distillation under reduced pressure separated 2.4 g. of excess *n*-heptylsilane from 2.5 g. (44% yield) of crude *n*-heptylcyanosilane, later redistilled to obtain a 1.36 g. center cut for measurements.

n-Heptylisothiocyanatosilane. Gradual addition of 11.5 g. of mercuric thiocyanate over 2 hr., with addition of 0.5 g. every 5 min., to 4.8 g. of *n*-heptylsilane in 15 g. of carbon tetrachloride and then 20 min. of reflux gave mercury, thiocyanic acid later polymerized to thiocyanuric acid and an organosilicon mixture. Filtration and washing of the thiocyanuric acid with carbon tetrachloride and then fractional distillation separated the solvent and then the excess *n*-heptylsilane from approximately 3.3 g. (48% yield) of crude *n*-heptylisothiocyanatosilane; redistillation gave a 1.5-g. center cut for measurements.

n-Heptyltriisothiocyanatosilane. One-hour reflux of 5.5 g. of *n*-heptyltrichlorosilane and 16 g. of silver thiocyanate in 20 g. of carbon tetrachloride, and the usual process[6,7] with fractional distillation under reduced pressure, furnished 6.1 g. (87% yield) of crude *n*-heptyltriisothiocyanatosilane; redistillation gave a 2.8-g. center cut.

n-Heptyltriisocyanatosilane. One-hour reflux of 6.57 g. of *n*-heptyltrichlorosilane and 18 g. of silver cyanate in 16 g. of carbon tetrachloride, and the usual process[6,7] with distillation under low pressure, furnished 5.8 g. (80% yield) of *n*-heptyltriisocyanatosilane. The 1.6-g. center cut served for measurements.

n-Heptylsilicon esters. Typically, 70-min. reflux of 3.95 g. of *n*-heptyltrichlorosilane and 14.6 g. (a 30% excess) of silver trifluoroacetate in 16 g. of carbon tetrachloride, and then filtration and washing of silver salts and distillation under low pressure, furnished 1.43 g. of slightly low *n*-heptyltris(trifluoroacetoxy)silane, then 3.28 g. of center cut ester for measurements, and lastly 1.57 g. of slightly higher boiling ester. All these esters hydrolyzed quite rapidly in air of 50% relative humidity at 20°. All the yields of fluoroesters were 70% or better. Similarly, 4.27 g. of *n*-heptyltrichlorosilane and 12.5 g. of silver acetate in 16 g. of carbon tetrachloride after a 45-min. reflux furnished 0.8 g. of low fraction and then 1.7 g. of center cut *n*-heptyltriacetoxysilane for measurements; 2.6 g. of dark colored undistilled residue remained. Excessive decomposition evidently reduced the yield to 46% and also prevented the measurement of the normal boiling point.

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The Triphenylsilyltriphenylborate Anion and Its Germanium Analog

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Our recent synthesis of B-tris(triphenylsilyl)-*N*-trimethylborazine,[1] the first compound containing a boron-silicon bond to be reported, prompted us to search for other systems in which a boron–other metal bond might be capable of existence. We report here another type of compound in which a boron atom is bonded to silicon or germanium.

The stability of the tetraphenylborate anion is well known,[2] and the reaction between an aryllithium compound and a triarylborane appears to be a general one. This suggested that triphenylsilyllithium[3] and its germanium analog[4] might react with triphenylborane to give lithium triphenylsilyltriphenylborate and the corresponding germanium compound. This expectation was supported by the report of Wittig and his co-workers that tritylsodium and triphenylborane form $Na[(C_6H_5)_3CB(C_6H_5)_3]$, a complex, which, due to steric hindrance, was barely stable in the solid state and nearly completely dissociated in solution,[5] but that replacement of the boron atom by the larger aluminum atom permits formation of the stable salt, $Na[(C_6H_5)_3CAl(C_6H_5)_3]$, from tritylsodium and triphenylaluminum.[6] In our case we are keeping the Group III atom constant and decreasing steric hindrance by replacing carbon by its larger congeners.

The reaction of triphenylsilyllithium and triphenylgermyllithium with triphenylborane resulted in the expected complexes.

$$(C_6H_5)_3MLi + (C_6H_5)_3B \longrightarrow Li[(C_6H_5)_3MB(C_6H_5)_3] \quad (M = Si \text{ or } Ge)$$

The germanium derivative is the first example of a compound containing a germanium-boron bond. Both complexes are very readily hydrolyzed. However, they are soluble and sufficiently stable in methanol to permit various precipitation reactions to be carried out. Like all tetraarylborates, they form insoluble compounds with large inorganic and organic cations, e.g., $[(CH_3)_4N][(C_6H_5)_3SiB(C_6H_5)_3]$. The tetramethylammonium salts of both compounds when suspended in chloroform readily decolorized bromine. In the case of $[(CH_3)_4N][(C_6H_5)_3GeB(C_6H_5)_3]$, tetramethylammonium bromide (subliming *ca.* 380–390° in an open tube) and triphenylgermanium bromide, m.p. 136°, were isolated from the bromination reaction.

EXPERIMENTAL[7]

Lithium triphenylsilyltriphenylborate and its derivatives. A solution of triphenylsilyllithium was prepared by cleavage of 15 g. (0.029 mole) of hexaphenyldisilane with 3.0 g. (0.43 g.

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TABLE I

ANALYSES OF SALTS OF THE $[(C_6H_5)_3M\text{-}B(C_6H_5)_3]^-$ ANIONS (M = Si OR Ge)

		Carbon		Hydrogen		M		Nitrogen	
M	Cation	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Si	$(CH_3)_4N$	83.45	82.98	7.36	7.30	4.88	4.60	2.43	2.41
Si	$(C_6H_5)_3PCH_3$	84.81	84.42	6.21	6.24				
Si	K	79.98	79.76	5.59	5.78				
Ge	$(CH_3)_4N$	77.46	77.16	6.83	6.75	11.71	11.63	2.26	2.13
Ge	$(C_6H_5)_3PCH_3$	80.33	80.24	5.88	5.91				

atom) of lithium wire cut into small pieces in 170 ml. of tetrahydrofuran (THF). One hundred-fifty milliliters of this solution was added to 11.3 g. (0.045 mole) of triphenylborane dissolved in 50 ml. of tetrahydrofuran, in a three-necked flask equipped with a mechanical stirrer, reflux condenser, addition funnel, and nitrogen inlet tube. A mildly exothermic reaction resulted in immediate decolorization of the silyllithium reagent as it was added. After the reaction mixture had been stirred at room temperature for 2 hr., fine, white crystals began to deposit. The mixture was allowed to stand overnight, during which time more white solid precipitated. Concentration of the solution gave additional product. The crude lithium triphenylsilyltriphenylborate thus obtained was dissolved in tetrahydrofuran; addition of hexane to this solution precipitated fine white needles (13.6 g.). This product was insoluble in hexane and carbon tetrachloride; moderately soluble in ether; and very soluble in methanol. The lithium salt itself was not obtained in analytical purity. However, three pure derivatives could be prepared by adding to a methanol solution of the crude lithium salt methanolic solutions of methyltriphenylphosphonium bromide and tetramethylammonium bromide, as well as a solution of potassium fluoride in aqueous methanol. All three salts precipitated in the form of white crystals; the phosphonium salt rapidly became yellow in color after its precipitation. None had a sharp melting point; all turned brown on heating and decomposed over a variable temperature range. Such decomposition began at *ca.* 100° with the crude lithium salt, above 200° with the methyltriphenylphosphonium salt. Analyses are given in Table I.

Lithium triphenylgermyltriphenylborate and its derivatives. A solution of triphenylgermyllithium, prepared in ethylene glycol dimethyl ether by the cleavage of hexaphenyldigermane with metallic lithium,[4] was added to 5 g. (0.0207 mole) of triphenylborane in 50 ml. of ethylene glycol dimethyl ether in the same manner as described above, until the triphenylgermyllithium reagent was no longer decolorized. A white crystalline precipitate was formed during this addition. The reaction mixture was stirred at room temperature overnight. The solid was filtered; here also the lithium salt was not isolated in a pure state. The tetramethylammonium and methyltriphenylphosphonium derivatives, however, were isolated in analytical purity by treatment of the crude lithium salt with the respective bromides in methanol solution. Analyses are given in Table I. Both salts showed behavior on heating similar to that observed with their silicon analogs, and the phosphonium salt also rapidly became yellow after its preparation.

A separate experiment in which the crude lithium salt was converted to the methanol-insoluble tetramethylammonium derivative showed that the triphenylgermyltriphenylborate anion had been formed in *ca.* 65% yield.

The reaction of phenyllithium with lithium triphenylsilyltriphenylborate. Three grams of crude lithium triphenylsilyltriphenylborate was suspended in ether, and 9.7 ml. of 0.81*M* phenyllithium solution was added with vigorous stirring. No color changes were apparent while the mixture was stirred for 2 hr. at room temperature and for 2 hr. at reflux. The solid was filtered and identified as starting material by conversion to the methyltriphenylphosphonium salt. Addition of bromobenzene to the filtrate produced no tetraphenylsilane. Similar results were obtained when the mixture was heated at reflux for 20 hr.

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Metalation of Triphenylgermane by Grignard Reagents

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Triphenylgermane was found to react with organolithium reagents in diethyl ether to give triphenylgermyllithium in good yields, together with some of the corresponding tetrasubstituted products.[1] Under comparable conditions, no reaction was observed with Grignard reagents such as allylmagnesium bromide and *n*-butylmagnesium bromide.

A somewhat similar reactivity had been noted with organosilicon hydrides, that is, organolithium reagents gave the respective substitution products,[2] but Grignard reagents were unreactive in the various solvents tried.[2b,3] Recent work, however, has shown that Grignard reagents do alkylate and/or arylate organosilicon hydrides in tetrahydrofuran.[4]

We have found that certain Grignard reagents will metalate triphenylgermane in refluxing tetrahydrofuran (THF). Reaction of triphenylgermane with allylmagnesium chloride in refluxing tetrahydrofuran gave triphenylgermylmagnesium chloride. The presence and structure of the Grignard reagent were confirmed by carbonation, which af-

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