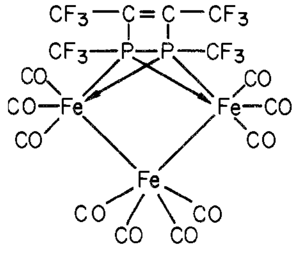
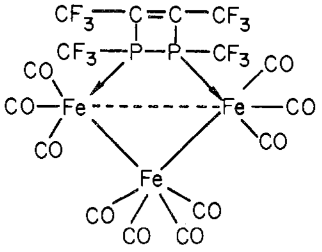


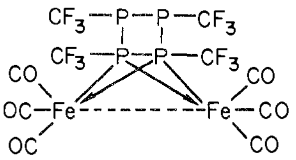
4a



4b

tene ring and an iron-iron bond as indicated in **4b**. The electronic spectrum of **4** (Table II) displays pronounced shifts compared with free **1**;[6] however, this evidence *per se* is not sufficient to establish the scission of the P-P bond. On the basis of these initial observations it would appear that the ligand behavior of **1** is quite different from that of 1,2-bis(trifluoromethyl)dithietene since there are no sulfur analogs of **3** or **4**.[2] Compound **4** is also noteworthy from the standpoint that all previously reported $Fe_3(CO)_{10}$ complexes involve bridging CO groups.[8]

The reaction of the cyclotetraphosphine, $(CF_3P)_4$, with $Fe_2(CO)_9$ results in a product of empirical composition $(CF_3P)_2Fe(CO)_3$. If the intense mass spectral peak at *m/e* 680 (Table I) is assigned to the parent ion, the molecular formula of **5** is $(CF_3P)_4Fe_2(CO)_6$. The *m/e* 680 peak is considered to be the parent peak because West, *et al.*,[3,9] have demonstrated that several other compounds of the general type $(RM)_4Fe_2(CO)_6$ (M = P, As; R = alkyl, aryl) exhibit intense molecular ion peaks. The correctness of these mass spectral assignments was confirmed by a subsequent X-ray crystallographic study[10] of $(CH_3As)_4Fe_2(CO)_6$. One additional mass spectral feature which **5** shares in common with other $(RM)_4Fe_2(CO)_6$ compounds[3,9] is a fragment corresponding to the species $(RM)_4Fe_2^+$. Furthermore, like the compounds reported by West, *et al.*,[3,9] **5** exhibits four intense ir bands in the C-O stretching region. The latter observation appears to be a characteristic feature of phosphido and arsenido bridging[11] and may be due to coupling between the two $Fe(CO)_3$ groups. By analogy with the bis(arsenido)-bridged structure of $(CH_3As)_4Fe_2(CO)_6$ the most reasonable structure for **5** is



5

The above structure is also consistent with the fact that two equally intense resonances are observed in the ^{19}F nmr spectrum of **5**. The "deceptively simple" appearance[12] of these resonances is due to the second-order nature of the nuclear spin coupling within the $(CF_3P)_4$ moiety.

Registry No. $Fe_2(CO)_9$, 15321-51-4; $(CF_3)_2C_2P_2(CF_3)_2Fe(CO)_4$, 39262-37-8; $(CF_3)_2C_2P_2(CF_3)_2Fe_3(CO)_{10}$, 39153-36-1; $(CF_3P)_4Fe_2(CO)_6$, 39153-37-2.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP-28634) and the Robert A. Welch Foundation for generous financial support.

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Displacement of Diborane from Pentaborane(9) by Strong Molecular Bases

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Received November 15, 1972

It has been demonstrated that the weak base dimethyl sulfide can act upon B_5H_9 to displace a BH_3 group as diborane or $(CH_3)_2SBH_3$.[1] It appeared that the driving force of the reaction was the attachment of $(CH_3)_2S$ to the remarkably strong Lewis acid B_4H_6 (through cleavage of two B-H-B bridges to remove one BH_3 from B_5H_9); then the resulting $(CH_3)_2S$-B_4H_6 complex would rapidly convert to unintelligible resins. The reaction thus was related to earlier work on the action of $(CH_3)_2NBH_2$ upon B_5H_9, whereby the displaced BH_3 group appeared as $(CH_3)_2NB_2H_5$.[2] More generally, it was assumed that any strong molecular base would capture each BH_3 group as soon as it was free, so that proof of the initial displacement of BH_3 from B_5H_9 would be more difficult than in the dimethyl sulfide case.

It now is found, however, that the relatively strong bases ammonia and methylamine, reacting with B_5H_9 during sudden heating at 160-180°, can displace as much as 0.25 B_2H_6 per B_5H_9 consumed. Thus we have interesting reactions in which strong bases act to liberate the strong Lewis acid diborane; that is, bases strong enough for irreversible attachment to BH_3 actually liberate this Lewis acid by action upon B_5H_9.

The final volatile products of these reactions included the borazine $(HNBH)_3$ or $(CH_3NBH)_3$ and the unstable μ-aminodiborane $H_2NB_2H_5$ or $CH_3NHB_2H_5$.[3,4] Thus steps such as the following may be suggested for all such reactions

$$n\mathrm{NH_3} + \mathrm{B_5H_9} \rightarrow \mathrm{BH_3} + \mathrm{B_4H_6}\cdot n\mathrm{NH_3} \rightarrow \text{resins} + \mathrm{H_2} \tag{1}$$

$$\mathrm{NH_3} + \mathrm{BH_3} \rightarrow \mathrm{H_3NBH_3} \rightarrow \mathrm{H_2} + \mathrm{H_2NBH_2} \tag{2}$$

$$\mathrm{H_2NBH_2} + \mathrm{BH_3} \rightarrow \mathrm{H_2NB_2H_5} \tag{3}$$

$$6\mathrm{H_2NB_2H_5} \rightarrow 3\mathrm{B_2H_6} + 2(\mathrm{H_2NBH_2})_3 \tag{4}$$

$$3(\mathrm{H_2NBH_2})_3 \rightarrow 3\mathrm{H_2} + (\mathrm{HNBH})_3 \tag{5}$$

Steps 1-3 would be fast and irreversible, leading to products known to be unstable in the sense of steps 4 and 5. On the assumption that these are the only processes which occur and that step 4 is complete, one would predict the formation of 0.25 B_2H_6 per B_5H_9 consumed, in good agreement with the results for the ammonia reaction. For methylamine, however, step 4 is far from complete (because the μ-aminodiborane is more stable), but the yield of diborane still can

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Table I. Base–Pentaborane(9) Flash Reactions

mmol of reactants[a]		Time, min	Temp, °C	Tube vol, ml	mmol of products			Empirical formula of residue
B_5H_9	Base				H_2	B_2H_6	Others	
3.362 −1.600 1.762	6.56 NH_3	4	180	80	10.756	0.184	1.07 $(HNBH)_3$, etc.	
2.454 −1.291 1.163	4.539 NH_3	5	163	80	6.634	0.292	0.596 $(HNBH)_3$ 0.067 $H_2NB_2H_5$ 0.09 B in X	$N_6B_8H_{11}$
2.717 −0.915 1.802	5.371 CH_3NH_2	10	160	80	(Lost)	0.460	1.065 $(CH_3NBH)_3$ 1.053 $CH_3NHB_2H_5$	$(CH_3N)_2B_5H_x$
2.072 −0.210 1.862	5.635 CH_3NH_2	5	170	70	4.707	0.296	1.052 $(CH_3NBH)_3$ 1.851 $CH_3NHB_2H_5$	$CH_3NB_2H_7$
0.847 −0.619 0.228	0.872 $CH_3NH_2 \cdot BH_3$ 0.029 CH_3NH_2	4	167	50	0.928	0.058	0.060 $(CH_3NBH)_3$ 0.506 $CH_3NHB_2H_5$	$(CH_3N)_2B_7H_{10}$
0.981 −0.177 0.804	2.101 CH_3NH_2 (combined <25°)	3	175	50	1.512	0.125	0.330 $(CH_3NBH)_3$ 0.887 $CH_3NHB_2H_5$	$(CH_3N)_2B_9H_{12}$
3.310 −0.773 2.537	6.708 $(CH_3)_2NH$	4	180	80	1.783	Nil	3.422 $(CH_3)_2NB_2H_5$ 2.736 $(CH_3)_2NBH_2$ 0.125 $[(CH_3)_2N]_2BH$	$(CH_3)_2NB_{10}H_{11}$?
5.230 −2.083 3.147	9.464 $(CH_3)_2NH$	5	150	80	1.859	Nil	4.769 $(CH_3)_2NB_2H_5$ 3.681 $(CH_3)_2NBH_2$ 0.085 $[(CH_3)_2N]_2BH$	$[(CH_3)_2N]_2B_5H_6$
2.352 −0.107 2.245	4.797 $(CH_3)_3N$	2	175	80	0.647	Nil	3.177 $(CH_3)_3NBH_3$	$(CH_3)_3NB_5H_{5.8}$
2.341 −1.334 1.007	2.427 $(CH_3)_3N$	1	170	50	1.057	Nil	1.329 $(CH_3)_3NBH_3$ 0.013 $(CH_3)_3NB_3H_7$	$(CH_3)_3NB_{4.8}H_{5.3}$
2.124 −1.130 0.994	4.596 CH_3PH_2 −1.611 2.985	2	190	50	2.388	Nil	0.272 $CH_3PH_2 \cdot BH_3$	$(CH_3P)_4B_7H_{13}$
1.892 −0.262 1.630	3.007 $(CH_3)_2PH$	3	175	50	(Lost)	0.009	0.887 $(CH_3)_2PH \cdot BH_3$ Trace $[(CH_3)_2PBH_2]_3$	$[(CH_3)_2P]_2B_7H_x$
2.811 −1.390 1.421	1.554 $(CH_3)_2PH$	3	178	50	3.040	0.011	0.095 $(CH_3)_2PH \cdot BH_3$	$[(CH_3)_2P]_3B_{14}H_{16}$
1.497 −0.361 1.136	1.689 $(CH_3)_3P$	3	173	50	1.575	0.006	0.373 $(CH_3)_3PBH_3$	$[(CH_3)_2P]_2B_8H_9$
0.395 −0.275 0.120	0.367 $(CH_3)_3PBH_3$ −0.180 0.187	10	166	15	0.378	0.0027		$(CH_3)_3PB_{4.2}H_{4.7}$

[a] Negative numbers represent unconsumed reactants.

be as high as 0.25 per B_5H_9 consumed. Hence it must be assumed that some B_4H_6 units liberate a second BH_3 group, as is known to occur to some extent in the liquid-phase $(CH_3)_2NBH_2$-B_5H_9 reaction.[2]

Indeed, with trimethylamine, for which the stability of the BH_3 complex would block reactions beyond the first part of step 2, one gets as many as 1.4 $(CH_3)_3NBH_3$ per B_5H_9 consumed. With dimethylamine, which cannot react beyond step 3 (because the aminodiborane is stable and the B_5H_9-assisted trimerization of the borazane occurs only in the liquid phase),[2] there is yet far more efficient conversion to volatile N-B-H compounds. Thus neither of these amines could liberate B_2H_6 from B_5H_9.

With $(CH_3)_3P$ one again would expect no reaction beyond the first part of 2, and so also with $(CH_3)_2PH$ because $(CH_3)_2PH \cdot BH_3$ produces H_2 too slowly at the temperatures here employed.[5] Thus it is curious that traces of diborane actually are found when either these phosphines or $(CH_3)_3PBH_3$ flash-react with B_5H_9 to form resins.

Experimental Methods and Results. For the results shown in Table I, the weighed or gas-measured reactants were condensed from the high-vacuum line into sealable Pyrex tubes of 25-mm diameter, with 1-mm walls for rapid heat response. Each sealed tube, with the reactants intact at −196°, was suddenly immersed in an oil bath, and the temperature was read as soon as it became sensibly constant. After a few minutes, the tube was immersed in liquid nitrogen. A vacuum tube opener was used to bring the tube contents to a series of −196° U traps, through which H_2 was delivered to the automatic Sprengel pump[6] for collection and measurement. The other volatile components were separated as well as possible by high-vacuum fractional condensation and identified by their known properties. Diborane was the only product passing a −150° U trap and condensing at −196°; for trace yields, its intense and highly characteristic infrared spectrum in the 2450-2500-cm^{-1} range was used for quantitative confirmation. Isolation was possible for all products except those having volatility near that of B_5H_9. For these, weighed mixtures were analyzed quantitatively by measuring the relative areas of their ^{11}B nmr signals at 32.1 Mc. The borazines

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$(HNBH)_3$ and $(CH_3NBH)_3$, as well as $(CH_3)_2NB_2H_5$, showed spectra agreeing well with the literature.[7] The unstable aminodiborane $H_2NB_2H_5$ showed the characteristic aminodiborane pattern,[7] with δ 43.9 ppm (upfield of methyl borate); $J_1 = 130$ cps; $J_2 = 29$ cps. A similar pattern for $CH_3NHB_2H_5$ appeared at δ 40.6 ppm; $J_1 = 129$ cps; $J_2 = 29$ cps. The ammonia reaction yielded a trace of a substance X, for which δ is 6.6 ppm ($J = 165$ cps, triplet); according to the literature, this could not have been $(H_2NBH_2)_3$, for which δ is $11.3 + 18.2 = 29.5$ ($J = 100$ cps).[8] However, the CH_3NH_2 reaction yielded a trace of slightly volatile crystals which could have been $(CH_3NHBH_2)_3$.

The results were not very different when the reactants CH_3NH_2 and B_5H_9 were first combined below 25° and then flash heated at 175°. Possibly much of the adduct was dissociated before step 1 made much progress, or step 1 could have gone through adduct formation in any case. Conjectures about the specific processes constituting step 1 do not seem useful.

It is interesting that the flash reaction of $CH_3NH_2 \cdot BH_3$ with B_5H_9 consumed a smaller proportion of B_5H_9 than the more direct CH_3NH_2–B_5H_9 reaction, but gave the same yield of B_2H_6 per B_5H_9 consumed. The chief difference was a far higher yield of $CH_3NHB_2H_5$ at the expense of $(CH_3NBH)_3$. In this case it is possible that the base which actually attacked the B_5H_9 was at least mostly CH_3NHBH_2.

The weakest base here employed was CH_3PH_2, which was far from all consumed by the excess B_5H_9. Then since the complex $CH_3PH_2 \cdot BH_3$ is stable against loss of BH_3, no diborane was obtained. The low yield of the BH_3 complex could have been due to loss of H_2 to form the CH_3PHBH_2 high polymers.[5]

It is interesting that one trimethylamine experiment yielded a trace of what seemed to be $(CH_3)_3N \cdot B_3H_7$, detected as an ^{11}B nmr signal at δ 33 ppm (lit.[9] δ $15 + 18 = 33$ ppm, unresolved). It could not be attributed to a B_5H_{11} impurity in the B_5H_9, which had been stored in glass for more than 12 years and was strictly pure.

The nonvolatile products of these experiments conform well to earlier observations of resins made of similar components.[10] They were destructively dissolved by acetone or partially extractable by benzene, in which they showed broad and unresolved ^{11}B nmr signals. Especially those involving phosphorus showed thermoplastic character on heating *in vacuo*: small evolution of volatiles caused large, viscous bubbles. There seemed to be plasticizing components of fairly low molecular weight range, sublimation of which at 250–300° left light brown, fragile, glassy residues richer in boron and poorer in hydrogen than average formulas such as (base)B_4H_5. Such glasses retained their light colors even above 400°, where the evolved noncondensable gases began to include methane. Such resins, showing more intrinsic thermal stability than the usual $(BH)_x$ polymers, seem worthy of further study if and when appropriate techniques become available.

Registry No. B_5H_9, 19624-22-7; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $CH_3NH_2 \cdot BH_3$, 1722-33-4; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; CH_3PH_2, 593-54-4; $(CH_3)_2PH$, 676-59-5; $(CH_3)_3P$, 594-09-2; $(CH_3)_3P \cdot BH_3$, 1898-77-7; H_2, 1333-74-0; B_2H_6, 19287-45-7; $(NHBH)_3$, 6569-51-3; $H_2NB_2H_5$, 39046-41-8; $(CH_3NBH)_3$, 1004-35-9; $CH_3NHB_2H_5$, 27073-27-4; $(CH_3)_2NB_2H_5$, 23273-02-1; $(CH_3)_2NBH_2$, 1838-13-7; $[(CH_3)_2N]_2BH$, 2386-98-3; $(CH_3)_3N \cdot BH_3$, 75-22-9; $(CH_3)_3N \cdot B_3H_7$, 12076-72-1; $H_3CPH_2 \cdot BH_3$, 14975-23-6; $(CH_3)_2PH \cdot BH_3$, 4268-35-3.

Acknowledgment. The generous support of this research by the Office of Naval Research is gratefully acknowledged.

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Iodination of Dicarbahexaboranes

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Received November 20, 1972

The chlorination or bromination of *nido*-4,5-dicarbahexaborane(8) ($C_2B_4H_8$) leads only to the enantiomorphs 3-$XC_2B_4H_7$ and 6-$XC_2B_4H_7$; the 1- or 2-halogenated derivatives seem to be excluded.[1] For the somewhat analogous B_5H_9, it appears that 1-halogenation occurs but that conversion to the 2 isomer is fairly easy. In contrast, 1-IB_5H_8 is decidedly more stable than 2-IB_5H_8.[2] Thus, it seemed that iodination of $C_2B_4H_8$ might produce 1-$IC_2B_4H_7$, since the ^{11}B nmr spectra indicate the 1-B atoms of B_5H_9 and $C_2B_4H_8$ to be very similar. In fact, however, we now have found the 25°, Al_2I_6-catalyzed iodination of $C_2B_4H_8$ to be like the chlorination or bromination: only the enantiomorphic mixture of 3-$IC_2B_4H_7$ and 6-$IC_2B_4H_7$ is obtained. The similar iodination of the *closo*-carborane $C_2B_4H_6$ yields only 2-$IC_2B_4H_5$; here only one species is possible, and no diiodo derivative could be observed.

Iodination of the *nido*-Carborane. The carborane $C_2B_4H_8$ was treated with iodine in a sealed tube wherein a trace of Al_2I_6 had been made from aluminum powder and iodine (24 hr at 180°). The iodination proceeded during 24 hr at 20° (with occasional shaking); the end of the process was indicated by a color change from violet to light brown. One H_2 was formed per I_2 consumed, and the yield of the colorless liquid $IC_2B_4H_7$ represented 25% of the consumed $C_2B_4H_8$. No HI was found, apparently because it would have been removed rapidly by reaction with $IC_2B_4H_7$ (but not $C_2B_4H_8$ at all) to form H_2. The main nonvolatile product had an ^{11}B nmr spectrum too broad and complex for interpretation. Boron triiodide was a minor by-product (^{11}B nmr spectrum, a singlet at 26.3 ppm upfield of methyl borate); it was easily removed when the iodocarborane was purified by high-vacuum fractional condensation.

The product $IC_2B_4H_7$ showed an equilibrium vapor pressure of 3.5 mm at 28°. Its vapor-phase molecular weight was 201.2 (calcd, 201.1). Its mass spectrum showed a parent ion with the right isotopic pattern for a 4-boron

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