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Chemistry of Decaborane–Phosphorus Compounds. I. Nucleophilic Substitutions of Bis-(chlorodiphenylphosphine)-decaborane

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Bis-(chlorodiphenylphosphine)-decaborane was prepared by the reaction of diphenylchlorophosphine with decaborane and, by a chemical method, was proved to have the phosphine ligands attached at the 6,9-positions of the $B_{10}H_{12}$ unit. The reaction of $B_{10}H_{12}((C_6H_5)_2PCl)_2$ with ammonia and primary aliphatic amines in alcohols has been found to give nearly quantitative yields of the respective amino compounds, $B_{10}H_{12}((C_6H_5)_2P{\cdot}NHR)_2$. The use of secondary aliphatic amines in alcohols or water, however, led to the replacement of chlorine with alkoxy and hydroxy, respectively, thus resulting in the formation of esters, $B_{10}H_{12}((C_6H_5)_2P{\cdot}OR)_2$, or the acid, $B_{10}H_{12}((C_6H_5)_2P{\cdot}OH)_2$. The di-azide, $B_{10}H_{12}((C_6H_5)_2P{\cdot}N_3)_2$, was obtained by treatment with sodium azide.

During the course of a study of reactions of phosphines with boron hydrides, it was found that decaborane (I) and diphenylchlorophosphine in ether or benzene solution entered into an addition reaction with the formation of bis-(chlorodiphenylphosphine)-decaborane (II) and one mole of hydrogen. The presence of chlorine atoms bound to phosphorus made this compound interesting as an intermediate for new decaborane derivatives provided that the chlorine atoms were susceptible to exchange reactions.

To date only one decaborane derivative of the type $B_{10}H_{12}$(ligand)$_2$ having phosphine ligands has been reported, namely bis-(triphenylphosphine)-decaborane (III).[1] Compound III is high melting, stable to hydrolysis, and unreactive in ligand replacement reactions.[1,2] In contrast to such chemical behavior, compound II (m.p. 212° dec.), which must be recrystallized from anhydrous solvents in order to avoid hydrolysis, appeared to be much more promising as a starting material for chemical reactions.

Attempts to substitute other groups ($-NH_2$, $-NHR$, $-NR_2$, $-CNO$, $-CNS$) for chlorine by reaction of II with NH_3, NH_2R, NHR_2, KCNO, and KCNS in acetone or refluxing benzene solution gave a mixture of products from which those we desired could not be isolated in pure form. However, when attention was turned to the use of alcohols as the reaction medium, more successful results were obtained. When ammonia was passed into a suspension of II in anhydrous ethanol at room temperature, the insoluble II dissolved completely within several minutes and the desired bis-(aminodiphenylphosphine)-decaborane (IV) precipitated almost quantitatively upon removal of excess ammonia; the ammonium chloride formed in this reaction remained in solution. It was found that this reaction takes place in primary, secondary, and tertiary alcohols, and that the reaction product is obtained quantitatively and in purest form in those alcohols in which the solubility of IV is least, *e.g.*, isopropyl or *n*-butyl. Hydrazine reacted as ammonia to give the bishydrazide (V).

When this method was extended to the reaction of II with primary and secondary aliphatic amines, only the former reacted as expected. Thus bis-(methylaminodiphenylphosphine)-decaborane (VI) and bis-(butylaminodiphenylphosphine)-decaborane (VII) were obtained.

In the case of reaction with secondary amines, the expected aminolysis did not occur but instead reaction with the solvent was effected. The resulting products then were the phosphinite esters derived from that alcohol which had been used. The methyl (VIII) and ethyl (IX) esters were prepared in this manner, and when the reaction was extended to the use of ethylene glycol, the corresponding hydroxyethyl ester (X) was obtained. Of the secondary amines investigated in this regard, only ethylenimine reacted as originally expected to form the bisaziridino compound (XI). The base strengths of the aliphatic amines employed, *e.g.*, methylamine, dimethylamine, and ethylenimine, are so similar that the difference in the observed reactivity cannot be explained on this basis. In an attempted re-

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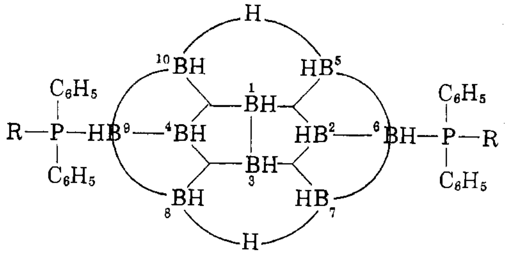
(1) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958).

(2) R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).

TABLE I

BIS-(CHLORODIPHENYLPHOSPHINE)-DECABORANE AND DERIVATIVES



	R	M.p., °C	Yield	Molecular weight	Carbon, % Calcd.	Carbon, % Found
II	Cl[a]	212	77.5	561.6	51.33	51.95
IV	NH_2	222	95–100	522.7	55.14	55.11
V	$NHNH_2$	214–215	95	552.7	52.15	51.20
VI	$NHCH_3$	226	90	550.8	56.70	56.82
VII	NHC_4H_9	165	92	634.9	60.53	60.43
VIII	OCH_3	227	90	552.7	56.49	56.30
IX	OC_2H_5	215–216	92	580.8	57.90	58.10
X	OCH_2CH_2OH	188	56	612.8	54.88	53.84
XI	$N(CH_2CH_2)$	202	94	574.8	58.51	58.23
XII	OH	216[b]	91	524.7	54.93	55.33
XIV	N_3	147	96	574.7	50.15	50.88

	Hydrogen, % Calcd.	Hydrogen, % Found	Boron, % Calcd.	Boron, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
II	5.74	6.15	19.27	19.20	. . .	. . .	11.03	11.00
IV	6.94	7.00	20.70	20.84	5.36	5.23	11.85	11.80
V	6.93	7.32	19.58	19.67	10.14	10.44	11.21	10.90
VI	7.32	7.30	19.65	19.71	5.08	5.09	11.25	11.00
VII	8.26	8.51	17.04	16.66	4.41	4.21	9.76	9.50
VIII	6.93	6.25	19.57	19.10	. . .	. . .	11.21	10.90
IX	7.29	7.24	18.63	18.68	. . .	. . .	10.67	10.70
X	6.91	7.08	17.66	17.28	. . .	. . .	10.11	10.10
XI	7.02	7.45	18.82	18.72	4.87	4.41	10.78	10.80
XII	6.53	6.78	20.62	20.66	. . .	. . .	11.81	11.60
XIV	5.61	6.74	18.83	17.84	14.63	14.60	10.78	10.60

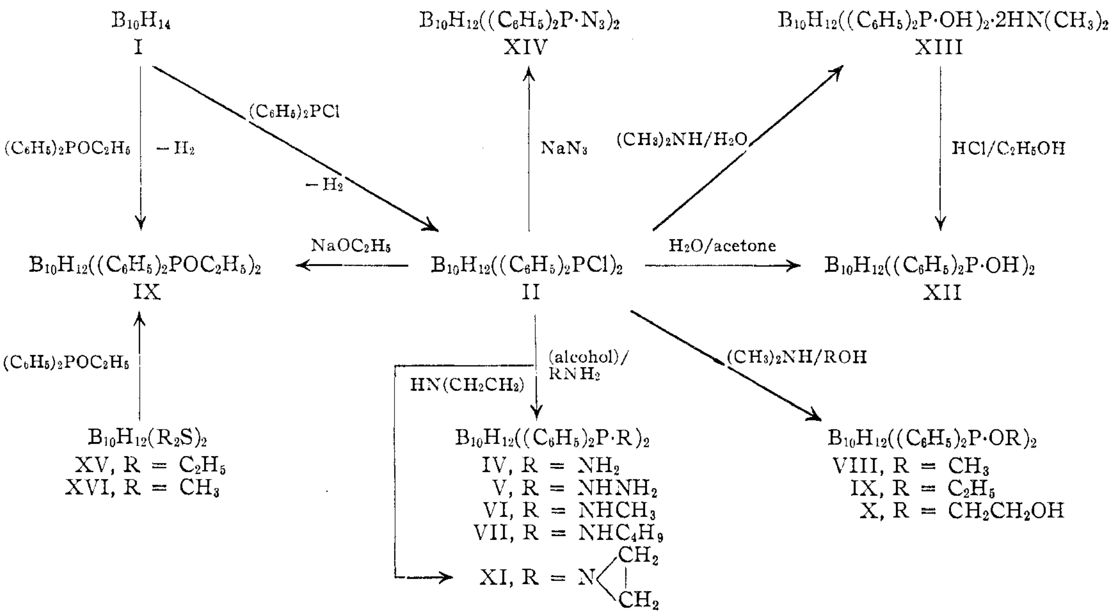
[a] Chlorine analysis: Calcd. 12.63; Found: 12.21. [b] See Experimental.

action with the weakly basic aniline neither reaction occurred.

Since dimethylamine was so effective in promoting the alcoholysis of II, it became of interest to ascertain whether hydrolysis could be similarly achieved. Upon treatment of a suspension of II in water with dimethylamine, the expected hydrolysis occurred, but the diacid (XII) formed immediately reacted with additional dimethylamine so that only the bisdimethylammonium salt (XIII) was recovered. When XIII was treated with alcoholic hydrochloric acid, the free acid XII was obtained. It subsequently was found that XII could be prepared directly by simply hydrolyzing II in acetone with water.

To determine whether such displacements also would occur with metal salts, an alcoholic suspension of II and sodium azide was stirred for a short period at 30°. The desired bisazide (XIV) was easily recovered in pure form by simply washing the separated solids with water. Compound XIV (m.p. 147°) was found not to explode on impact or friction, but it did flash on ignition. The azide was found to decompose on standing in sunlight. Physical and analytical data for the dichloro compound (II) and the products of the reported reactions are compiled in Table I.

It was of interest to determine those positions of the decaborane nucleus at which the ligands of II and its derivatives were attached. It was supposed that they were bonded at the 6 and 9 boron atoms, as has been established for bis-(acetonitrile)-decaborane[3] and for bis-(dimethyl sulfide)-decaborane (XV).[4] As described above,



compound II had been prepared directly from decaborane by treatment with diphenylchlorophosphine. Simple alcoholysis converted II into the ester IX. But compound IX also resulted from the direct reaction of decaborane with ethyl diphenylphosphinite.[5] This established unequivocally the similarity of the reactions of decaborane with diphenylchlorophosphine and with ethyl diphenylphosphinite. Finally, the ester IX was conclusively related to bis-(diethyl sulfide)-decaborane (XV)[6] and bis-(dimethyl sulfide)-decaborane (XVI), since these compounds on treatment with ethyl diphenylphosphinite in simple ligand displacement reactions afforded compound IX, which had been prepared from II.

Experimental[7]

Starting Materials.—Decaborane was purified by vacuum sublimation. Diphenylchlorophosphine was prepared from commercially available phenyldichlorophosphine by disproportionation with aluminum chloride.[8]

Bis-(chlorodiphenylphosphine)-decaborane (II).—A solution of diphenylchlorophosphine (88 g., 0.4 mole) in ether (100 ml.) was added to a solution of decaborane (I, 22.4 g., 0.2 mole) in ether (200 ml.). Hydrogen was evolved slowly and, after stirring for 20 hr. at 25°, 98 g. of reaction product had precipitated. Recrystallization from anhydrous ethyl acetate gave 87 g. of pure II.

Amination of Bis-(chlorodiphenylphosphine)-decaborane (II). Bis-(aminodiphenylphosphine)-decaborane (IV).—Gaseous ammonia was passed into a stirred suspension of II (1.4 g., 0.0025 mole) in anhydrous ethanol (60 ml.). The temperature was kept at 20° by cooling and complete solution occurred after 15 min. Excess ammonia then was evaporated and 1.3 g. (100%) of crude II (m.p. 214–216°) precipitated. Recrystallization from benzene raised the m.p. to 222°.

When the experiment was repeated under the same conditions but employing methanol instead of ethanol, only 60% yield of IV was obtained. The use of isopropyl alcohol or *t*-butyl alcohol gave rather pure IV (m.p. 219–220°) in 95% yield. *n*-Butyl alcohol was found to be the most suitable alcohol for this reaction. In a typical experiment, 5 g. of II suspended in 200 ml. of butyl alcohol was converted into pure IV (m.p. 222°) in 98% yield; in a second experiment the yield was 100%.

Bis-(methylaminodiphenylphosphine)-decaborane (VI) was prepared in the same manner employing gaseous methylamine instead of ammonia; the precipitated crude product was recrystallized from benzene.

Bis-(aziridinodiphenylphosphine)-decaborane (XI).—An excess of ethylenimine (1.29 g., 0.03 mole) in ethanol (20 ml.) was added, with stirring, within 5 min. to a suspension of II (2.81 g., 0.005 mole) in ethanol (80 ml.). The mixture was stirred at 15° for 30 min., then at 35° for another 30 min. Solution did not occur. Compound IX was recovered by filtration and merely washed with petroleum ether.

Bis-(butylaminodiphenylphosphine)-decaborane (VII) **and bis-(hydrazinodiphenylphosphine)-decaborane** (V) were prepared by the same procedure as for XI except for substitution of butylamine and hydrazine, respectively, for ethylenimine. The former compound (VII) was recrystallized from ethanol, while compound V was recrystallized from chloroform.

Alkoxylation of Bis-(chlorodiphenylphosphine)-decaborane (II). Bis-(ethoxydiphenylphosphine)-decaborane (IX).—(a) A solution of $(C_6H_5)_2POC_2H_5$ (4.6 g., 0.02 mole) in ether (10 ml.) was added, with stirring, to a solution of

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(3) J. M. Reddy and W. N. Lipscomb, *J. Am. Chem. Soc.*, **81**, 754 (1959).

(4) D. E. Sand and A. Zalkin, Abstract of Papers, International Congress of Crystallography, 1960.

(5) H. Schroeder, forthcoming publication.

(6) R. J. Polak and T. L. Heying, *J. Org. Chem.*, **27**, 1483 (1962).

(7) Melting points are uncorrected (Fisher-Johns); analyses were by R. Rittner, R. Culmo, and F. O. Geenty of the Olin microchemical section.

(8) M. P. Brown and H. B. Silver, *Chem. Ind.* (London), 24 (1961).

decaborane (I, 1.22 g., 0.01 mole) in ether (40 ml.). The reaction product (m.p. 203–208°) precipitated quantitatively within 90 min. at 20°. Purification could be achieved by recrystallization from benzene, but preferably from ethyl acetate. When the latter solvent was used, the reaction product contained approximately 0.5 mole of ethyl acetate, which was removed by heating the substance for a short time *above 145° in vacuo.*

(b) To a suspension of bis-(diphenylchlorophosphine)-decaborane (II, 2.81 g., 0.005 mole) in anhydrous ethanol (50 ml.) was added a solution formed by dissolving sodium (0.23 g., 0.01 mole) in ethanol (20 ml.). The mixture was stirred for 30 min., then evaporated to dryness. The reaction product was washed with water, recrystallized from ethyl acetate, and dried at 160° *in vacuo;* yield of IX: 2 g. (69%).

(c) Gaseous dimethylamine was passed into a suspension of bis-(chlorodiphenylphosphine)-decaborane (II, 5.61 g., 0.01 mole) in ethanol (200 ml.) for 30 min. After evaporation of excess dimethylamine, the crude IX was recovered by filtration and recrystallized from ethyl acetate.

Bis-(methoxydiphenylphosphine)-decaborane (VIII) and bis-(β-hydroxyethoxydiphenylphosphine)-decaborane (X) were prepared by the same general procedure, passing dimethylamine into a suspension of II in the respective alcohol. Compound VII was recrystallized from acetonitrile, whereas X merely was washed with methanol and petroleum ether.

Bis-(hydroxydiphenylphosphine)-decaborane Bis-dimethylammonium Salt (XIII).—Gaseous dimethylamine was bubbled through a suspension of bis-(chlorodiphenylphosphine)-decaborane (II, 5.61 g., 0.01 mole) in water (50 ml.). The mixture was stirred with cooling and solution occurred after 15 min. Upon evaporation of excess dimethylamine, compound XIII separated, was filtered, and dried *in vacuo*. The yield of crude product was 5.1 g. (93.5%). Recrystallization from 300 ml. of a mixture of dimethylformamide and acetonitrile (2:1) gave 4.2 g. (77%) of pure XIII, m.p. 224–226°.

Anal. Calcd. for $C_{28}H_{48}B_{10}N_2O_2P_2$ (614.8): C, 54.69; H, 7.87; B, 17.60; N, 4.56; P, 10.08. Found: C, 55.08; H, 8.26; B, 17.66; N, 4.62; P, 9.90.

Bis-(hydroxydiphenylphosphine)-decaborane (XII).—(a) To a suspension of bis-(hydroxydiphenylphosphine)-decaborane bisdimethylammonium salt (XIII, 1.23 g., 0.002 mole) in ethanol (10 ml.), 5% alcoholic hydrochloric acid was added dropwise with stirring. The salt dissolved gradually and complete solution was effected after the theoretical amount of acid had been added. The solution thus obtained was evaporated to dryness, and the remaining semi-solid product was treated with hot water (20 ml.) to give 0.84 g. (80%) of crude XII. After recrystallization from xylene (50 ml.), the yield of pure XII was 0.72 g. (69%). Instead of showing a sharp melting point, the product softened somewhat at 216° but still had not melted at 300°. Compound XII is soluble in alcohols, acetone, and ethyl acetate.

(b) Bis-(chlorodiphenylphosphine)-decaborane (II, 5.61 g., 0.01 mole) was dissolved at 40° in acetone (220 ml.). After cooling to 25°, water (10 ml.) was added to the slightly yellow solution. Upon stirring for approximately 5 min., the solution turned colorless and then was evaporated to dryness. The residue consisted of almost pure XII.

Bis-(azidodiphenylphosphine)-decaborane (XIV).—A suspension of bis-(chlorodiphenylphosphine)-decaborane (II, 0.56 g., 0.001 mole) and sodium azide (0.195 g., 0.003 mole) in ethanol (25 ml.) was stirred for 1 hr. at 30°. The solid reaction products were recovered by filtration, washed thoroughly with water (50 ml.), and dried *in vacuo* over diphosphorus pentoxide. Recrystallization from ethanol did not raise the melting point.

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