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Complex Formation by 1,2-Bis(dimethylarsino)tetrafluorocyclobutene and Its Diphenylphosphino Analog[1]

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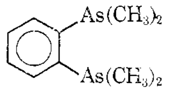
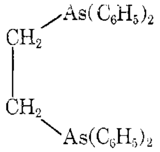
A survey of the chelating properties of the novel compounds $R\overline{C{=}CRCF_2CF_2}$ [R = $(CH_3)_2As$ (ffars) or $(C_6H_5)_2P$ (ffos)] is described. They form complexes such as $ffosHgCl_2$, $ffosPdCl_2$, $ffosPtCl_2$, and $(ffars)_2RhCl_3$ but do not easily coordinate with salts of metals of the first transition series. They react more readily with metal carbonyls than unfluorinated di(tertiary phosphines or arsines) to give compounds such as $ffosCr(CO)_4$, $ffarsMo(CO)_4$, and $ffosNi(CO)_2$. Under mild conditions ffars displaces all of the carbonyl groups from nickel carbonyl.

Introduction

The chelating properties of di(tertiary arsines) such as *o*-phenylenebis(dimethylarsine) (I), 1,2-bis(diphenylarsino)ethane (II), and related di(tertiary phosphines)

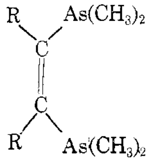


I

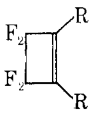


II

have been extensively studied.[2] The metal complexes of unsaturated tertiary phosphines and arsines such as 2-allylphenyldiphenylphosphine are also being investigated.[3] However, it seemed that replacement of the *o*-phenylene group in I by an electronegative alicyclic group might give rise to significant changes in properties. Furthermore, since nothing was known of the complexing abilities of di(tertiary arsine) derivatives of ethylene such as III it seemed desirabe to synthesize compounds of this type for study. These two interesting structural variations have been combined in the same molecule as the result of the synthesis of 1,2-bis(dimethylarsino)tetrafluorocyclobutene[4] (IVa)



III



IVa, R = $As(CH_3)_2$
b, R = $P(C_6H_5)_2$

and the corresponding diphenylphosphino compound[5] (IVb). The di(tertiary arsine), IVa (ffars), has already shown unusual reactivity in forming the complex $ffars[Fe(CO)_3]_2$ in which the double bond coordinates with one $Fe(CO)_3$ group while the two arsenic atoms bond to the other.[6] It seems that ffos (IVb) reacts similarly with iron and ruthenium carbonyls.[7] The present paper is concerned with a survey of the reactions of ffos and ffars.

Recently *trans*-1,2-bis(dimethylarsino)ethylene has been prepared and it has been found to coordinate with Pt(II) in the *trans* configuration. However, irradiation can cause isomerization to the chelated derivatives of the *cis*-di(tertiary arsine) III (R = H).[8] Reaction of the *trans* ligand with Ni(II) and Pd(II) results in the direct formation of complexes of the *cis* ligand.[8] It should also be mentioned here that 1,2-bis(dimethylarsino)-3,4,5,6-tetrafluorobenzene (F-diars), a compound related to both diars (I) and ffars (IVa), has recently been prepared and preliminary results indicate that the effect of the fluorine atoms on the coordinating properties of the arsenic atoms is much more marked than might have been expected.[9]

Experimental Section

The preparation of the two ligands ffos and ffars has been described.[4,5] The di(tertiary arsine) was also obtained by heating dimethylarsine with 1,2-dichlorotetrafluorocyclobutene in a sealed tube at 130°, in the presence of diphenylamine. Infrared spectra were obtained using Perkin-Elmer Model 21 and 421 instruments, and nmr spectra were run using Varian A-60, HR-60, and HA-100 spectrometers. Chemical shifts are reported in ppm downfield from external tetramethylsilane (^1H) and upfield from external trichlorofluoromethane (^{19}F). Analytical and some spectroscopic data for new compounds are listed in Tables I–III and in the text below. Microanalyses were done by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany, by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., by Drs. F. and A. Pascher, Microanalytisches Laboratorium, Bonn, West Germany, and by Mr. P. Borda, Chemistry Department, University of British Columbia.

(1) **Complexes of 1,2-Bis(diphenylphosphino)tetrafluorocyclobutene (ffos).**—(a) Molybdenum carbonyl (0.6 g) and ffos (0.3 g) were refluxed in benzene (50 ml) for 6 hr. The solution became yellow after 5 min and brown after 6 hr. The solvent was

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(1) Presented in part at the Northwestern Regional Meeting of the American Chemical Society, Vancouver, British Columbia, Canada, June 1966.

(2) (a) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964); (b) T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

(3) L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, **5**, 2213 (1966), and references quoted therein.

(4) W. R. Cullen, P. S. Dhaliwal, and G. E. Styan, *J. Organometal. Chem.* (Amsterdam), **6**, 633 (1966).

(5) W. R. Cullen, D. S. Dawson, and P. S. Dhaliwal, *Can. J. Chem.*, **45**, 683 (1967).

(6) F. W. B. Einstein, W. R. Cullen, and J. Trotter, *J. Am. Chem. Soc.*, **88**, 5670 (1966); F. W. B. Einstein and J. Trotter, *J. Chem. Soc., Sect. A*, 824 (1967).

(7) W. R. Cullen and C. J. Stewart, unpublished work.

(8) M. A. Bennett, G. J. Erskine, and J. Wild, in preparation.

(9) N. V. Duffy, A. J. Layton, R. S. Nyholm, D. Powell, and M. L. Tobe, *Nature*, **212**, 177 (1966).

evaporated and the crude product was recrystallized from toluene–ethanol to give the bright yellow complex ffosMo(CO)$_4$ in 63% yield.

(b) Chromium carbonyl (0.6 g) and ffos (0.3 g) were refluxed in toluene (10 ml) for 13 hr. On cooling the brown solution to 0° chromium carbonyl precipitated. The toluene solution was evaporated and the crude product was recrystallized from benzene–ethanol to give the orange complex ffosCr(CO)$_4$ in 85% yield.

(c) Tungsten carbonyl (0.6 g) and ffos (0.3 g) were refluxed in toluene (10 ml) for 6 hr. The solvent was removed and X-ray powder photographs of the remaining solid indicated that very little, if any, reaction had occurred.

(d) Nickel carbonyl (5 ml) and ffos (0.2 g) on mixing in a sealed tube at 20° gave a blue solution. The volatile contents of the tube were removed after 20 hr at 20° and the solid residue was extracted with benzene to give 0.1 g of benzene-soluble orange-yellow crystals. Those were recrystallized 3 times from ethanol–benzene and finally purified by chromatography on alumina using benzene as eluent. The final yield of the pure complex ffosNi(CO)$_2$ was 0.005 g.

(e) When a solution of ffos (0.3 g) in hot acetone was added to a hot aqueous solution of ammonium tetrachloropalladate(II) (0.5 g), a precipitate was obtained which was removed by filtration. The pale yellow solution on cooling yielded yellow crystals which were recrystallized twice from acetone and identified as ffosPdCl$_2$ (37% yield).

(f) ffos (0.3 g) in hot acetone was added to 0.35 g of potassium tetrachloroplatinate(II) in hot water. The mixture was refluxed (0.5 hr) and the solution was concentrated to give tan crystals. These were recrystallized twice from acetone and identified as ffosPtCl$_2$ (40% yield).

(g) Similarly ffos (1.5 g) and a hot aqueous olution of RhCl$_3$·3H$_2$O (0.5 g) gave a yellow precipitate. This was isolated and recrystallized from ethanol and identified as (ffos)$_2$RhCl$_3$.

(h) Mercuric chloride (0.6 g) in acetone (10 ml) was mixed with a solution of ffos (1.0 g) in the same solvent (15 ml) to give a yellow precipitate. The solid was recrystallized four times from acetone to give a 71% yield of ffosHgCl$_2$.

(2) **Complexes of 1,2-Bis(dimethylarsino)tetrafluorocyclobutene (ffars).**—(a) ffars (0.4 g) and molybdenum carbonyl (0.5 g) were refluxed in tetrahydrofuran (40 ml) for 2 hr. Evaporation of the blue solution gave pale blue crystals which were recrystallized from tetrahydrofuran and identified as ffarsMo(CO)$_4$. The ^{1}H nmr spectrum in nitrobenzene showed a single peak at 1.12 ppm and the ^{19}F spectrum a singlet at 109.5 ppm.

(b) ffars (1.5 g) and an excess of nickel carbonyl (5.0 g) were mixed in benzene solution (40 ml) at 20°. After 12 hr a yellow precipitate had appeared and after 10 days sufficient of the solid was obtained for investigation. The dry, dark yellow powder did not melt below 360° and did not sublime under vacuum. It was insoluble in a wide range of polar and nonpolar solvents. *Anal.* Found: C, 16.7; H, 3.5; As, 15.2; F, 11.4; Ni, 20.8.

(c) An ethanolic solution (50 ml) of ffars (4.5 g) was added to hydrated rhodium(III) chloride (1.0 g) in ethanol and the solution was refluxed for 12 hr. The yellow solution was evaporated yielding a yellow solid which was recrystallized from ethanol and identified as (ffars)$_2$RhCl$_3$. The nmr spectra show singlets at 2.06 ppm (^{1}H) and 109.5 ppm (^{19}F) when measured in *sym*-1,3-dichlorotetrafluoro-2,2-deuteriopropanediol solution.

(d) When an acetone solution (6 ml) of ffars (0.8) and an aqueous solution of ammonium tetrachloropalladate(II) (0.5 g in 40 ml) were mixed, a red precipitate was obtained. The crystals were recrystallized from acetone and then from chloroform and dried under vacuum. Their color then changed from red to yellow. The yellow solid analyzed for ffarsPdCl$_2$. The same compound was obtained from ffars and palladium dichloride in refluxing acetone.

(e) On mixing acetone solutions of ffars (0.9 g) and mercuric chloride (0.5 g) at 20° a white solid slowly precipitated. The solid was recrystallized from acetone and identified as ffarsHgCl$_2$.

(f) An ethanol solution of ffars (1.8 g) and cadmium bromide (1.1 g) was refluxed for 10 hr to give a white crystalline solid. Loss of ffars from the solid occurred on attempted recrystallization.

Discussion

One of the notable features of diars (I) is its ability to coordinate with a wide range of metal salts, covalent metal halides, and metal carbonyls.[2] However from preliminary experiments it seems that ffars and ffos are much more reluctant to form complexes with first-row transition metal salts. Thus they do not react with Ni(II), Fe(II), or Fe(III) compounds in a wide variety of solvents. In refluxing dioxane both gave a red color with nickel(II) nitrate indicative of reaction, but no complex could be isolated. diars also complexes readily with Zn(II), Cd(II), and Hg(II) halides.[10] ffars forms an analogous compound with mercuric chloride (Table I) but the cadmium bromide complex loses ligand very easily. The compound ffarsZnCl$_2$ does not seem to be formed. Since F-diars, 1,2-bis(dimethylarsino)-3,4,5,6-tetrafluorobenzene, forms complexes with Fe(II), Fe(III), Ni(II), and Co(II), it seems that the inductive effect of the bridging group in the di(tertiary arsine) is not largely responsible for the failure of ffars (and ffos) to complex with metal ions of the early transition metals. It is suggested that geometric factors such as the size of the ion and the arsenic-to-arsenic distance may be more important.

The compounds obtained in the present investigation are listed in Table I and the main bands of the infrared spectra of the complexes of ffos are shown in Table II. These bands are very similar to those of the uncomplexed di(tertiary phosphine)[5] and their similarity strongly suggests that ffos is acting as a chelating ligand in all of the complexes. A similar table could be drawn up for the complexes of ffars.

The presumably tetrahedral mercury complexes are analogous to those obtained with diars,[10] and even multidentate ligands seem to prefer to behave as bidentate ones with respect to Hg(II), Zn(II), and Cd(II).[11] ffosHgCl$_2$ appears to be completely dissociated in tetrahydrofuran although the complex is stable in dichloromethane. The analytical results of Table I suggest that a partial loss of ligand from ffarsHgCl$_2$ may have occurred. Ligand is easily lost from ffarsCdBr$_2$ which as yet has only been identified on the basis of its infrared spectrum which is almost identical with that of ffarsHgCl$_2$.

The presumably square-planar platinum and palladium complexes of ffos and ffars (Table I) are easily obtained although the usual products of the reaction of di(tertiary phosphines and arsines) with salts of Pt(II) and Pd(II) are salts containing ions of the type Pd(diars)$_2^{2+}$.[2] F-diars also yields Pd(F-diars)X$_2$ and Pt(F-diars)X$_2$ as well as complexes of the series M(F-diars)$_2$X$_2$.[9] Thus F-diars is somewhat similar in its coordinating properties to ffars and ffos. It should be

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[10] J. Lewis, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 2177 (1962).

[11] G. Dyer, D. C. Goodall, R. H. B. Mais, H. M. Powell, and L. M. Venanzi, *ibid., Sect. A*, 1110 (1966).

Table I

Analytical Data

			% found						% calcd					
Compound	Color	Mp, °C	C	H	F	P (As)	M	Cl	C	H	F	P (As)	M	Cl
ffos$PtCl_2$	Light brown	334–337	44.4	2.85	...	8.02	...	...	44.2	2.63	...	8.16	...	...
ffos$PdCl_2$	Yellow	~320[a]	49.8	3.21	...	9.15	...	...	50.0	2.78	...	9.24	...	...
ffos$HgCl_2$[b]	Yellow	230–232	43.6	2.33	10.2	8.00	...	9.48	43.9	2.61	9.92	8.01	...	9.27
(ffos)$_2RhCl_3$	Yellow	229–235[a]	54.8	3.59	14.5	9.37	9.25	8.55	56.2	3.46	12.7	10.3	8.63	8.90
ffos$Ni(CO)_2$	Yellow	...	59.4	3.48	...	...	...	...	59.2	3.29	...	...	...	...
ffos$Cr(CO)_4$	Orange	217	58.7	2.86	...	9.18	...	...	58.4	3.08	...	9.42	...	...
ffos$Mo(CO)_4$	Yellow	194	54.5	3.08	...	8.74	...	...	54.7	2.85	...	8.84	...	...
ffars$PdCl_2$[c]	Yellow	220	19.4	2.61	14.0	29.3	20.8	13.9	18.8	2.35	14.9	29.4	20.7	13.9
ffars$HgCl_2$	White	123	13.8	2.42	9.50	24.2	37.0	12.9	15.8	1.98	12.6	24.8	33.1	11.6
(ffars)$_2RhCl_3$	Yellow	...[d]	21.1	2.89	17.4	34.4	11.5	12.3	22.0	2.74	17.4	34.3	11.5	12.1
ffars$Mo(CO)_4$[e]	Pale blue	147	27.2	2.42	13.8	27.8	17.9	...	26.6	2.22	14.0	27.7	17.9	...

[a] With preliminary charring. [b] Molecular weight: found, 685 (dichloromethane), 380 (tetrahydrofuran); calcd, 776. [c] Molecular weight: found, 560; calcd, 511. [d] At 200° solid becomes orange. It chars at higher temperatures. [e] Molecular weight: found, 542; calcd, 511.

Table II

Infrared Spectra of Some ffos Complexes (cm^{-1})[a]

ffos-$PtCl_2$	ffos-$PdCl_2$	ffos-$HgCl_2$	(ffos)$_2$-$RhCl_3$	ffos-$Cr(CO)_4$	ffos-$Mo(CO)_4$
1476 s	1475 s	1480 s	1476 m	1487 s	1478 s
1435 s	1430 s	1432 s	1429 s	1434 s	1435 s
1305 vs[b]	1303 vs[b]	1300 vs[b]	1303 s	1304 vs	1305 vs[b]
1240 s	1236 s	1228 vs	1235 m	1228 s	1227 s
1150 s	1155 s	1145 vs[c]	1155 m	1148 s	1145 s
1130 vs	1127 vs	1130 vs[b]	1127 vs	1125 vs	1120 vs[b]
1098 s	1098 s	1090 vs[c]	(1108, 1093) vs	1090 s	1088 s
856 s	850 s	845 m	830 s	848 s	825 m
745 s	738 s	740 s	740 s	745 s	730 s
718 s	715 s	720 m	711 s	715 s	712 m
685 s	683 s	685 s	687 s	692 s	690 s

[a] Main bands only from spectra in KBr disks. Carbonyl bands are listed in Table III. [b] Broad. [c] Shoulder.

mentioned that the reaction of ffars with Pt(II) salts is complex and that, although Pt(ffars)X_2 seems to be formed, the results are not reproducible.[12,13]

ffos reacts easily with nickel carbonyl replacing two carbonyl groups and yielding ffos$Ni(CO)_2$. Other di(tertiary phosphines) such as the phosphorus analog of II react similarly, though under more forcing conditions (150–200°) it is possible to displace all four carbonyl groups.[14] This further reaction has not yet been studied with ffos. The compounds $LNi(CO)_2$ [L = di(tertiary arsine)] are also readily obtained[2,9] but the formation of (diars)$_2$Ni by further substitution is apparently rather difficult.[15] Therefore it is surprising to find that ffars reacts with nickel carbonyl at 20° to give a solid which apparently contains no carbonyl groups. This solid does not analyze for the possible product (ffars)$_2$Ni but its insolubility and thermal stability suggest that it is polymeric. In this case ffars might be acting as a tridentate group (two arsenic atoms and one double bond) in a similar manner to that found in ffars$(Fe(CO)_3)_2$.[6]

Both ffos and ffars seem to react with chromium and molybdenum hexacarbonyls, to displace two carbonyl groups, more easily than unfluorinated chelating agents. A similar observation has been made with respect to F-diars. The product ffars$Mo(CO)_4$ is unusual in that it is blue. Derivatives of this sort are usually yellow[2] and the blue color may be due to partial oxidation. After 36 hr in refluxing tetrahydrofuran ffars apparently displaces all of the carbonyl groups from molybdenum hexacarbonyl to yield a pink solid which is probably related to the product obtained from ffars and nickel carbonyl.[12] Complete replacement of carbonyl groups from group VI carbonyls has not been achieved using the usual di(tertiary arsines or phosphines).[2b] Reactions of ffos with tungsten hexacarbonyl did not, however, take place under the same mild conditions. Presumably the usual more vigorous conditions will be needed.

Table III lists the CO stretching frequencies of some of the new complexes as well as those of some related derivatives. It is seen that the frequencies of the chromium complexes are lower than those of the molybdenum complexes with the same ligand. More importantly the frequencies of the ffos complexes are higher than those of the others which suggests that the electronegative cyclobutene bridging group causes the phosphorus atoms to act as good π acceptors. The figures for the di(tertiary arsine) complexes indicate that there is not much difference in the π-acceptor properties of the two ligands ffars and diars. However F-diars seems to be better than both. The frequency

Table III

Some Carbonyl Infrared Absorption Frequencies (cm^{-1})

ffos$Cr(CO)_4$[a]	2015, 1937, 1916, 1907[b]
$C_2H_4(P(C_6H_5)_2)_2Cr(CO)_4$[c]	2009, 1914, 1899, 1877
o-$C_6H_4(P(C_2H_5)_2)_2Cr(CO)_4$[c]	2001, 1906, 1884
ffos$Mo(CO)_4$[a]	2030 1944 1927, 1918[b]
$C_2H_4(P(C_6H_5)_2)_2Mo(CO)_4$[c]	2020, 1919, 1907, 1881
o-$C_6H_4(P(C_2H_5)_2)_2Mo(CO)_4$[c]	2014, 1912,[b] 1896
ffars$Mo(CO)_4$[a]	2025, 1937, 1917
o-$C_6H_4(As(CH_3)_2)_2Mo(CO)_4$[d]	2026, 1938, 1923, 1914
o-$C_6F_4(As(CH_3)_2)_2Mo(CO)_4$[e]	2032, 1946, 1921, 1892

[a] In CCl_4 solution. [b] Shoulder. [c] In 1,2-$C_2H_4Cl_2$ solution: J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961). [d] In C_6H_{12} solution: C. C. Baraclough, J. Lewis, and R. S. Nyholm, *ibid.*, 2582 (1961). [e] In C_6H_{12} solution: A. J. Layton, personal communication.

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(12) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, unpublished work.

(13) X-Ray powder photographs of supposedly identical products are not identical. G. W. Watt and R. Layton, *Inorg. Chem.*, **1**, 496 (1962), have noted similar behavior in some Pd(II) complexes of di(tertiary arsines) related to II.

(14) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(15) D. V. R. Rao and R. S. Nyholm, unpublished observations quoted by C. M. Harris, R. S. Nyholm, and D. J. Phillips, *ibid.*, 4379 (1960).

shifts in the complexes could equally well be caused by the electronegative bridging groups reducing the σ-bonding ability of the ligands. It should be noted that some comparisons are being made here between frequencies obtained from different solvents and hence the conclusions may not be meaningful.

The final compounds to be discussed are the products (ffars)$_2$RhCl$_3$ and (ffos)$_2$RhCl$_3$. The analytical data for the ffos complex (Table I) are not very good; in fact, it seems difficult to get consistent analysis figures for this type of complex. However, there is little doubt that the formula is correct. The infrared spectrum of Table II indicates that the di(tertiary phosphine) is bonded in the usual way and the structures are probably the same as that of the analogous diars complex which Nyholm[16] found to be a 1:1 electrolyte and formulated as [(diars)$_2$RhCl$_2$]$^+$Cl$^-$.

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(16) R. S. Nyholm, *J. Chem. Soc.*, 857 (1950).

Notes

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The Tetrakis(dimethylamino)diborane(4)–Diborane(6) System[1,2]

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The similarity in the structures of tetrakis(dimethylamino)diborane(4) and of tetrakis(dimethylamino)ethene and the possibility of forming some novel aminoboron hydrides prompted us to investigate the tetrakis(dimethylamino)diborane(4)–diborane(6) system.

Tetrakis(dimethylamino)diborane(4) dissolved in 2-methylbutane reacts with 1 mole of diborane(6) at −78° to form a white insoluble solid. On warming to −23°, 1 mole of dimethylaminoborane is formed along with a colorless nonvolatile liquid which slowly converts to a yellow glass. At temperatures above −78°, the diborane(6) to tetrakis(dimethylamino)diborane(4) mole ratio varies from 1:1 to 2:1 owing primarily to the formation of dimethylaminodiborane(6). Similar results were obtained although not as reproducibily in the absence of a solvent, in hydrocarbon solvents, and in methyl ether.

Physical data which give direct evidence for the structure of the 1:1 adduct could not be obtained owing to its insolubility and its thermal instability. However, on the basis of chemical arguments, it is reasonable to propose that the adduct has a tetraborane(10)-like structure which results from the symmetrical cleavage of diborane(6) by tetrakis(dimethylamino)diborane(4). This adduct then loses 1 mole of dimethylaminoborane on warming and the remaining B–B bonded fragment polymerizes into the nonvolatile liquid. With this hypothesis in mind, two attempts, both unsuccessful, were made to minimize polymerization and isolate a stable monomeric species. Apparently if the adduct has a tetraborane(10)-like structure, the B–B bonded fragment polymerizes too rapidly and thus prevents the formation of stable monomers.

Experimental Section

Standard high-vacuum line and inert-atmosphere techniques were used to carry out the experiments described below. Tetra(dimethylamino)diborane(4)[4] was used without further purification. The desired amount of reagent was measured volumetrically to the nearest 0.001 ml with a 2-ml micrometer syringe. The density of the liquid at room temperature (0.858 g/ml) was determined by weighing liquid delivered by the syringe. No corrections were made for changes in density due to temperature fluctuations. All solvents were fractionally distilled and stored over either metallic sodium, calcium hydride, or lithium aluminum hydride under vacuum. The diborane(6) (pressure at −111°, 225 mm; lit.[5] 225 mm) was always fractionally distilled in the vacuum line just prior to use.

B_2H_6 + $[(CH_3)_2N]_4B_2$ in Hydrocarbon Solvents.—In a typical run 5.36 mmoles of B_2H_6 were added at −78° to 0.852 mmole of $[(CH_3)_2N]_4B_2$ dissolved in 5 ml of 2-methylbutane. The formation of a white precipitate and a drop in pressure indicated that a reaction had occurred. After allowing the reaction mixture to stand at −78° for several hours, the substances volatile at −78° were removed. Hydrolysis of the nonvolatile substances in aqueous NaOH yielded 5.92 mmoles of hydrogen, in good agreement with the 5.96 mmoles expected if 0.852 mmole of $B_2H_6 \cdot [(CH_3)_2N]_4B_2$ had formed.

In three other experiments the $B_2H_6 : [(CH_3)_2N]_4B_2$ ratio in the nonvolatile solid was found to be 1.17:1, 1.11:1, and 1.02:1. The ratio was determined by acid hydrolysis of the unreacted diborane in these runs.

When the temperature of the reaction mixture was allowed to rise above −78° for even a few minutes, higher ratios (1.45:1 and 1.8:1) were obtained.

Similar results were obtained in the absence of a solvent, in methyl ether, and in other hydrocarbon solvents such as 3-methylpentane, methylcyclohexane, and toluene.

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(1) Taken in part from the Ph.D. thesis of J. D. C., University of New Mexico, Sept 1966.

(2) A report on a brief study of this sytem by J. L. Boone and co-workers, U. S. Borax Research Corp., Anaheim, Calif. 92803, is contained among the U. S. Government classified literature.

(3) Communications should be addressed to this author at Eastern Michigan University Ypsilanti, Mich. 48197.

(4) Complimentary sample from the U. S. Borax Co., Anaheim, Calif.

(5) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).