, 1975.
[2] H.Binder, P.Melidis, S.Söylemez, and G.Heckmann, J.Chem.Soc., Chem.Commun. in press.
[3] D.F.Gaines and J.C.Kunz, Inorg.Chem. 27, 1839 (1988).
[4] H.Binder and B.Brellochs, Z.Naturforsch. 43b, 648 (1988).