

$(\text{CH}_3)_3$ $[(\text{CH}_3)_3\text{SnBr}_2]$ formed before the solution was concentrated to half of the original volume. The crystals were dried over concentrated sulfuric acid for two weeks. They decomposed over a wide temperature range, starting at 152° .

Anal. Calcd. for $\text{C}_{26}\text{H}_{36}\text{Br}_2\text{PSn}_2$: C, 39.31; H, 4.62. Found: C, 39.79; H, 4.69.

A sample of pure product was dissolved in water and added to an aqueous solution of reinecke salt. The resulting insoluble reineckate, m.p. $123\text{--}125^\circ$, was washed with water and dried.

Anal. Calcd. for $\text{C}_{26}\text{H}_{32}\text{N}_8\text{S}_4\text{PSnCr}$: C, 41.20; H, 4.26. Found: C, 41.42; H, 4.38.

A second sample was dissolved in dilute HBr and added to an aqueous solution of mercuric bromide. The mixture became turbid, and a sticky precipitate formed. The latter solidified on standing and was pulverized with a stirring rod, filtered, washed with water and dried to give pure $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Sn}(\text{CH}_3)_3][\text{HgBr}_3]$, m.p. $165\text{--}168^\circ$.

Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{Br}_3\text{PSnHg}$: C, 30.02; H, 2.98; Hg, 22.78. Found: C, 30.28; H, 2.84; Hg, 22.70.

The Reaction of Trimethyltin Bromide with Tetraethylammonium Bromide.—Tetraethylammonium bromide (1.05 g., 0.005 mole) was dissolved in 3 ml. of water, and 6.10 g. (0.025 mole) of trimethyltin bromide was added. Two layers formed, which on addition of 2 ml. of water formed a homogeneous solution. The solution was concentrated at reduced pressure (23 mm.) using a rotary evaporator at room temperature. Eventually crystals formed; these were filtered, washed with a methanol-ether mixture and then with ether alone. The crystals, $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{CH}_3)_3\text{SnBr}_2]$, were dried for one hr. at 73° ; when heated in a sealed tube, they decomposed between $150\text{--}165^\circ$.

Anal. Calcd. for $\text{C}_{11}\text{H}_{29}\text{NBr}_2\text{Sn}$: C, 29.11; H, 6.44; N, 3.08. Found: C, 29.47, 29.41; H, 6.32, 6.57; N, 2.86.

Reaction of Triphenylphosphinemethylene with Dimethyltin Dichloride.—Dimethyltin dichloride (0.04 mole) was dissolved in 350 ml. of ether and placed in a 1-liter reaction flask. Triphenylphosphinemethylene solution (*ca.* 0.04 mole) was added *via* a transfer tube under nitrogen pressure. Its yellow color was discharged immediately, and white solid precipitated. The crude product weighed 18 g., and attempts to purify it failed.

A small amount (0.5 g.) of the crude product was dissolved in 100 ml. of water, and a freshly prepared aqueous solution of sodium tetraphenylborate was added. The white precipitate, $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Sn}(\text{CH}_3)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$, m.p. $78\text{--}81^\circ$, was collected, washed with water and dried in vacuum over phosphorus pentoxide at room temperature.

Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{P}_2\text{B}_2\text{Sn}$: C, 78.88; H, 6.02. Found: C, 78.95; H, 6.04.

The water-insoluble di-reineckate, m.p. $115\text{--}119^\circ$, was prepared in a similar manner.

Anal. Calcd. for $\text{C}_{48}\text{H}_{52}\text{N}_{12}\text{S}_3\text{P}_2\text{SnCr}_2$: C, 43.08; H, 3.92. Found: C, 43.33; H, 4.06.

An ethanolic solution of mercuric bromide was added to 0.2 g. of the crude product dissolved in ethanol. A white precipitate formed, which dissolved when the solution was heated. On cooling, crystals of the bis-dibromochloromercurate formed. These were filtered, washed with ethanol and dried at 60° in vacuum for 3 hr.; m.p. $139\text{--}140^\circ$.

Anal. Calcd. for $\text{C}_{40}\text{H}_{40}\text{Cl}_2\text{Br}_4\text{P}_2\text{SnHg}_2$: C, 32.17; H, 2.70; Hg, 26.87. Found: C, 32.77; H, 2.94; Hg, 27.83.

Reaction of Triphenylphosphinemethylene with Dimethyltin Dibromide.—The reaction of triphenylphosphinemethylene with dimethyltin dibromide in 1:1 molar ratio was carried out on a 0.032 mole scale. The product weighed 10.9 g. A sample was recrystallized from dilute hydrobromic acid by evaporation using a rotary evaporator until crystals of $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Sn}(\text{CH}_3)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3][(\text{CH}_3)_2\text{SnBr}_4]$ formed. This compound was stored over phosphorus pentoxide for three weeks before it was analyzed; it decomposed over a wide range, beginning at 135° .

Anal. Calcd. for $\text{C}_{42}\text{H}_{46}\text{Br}_4\text{P}_2\text{Sn}_2$: C, 43.12; H, 3.96. Found: C, 43.35; H, 3.97.

Reaction of Triphenylphosphinemethylene with Mercuric Bromide.—A solution of 7 g. (0.02 mole) of mercuric bromide in 400 ml. of ether was added rapidly with stirring to 0.04 mole of triphenylphosphinemethylene in ether. A large amount of white solid precipitated immediately. The mixture was stirred for 15 min. and then was filtered under nitrogen. The residue was washed with ether. The dried product, 15.3 g., was not appreciably soluble in water, acetone or ethanol but was somewhat soluble in hot methanol.

Only part of a 0.4 g. sample of the product dissolved in 30 ml. of boiling methanol. The undissolved solid was filtered off, and the filtrate was added to a hot, concentrated solution of mercuric bromide in methanol. On cooling, a white powder, $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{HgCH}_2\text{P}(\text{C}_6\text{H}_5)_3][\text{HgBr}_3]_2$, m.p. $123\text{--}126^\circ$, came out of solution.

Anal. Calcd. for $\text{C}_{38}\text{H}_{34}\text{Br}_4\text{P}_2\text{Hg}_2$: C, 27.93; H, 2.10; Hg, 36.83. Found: C, 28.04; H, 2.22; Hg, 37.02.

One gram of the crude product dissolved only partially in 100 ml. of a 70:30 methanol-water solution. The mixture was filtered, and to the filtrate was added a concentrated solution of sodium tetraphenylborate in the same solvent mixture. The precipitate which formed was centrifuged and washed with methanol and water until the wash water no longer gave a positive bromide ion test. The white bis-tetraphenylborate melted at $101\text{--}104^\circ$.

Anal. Calcd. for $\text{C}_{86}\text{H}_{74}\text{P}_2\text{B}_2\text{Hg}$: C, 74.22; H, 5.36; Hg, 14.41. Found: C, 74.68; H, 5.52; Hg, 14.20.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE MASSACHUSETTS]

Studies in Phosphinemethylene Chemistry. II. Adducts of Triphenylphosphinemethylene with Boron Compounds¹

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Stable solid adducts are formed between triphenylphosphinemethylene and boron trifluoride, boron trichloride, triphenylborane and borane; between triphenylphosphineethylidene and boron trifluoride and triphenylborane; and between triphenylphosphinechloromethylene and triphenylborane. Triphenylphosphinemethylenetrifluoroborane may be reduced to the B-trihydro compound with lithium aluminum hydride and arylated to B-triaryl compounds with aryl Grignard reagents. Triphenylphosphinemethylene does not appear to form stable adducts with trialkylboranes.

In a previous study² it was shown that triphenylphosphinemethylene reacts with metallic and

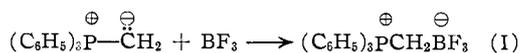
(1) This work was summarized in part in a paper presented at the XVII Congress of Pure and Applied Chemistry, München, August 30–September 6, 1959; *cf. Angew. Chem.*, **72**, 36 (1960).

organometallic halides of Periodic Groups II and IV to form organometallic-substituted phosphonium salts by a displacement mechanism which,

(2) S. O. Grim and D. Seyferth, *Chem. and Ind. (London)*, 849 (1959); Part I of this series, *J. Am. Chem. Soc.*, **83**, 1610 (1961).

according to current ideas regarding nucleophilic displacement reactions of Group IV halides, may involve initial coordination of the reagent by participation of vacant metal d orbitals. The boron halides, with an available vacant p orbital, readily form 1:1 coordination compounds with a variety of electron pair donors. This suggested that triphenylphosphinemethylene might react with boron halides to form 1:1 adducts without subsequent displacement of halide ion.

This was found to be the case in this study. Triphenylphosphinemethylene reacted with boron trifluoride diethyl etherate in ether solution to form the very stable ether-insoluble adduct triphenylphosphinemethylenetrifluoroborane (I). While



this work was in progress, Hawthorne reported a similar adduct, triphenylphosphinemethyleneborane, as the product of the reaction between triphenylphosphinemethylene and diborane.³ The compound triphenylphosphinemethylenetriphenylborane was mentioned in a review article by Wittig,⁴ but no details concerning its preparation or properties were given.

Triphenylphosphinemethylenetrifluoroborane is unaffected by water and is rather stable thermally, decomposing at 221°. It is very soluble in methylene chloride and soluble in acetone; sparingly soluble in methanol, ethanol and benzene; insoluble in water. Its molecular weight, determined by isothermal distillation in methylene chloride, indicated it to be monomeric; however, its molecular weight decreased with time, probably due to a slow decomposition. Its cryoscopic molecular weight in nitrobenzene also indicated that the adduct was monomeric.

The reaction of boron trichloride with triphenylphosphinemethylene afforded the expected adduct, triphenylphosphinemethylenetrichloroborane. This compound appeared to be stable toward water because of its insolubility, but in the presence of a cosolvent it decomposed, giving a sticky mass which had a pungent odor.

Trimethylamine-borane reacted with triphenylphosphinemethylene in diethylene glycol dimethyl ether at *ca.* 100°, giving the B-trihydro adduct previously reported.³ Subsequent to our report of this reaction,¹ Hawthorne demonstrated the general nature of this reaction by preparing a number of triphenylphosphinemethylene-monoorganoborane adducts by similar displacement of trimethylamine from trimethylamine-alkylboranes.⁵

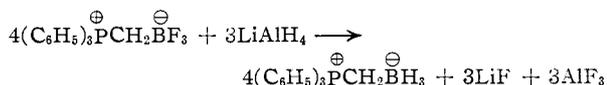
While triphenylphosphinemethylene reacted readily with triphenylborane in ether solution to give triphenylphosphinemethylenetriphenylborane in good yield, the addition of triethyl- and tri-*n*-butylborane to triphenylphosphinemethylene did not produce similar adducts; the characteristic yellow color of the phosphinemethylene solution was not discharged, and no precipitate was formed. Adducts of triphenylborane with triphenylphos-

phineethylidene and triphenylphosphinechloromethylene⁶ also were prepared.

The reaction of triphenylphosphinemethylenetrifluoroborane with aryl Grignard or lithium reagents provided a new synthesis of the B-triaryl adducts. For example, treatment of the B-trifluoro adduct with *m*- α,α -trifluorotolylmagnesium bromide in ether gave ether-soluble triphenylphosphinemethylene-tris-(*m*- α,α -trifluorotolyl)-borane in 48% yield. The B-triaryl compound was prepared readily in a similar manner, and triphenylphosphinemethylenetrichloroborane also could be arylated.

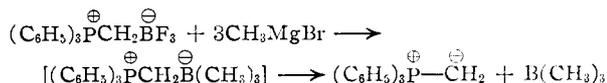
The attempted alkylation of triphenylphosphinemethylenetrifluoroborane provided further evidence for the instability of the B-trialkyl adducts. The reaction of methylmagnesium bromide with the B-trifluoro compound in di-*n*-butyl ether gave trimethylborane, which was identified as crystalline trimethylamine-trimethylborane.

Reduction of triphenylphosphinemethylenetrifluoroborane with lithium aluminum hydride resulted in formation of the B-trihydro compound in 65% yield.



The reduction and the arylation of triphenylphosphinemethylenetrifluoroborane conceivably could proceed by two different paths: (1) reaction of the undissociated complex with the Grignard reagent or with lithium aluminum hydride, or (2) dissociation of the complex, followed by arylation or reduction of boron trifluoride and recombination of the triarylborane or diborane thus produced with triphenylphosphinemethylene. We have no experimental evidence which allows the exclusion of either possibility. This question is under active investigation.

The stability of the adducts formed between triphenylphosphinemethylene and boron compounds is undoubtedly determined both by steric and electronic factors. It might be expected that those adducts in which the substituents on boron are best able to draw off the formal negative charge placed on boron when coordination takes place would be the most stable. In agreement with this view is the great stability of the B-trifluoro compound and the poorer stability of the B-trichloro compound, as well as the failure to isolate a B-trialkyl derivative. In the reaction of the methyl Grignard reagent with triphenylphosphinemethylenetrifluoroborane, partial or total methylation of the latter very probably takes place, but the presence of methyl groups in the complex leads to instability and dissociation. A study of the reaction of tri-



phenylphosphinemethylene with methyl difluoroborane and dimethyl fluoroborane has been initiated in order to determine at what degree of methylation instability becomes important.

(3) M. F. Hawthorne, *J. Am. Chem. Soc.*, **80**, 3480 (1958).

(4) G. Wittig, *Angew. Chem.*, **70**, 65 (1958).

(5) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 833 (1961).

(6) D. Seyferth, S. O. Grim and T. O. Read, *ibid.*, **82**, 1510 (1960).

Triphenylphosphinemethylenetrifluoroborane reacts smoothly with four equivalents of phenyllithium in an ether-tetrahydrofuran mixture to give a red-brown solution containing triphenylphosphinelithiomethylenetriphenylborane, $(C_6H_5)_3PCHLi^{\ominus}(C_6H_5)_3$. The reactions of this novel lithium compound will be described in a later paper.

Experimental⁷

(1) **Reactions of Triphenylphosphinealkylidenes with Boron Compounds. Reactions of Triphenylphosphinemethylene with Boron Trifluoride Etherate.**—The ethereal triphenylphosphinemethylene solution prepared from 0.04 mole of methyltriphenylphosphonium bromide and 0.04 mole of phenyllithium⁸ was filtered under nitrogen into a reaction flask equipped with a nitrogen inlet tube, a mechanical stirrer and a tube capped with a "no-air" rubber stopper. Boron trifluoride diethyl etherate (5 g., 0.035 mole), which had been freshly distilled into a Schlenk tube, was removed with a hypodermic syringe and injected into the stirred triphenylphosphinemethylene solution. The yellow solution momentarily became a deeper orange in color, and a large amount of precipitate formed. The yellow mixture was stirred for 15 min., filtered and washed with ether. The dried solid weighed 12.5 g.; it was soluble in hot ethanol, acetone and methylene chloride and insoluble in water. An 11.5 g. sample of the crude product was washed with water, dissolved in 200 ml. of hot acetone and reprecipitated by adding 100 ml. of water. The mixture was evaporated to about one third of its original volume at reduced pressure using a rotary evaporator. The dried solid weighed 4.8 g. Two recrystallizations gave triphenylphosphinemethylenetrifluoroborane, which decomposed to a red melt at 199–201°. Further recrystallization from methylene chloride–benzene gave material of m.p. 218–221° (sealed tube).

This reaction was repeated five times on a larger scale, and the average recrystallized yield was 41%.

Anal. Calcd. for $C_{19}H_{17}F_3PB$: C, 66.31; H, 4.98; P, 9.00; F, 16.56. Found: C, 66.45; H, 5.16; P, 9.16; F, 16.47.

NOTE ADDED IN PROOF.—A further study of the chemical properties of adducts of this type by Dr. E. Hahn in this Laboratory has resulted in observations which have led to improved preparative and purification procedures. These will be described in a forthcoming publication.

When boron trifluoride etherate was injected directly into the unfiltered phosphinemethylene solution during one preparation, a low yield of methyltriphenylphosphonium tetrafluoroborate was isolated in addition to a 41% yield of triphenylphosphinemethylenetrifluoroborane. The former may have been formed by the reaction of some unconverted methyltriphenylphosphonium bromide with boron trifluoride. The crude tetrafluoroborate, m.p. 114–122°, was recrystallized from ethanol–ether to give the pure compound, m.p. 133–134°.

Anal. Calcd. for $C_{19}H_{18}F_4PB$: C, 62.67; H, 4.98; F, 20.87. Found: C, 62.80; H, 4.95; F, 20.26.

A molecular weight determination of triphenylphosphinemethylenetrifluoroborane was made by an isothermal distillation. Methylene chloride was used as the solvent and azobenzene as the standard. Azobenzene, 0.0145 g. (7.96×10^{-5} mole) and the B-trifluoro compound, 0.0274 g. (7.96×10^{-5} mole) were placed in the respective arms of the apparatus, and each was dissolved in about 4 ml. of methylene chloride. The apparatus was cooled in a Dry-Ice-acetone bath, evacuated to ca. 1 mm. and then placed in a constant temperature room. The heights of the two solutions were measured at the times tabulated. The calculated molecular weight for the B-trifluoro compound is 344.

(7) Analyses were performed by Dr. S. M. Nagy (M.I.T.) and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were determined using a Mel-Temp melting point apparatus. All reactions were carried out in an atmosphere of prepurified nitrogen, and all possible precautions were taken to exclude air and moisture from the reaction system before, during and after the reaction. Starting materials either were purchased and, if necessary, subjected to further purification, or were prepared by standard methods described in the literature.

Time	Ht.,	Ht.,	Mol. wt.,
	$Ph_3PCH_2BF_3$	azobenzene	$Ph_3PCH_2BF_3$
5 hr.	14.0	15.0	369
28 hr.	15.2	13.7	311
14 days	16.7	12.4	256
22 days	17.6	11.2	220

Several determinations of the cryoscopic molecular weight in nitrobenzene gave 296 as an average value; the best value was 320.

Reaction of Triphenylphosphinemethylene with Boron Trichloride.—The triphenylphosphinemethylene solution (ca. 0.04 mole) was filtered into a reaction flask similar to that described above. Boron trichloride (2.1 g., 0.018 mole), cooled to -50° , was injected with a precooled hypodermic syringe. A precipitate formed immediately, and the solution remained yellow. After the mixture had stood for 3 hr., the solid was filtered off under nitrogen. Drying gave 6.2 g. of crude product. A water-washed sample of the crude product was dried over phosphorus pentoxide in a vacuum oven and then was recrystallized under a nitrogen atmosphere from methylene chloride–ether. The still impure triphenylphosphinemethylenetrichloroborane softened at 170° and melted at $225-228^\circ$ (dec).

Anal. Calcd. for $C_{19}H_{17}Cl_3PB$: C, 58.01; H, 4.36; Cl, 27.04; P, 7.88. Found: C, 57.04; H, 4.79; Cl, 25.41; P, 7.69.

Reaction of Triphenylphosphineethylidene with Boron Trifluoride.—The triphenylphosphineethylidene was prepared in 200 ml. of ether from 0.054 mole of ethyltriphenylphosphonium bromide and 0.052 mole of phenyllithium. After the residual solid had been allowed to settle, the red solution was pipetted into the usual reaction flask. Freshly distilled boron trifluoride etherate, 5.5 ml. (0.043 mole), was injected into the red solution. The resulting solid was filtered and washed with ether to give 17.6 g. of crude product. This was not very soluble in hot acetone (ca. 1 g. in 100 ml.). Addition of ether to a methylene chloride solution of the crude product did not precipitate solid in any great quantity; however on concentration of this solution at reduced pressure, 8.1 g. of white powder (55% yield) was obtained. A small sample was recrystallized from acetone–water to give the analytically pure triphenylphosphineethylidene-trifluoroborane, m.p. $207-208^\circ$ to a red liquid.

Anal. Calcd. for $C_{20}H_{18}F_3PB$: C, 67.07; H, 5.35; F, 15.91. Found: C, 67.25; H, 5.69; F, 15.67.

Reaction of Triphenylphosphinemethylene with Trimethylamine-borane.—Trimethylamine-borane (2.84 g., 0.038 mole) was dissolved in 60 ml. of anhydrous ether in the usual reaction flask and ca. 0.04 mole of triphenylphosphinemethylene solution was added. A very slight precipitate formed, but no other reaction was apparent. Eighty ml. of freshly distilled anhydrous diethylene glycol dimethyl ether was added to the solution, and the diethyl ether was removed by distillation until the pot temperature reached 100° . The resulting dark orange solution was heated at $95-105^\circ$ for 6 hr. On cooling, a slight precipitate formed. Fifty ml. of water and 50 ml. of methylene chloride were added. The layers were separated, and an organic layer was evaporated at reduced pressure. Triphenylphosphinemethyleneborane, 2.53 g. (25%), was thus obtained. The sample was recrystallized from acetone by adding water and from an ether–methylene chloride mixture to give pure material, m.p. $190-191^\circ$ (lit.³ $191-192^\circ$). The infrared spectrum of this compound showed strong bands arising from the B–H vibrations at 2210 and 2375 cm^{-1} .

Anal. Calcd. for $C_{19}H_{20}PB$: C, 78.65; H, 6.95. Found: C, 78.63; H, 6.96.

Reaction of Triphenylphosphinemethylene with Triphenylborane.—To a solution of 0.016 mole of triphenylborane in 50 ml. of benzene and 150 ml. of ether in the usual reaction flask was added a filtered ethereal solution of ca. 0.02 mole of triphenylphosphinemethylene. The resulting white precipitate was filtered after the reaction mixture had been allowed to stand overnight. Triphenylphosphinemethylenetriphenylborane was obtained in 93% crude yield (7.8 g.). The product was extremely soluble in methylene chloride and acetone, sparingly soluble in methanol and insoluble in water. The yellow product was washed under

nitrogen first with ether, then with warm benzene, to give the pure adduct in 70% yield, m.p. 215–217° in a nitrogen-filled sealed capillary. This nearly white solid could be recrystallized from acetone by adding water, but only with severe losses.

Anal. Calcd. for $C_{37}H_{32}PB$: C, 85.71; H, 6.22; P, 5.97; B, 2.09. Found: C, 85.57; H, 6.31; P, 5.84; B, 2.10.

Its infrared spectrum showed a closely spaced doublet at 1105 and 1110 cm^{-1} ; P-Ph band at 1430 cm^{-1} has a small shoulder at 1420 cm^{-1} , possibly due to B-Ph absorption. This shoulder can also be noticed in tetraphenylborate derivatives of phosphonium salts.

Reaction of Triphenylphosphineethylidene with Triphenylborane.—The reaction of 0.066 mole of triphenylborane with *ca.* 0.009 mole of triphenylphosphineethylidene was carried out in a manner similar to the experiment described above. The granular solid produced weighed 1.98 g. (56%); it was washed with methanol and ether. Attempts to recrystallize the product from acetone-water or methylene chloride-ether resulted in oils. The methanol-washed sample decomposed and turned orange between 120 and 145°; a sample introduced at 145° did not collapse until 161°. A small sample was washed repeatedly with methanol, dried and submitted for analysis.

Anal. Calcd. for $C_{38}H_{34}PB$: C, 85.71; H, 6.44. Found: C, 85.53; H, 6.62.

Reaction of Triphenylphosphinechloromethylene with Triphenylborane.—The deep orange ether solution prepared from 0.0098 mole of chloromethyltriphenylphosphonium bromide and 0.0099 mole of phenyllithium was added to 0.009 mole of triphenylborane dissolved in 20 ml. of 1:1 benzene-ether in the usual apparatus. At the beginning of the addition the color was discharged, and a sticky oil formed, which later solidified. After about one-fourth of the triphenylphosphinechloromethylene had been added, the color was no longer discharged. The addition was completed and the mixture refluxed for 45 min. On cooling, the yellow color was discharged, and the small amount of solid which was present was filtered, washed with ether and dried. A yield of 0.72 g. was obtained. The product was washed with methanol and dried to give fairly pure triphenylphosphinechloromethylenetriphenylborane, which gave a deep red melt at 122–125°.

Anal. Calcd. for $C_{37}H_{31}ClPB$: C, 80.37; H, 5.65; Cl, 6.41. Found: C, 80.16; H, 5.87; Cl, 6.18.

(2) **Reactions of Triphenylphosphinemethylenetrifluoroborane.** **Reaction of Triphenylphosphinemethylenetrifluoroborane with Lithium Aluminum Hydride.**—Two g. (0.0058 mole) of triphenylphosphinemethylenetrifluoroborane was suspended in 15 ml. of ether in a 100 ml. flask fitted with a stirrer, solids addition tube with a side arm for a nitrogen inlet and a condenser provided with an outlet tube to a trap containing aqueous caustic. About 0.5 g. of lithium aluminum hydride was added slowly to the flask through the addition tube. No apparent reaction was observed. On addition of 15 ml. of methylene chloride a slightly exothermic reaction commenced. The mixture was stirred for 10 min. and then cautiously hydrolyzed. After another portion of methylene chloride had been added, the mixture was filtered and ether added to the filtrate. Evaporation of the latter gave white solid triphenylphosphinemethylenetrifluoroborane, m.p. 190–195° in 65% yield. Its infrared spectrum was identical with that of the product of the trimethylamine-borane/triphenylphosphinemethylene reaction.

Reaction of Triphenylphosphinemethylenetrifluoroborane with Phenyl Grignard Reagent.—Twenty ml. of 1.15 *M* phenylmagnesium bromide (0.023 mole) in ether was added rapidly to 2.0 g. (0.0058 mole) of triphenylphosphinemethylenetrifluoroborane suspended in 20 ml. of ether.

An exothermic reaction commenced, causing gentle reflux, and the originally finely dispersed solid gathered into larger particles. The mixture was refluxed for 10 min. and filtered. The solid, a mixture of product and magnesium salts, weighed 5.1 g. Recrystallization was effected by adding water to an acetone solution of the crude product. The resulting crystals weighed 0.32 g. (11%) and had an infrared spectrum identical with that of triphenylphosphinemethylenetriphenylborane prepared by the reaction of triphenylborane with triphenylphosphinemethylene.

Reaction of Triphenylphosphinemethylenetrifluoroborane with the Grignard Reagent from *m*-Bromo- α,α,α -trifluorotoluene.—Twenty-two ml. of 0.019 *M* (0.02) mole of the Grignard reagent prepared in ether from *m*-bromo- α,α,α -trifluorotoluene and magnesium was added to a suspension of 2.0 g. (0.0058 mole) of triphenylphosphinemethylenetrifluoroborane in 20 ml. of ether. At first, addition of the deep brown Grignard solution seemed to change the white powder to yellow-brown crystals. On further addition, the solution became red-brown, and the crystals were converted to a brown, sticky tar. A mildly exothermic reaction commenced, and the ether refluxed gently. The reaction mixture was stirred for 10 min. without heating and subsequently hydrolyzed. The deep yellow ether layer was separated and evaporated to near dryness. A yellow, sticky mass resulted; this was redissolved in ether, and the ether solution was concentrated very slowly. Pale yellow crystals of triphenylphosphinemethylene-tris-(*m*- α,α,α -trifluorotolyl)-borane formed, which were filtered, washed with methylene chloride-pentane and dried. A yield of 1.7 g. (48%) was realized. The sample was recrystallized from ether to give the pure compound, m.p. 159–160°.

Anal. Calcd. for $C_{42}H_{29}F_9PB$: C, 66.50; H, 4.05; F, 23.67. Found: C, 66.44; H, 3.98; F, 23.28.

Triphenylphosphinemethylenetrifluoroborane reacted with the same Grignard reagent to give the B-triaryl compound in 34% yield.

Reaction of Triphenylphosphinemethylenetrifluoroborane with Methylmagnesium Bromide.—A sample of the B-trifluoro adduct (2.16 g., 0.0063 mole) was placed in a 200 ml., three-necked flask fitted with an addition funnel, condenser and a magnetic stirrer. A connecting tube led from the top of the condenser to a jointed trap. The lower part of the trap was a Schlenk tube with a three-way stopcock (for nitrogen or vacuum alternatively). The trap contained 5 g. of trimethylamine and was cooled to -78°. Butyl ether (40 ml.), freshly distilled from lithium aluminum hydride, was added to the solid, and then 17 ml. of 1.42 *M* CH_3MgBr (0.024 mole) in butyl ether was added. The mixture was heated to *ca.* 80° for 4 hr. After cooling, the pressure in the system was reduced to 17 mm. for 1 hr. A white solid had formed in the trap, which was then allowed to warm to room temperature to remove excess trimethylamine. The upper part of the trap was replaced with a small low-temperature condenser (maintained at -78°). The pressure was reduced to 20 mm. and the trap heated to 60°. Long white crystals of trimethylamine-trimethylborane sublimed into the condenser. These were sealed under nitrogen in a small vial and submitted for analysis.

Anal. Calcd. for $C_8H_{13}NB$: C, 62.64; H, 15.77. Found: C, 62.22; H, 15.98.

Infrared Spectra.—The infrared spectra of the triphenylphosphinealkylideneboranes described above are available in the Ph.D. Thesis (Massachusetts Institute of Technology, September 1960) of S. O. G.

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