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Arsinocarboranes. Synthesis and Characterization of 1,2-Bis(dimethylarsino)-[1] and 1,2-Bis(diphenylarsino)-*o*-carboranes

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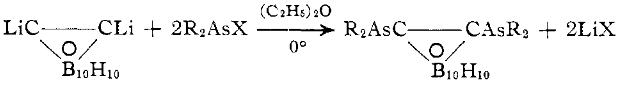
The carborane[2] moiety, because of its unusual geometry and stability, is being extensively explored both from the standpoint of its own chemical reactivity as well as its function as a substituent. A stimulating review of the developments in carborane chemistry through 1967 is given by Muetterties and Knoth in a recent publication.[3]

Our interest has been in the development of potential ligand systems in which the *o*-carborane nucleus functions as a backbone, the carbon atoms containing the ligands. We have previously reported the synthesis and reactivities of phosphino and mercapto derivatives of *o*-carborane.[4-7]

We wish now to report the synthesis and characterization of the analogous arsine derivatives of *o*-carborane. The ligands were prepared *via* the low-temperature reaction of dilithio-*o*-carborane[8] with the appropriate arsine in diethyl ether



$$\underset{\substack{\diagdown O \diagup \\ B_{10}H_{10}}}{\mathrm{LiC{-\!-\!-}CLi}} + 2R_2AsX \xrightarrow[0^\circ]{(C_2H_5)_2O} \underset{\substack{\diagdown O \diagup \\ B_{10}H_{10}}}{\mathrm{R_2AsC{-\!-\!-}CAsR_2}} + 2LiX$$

I, II

where $R = CH_3$ (I) or C_6H_5 (II).

Both the methyl (I) and phenyl (II) derivatives were white, crystalline, air-stable solids. Isolation of I was effected by removal of the ether solvent under vacuum or by distillation and by subsequent extraction and recrystallization of the product with hot hexane. When pure, I melts sharply at 111°. The infrared spectrum in the B–H stretching region showed strong absorptions at 2547, 2570, 2580 (sh), and 2610 cm^{-1}. The characteristic B–H skeletal absorption occurs at 727–740 cm^{-1}. Table I lists the infrared bands associated with the compounds prepared in this work.

Further characterization of I was afforded by its elemental analysis and ^1H and ^{11}B nmr spectra. A single methyl resonance was observed at τ 9.13 (60 Mc/sec in benzene) and at τ 8.61 in carbon disulfide. The ^{11}B spectrum at 32 Mc/sec showed four peaks of area ratio 1:2:4:3, typical of the *o*-carborane cage systems at 32 Mc/sec. The chemical shift of the high-field doublet[9] relative to $(C_2H_5O)_3B$ was 28.4 ppm and the ^{11}B–^1H coupling constant of the two high-field peaks was 151 cps when measured in acetonitrile. (For comparison, *o*-carborane in CH_3CN gave a value of δ 30.7 ppm and a ^{11}B–^1H coupling constant of 160 cps.)

The phenyl analog (II) was only slightly soluble in diethyl ether and therefore precipitated during the reaction (eq 1). Recrystallization from chloroform–hexane yielded crystals which melted at 205 ± 0.5°. Because of the limited solubility of II in suitable solvents, the nmr spectra could not be obtained.

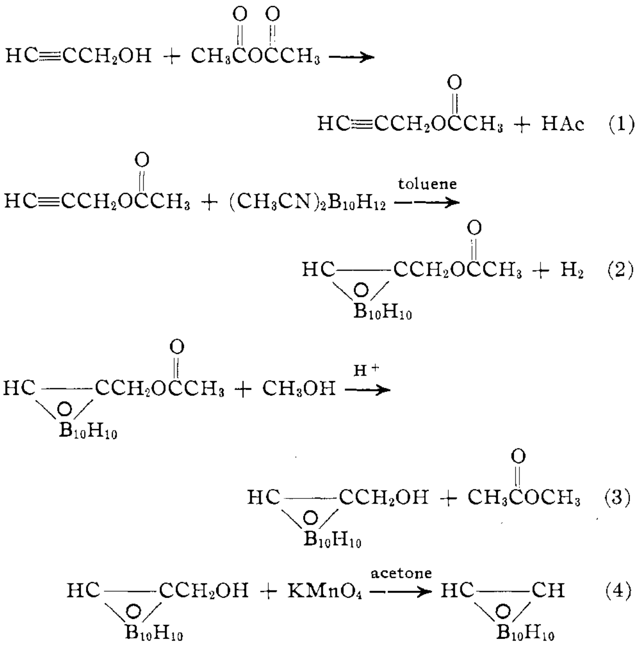
Two palladium complexes of II were isolated. The chloride was obtained by heating the benzonitrile complex of palladium chloride with II in chloroform, and the iodide was obtained by reaction of the chloride with potassium iodide in acetone–water. Analysis of the $PdCl_2$ complex was in accord with the formula $B_{10}H_{10}C_2[As(C_6H_5)_2]_2PdCl_2$.

Difficulty was encountered when complexation of I with $NiCl_2$ was attempted. In acetone or nitromethane a red solution formed from which a light green unstable solid was isolated. This solid has not yet been characterized.

Experimental Section

***o*-Carborane.**—A series of publications by Zakharkin and coworkers,[10,11] suggested a convenient route to *o*-carborane. Our adaptation of the Zakharkin reactions follows. However, a recently published procedure by Kutal, Owen, and Todd[12] essentially details our procedure.

The reactions involved were



$$HC{\equiv}CCH_2OH + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow HC{\equiv}CCH_2O\overset{O}{\overset{\|}{C}}CH_3 + HAc \quad (1)$$

$$HC{\equiv}CCH_2O\overset{O}{\overset{\|}{C}}CH_3 + (CH_3CN)_2B_{10}H_{12} \xrightarrow{\text{toluene}} \underset{\substack{\diagdown O \diagup \\ B_{10}H_{10}}}{\mathrm{HC{-\!-\!-}CCH_2O\overset{O}{\overset{\|}{C}}CH_3}} + H_2 \quad (2)$$

$$\underset{\substack{\diagdown O \diagup \\ B_{10}H_{10}}}{\mathrm{HC{-\!-\!-}CCH_2O\overset{O}{\overset{\|}{C}}CH_3}} + CH_3OH \xrightarrow{H^+} \underset{\substack{\diagdown O \diagup \\ B_{10}H_{10}}}{\mathrm{HC{-\!-\!-}CCH_2OH}} + CH_3\overset{O}{\overset{\|}{C}}OCH_3 \quad (3)$$

$$\underset{\substack{\diagdown O \diagup \\ B_{10}H_{10}}}{\mathrm{HC{-\!-\!-}CCH_2OH}} + KMnO_4 \xrightarrow{\text{acetone}} \underset{\substack{\diagdown O \diagup \\ B_{10}H_{10}}}{\mathrm{HC{-\!-\!-}CH}} \quad (4)$$

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[1] Prepared previously by R. Schaeffer, private communication.

[2] For brevity the term carborane is used for dicarbaclovododecaborane(12).

[3] E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968.

[4] H. D. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 1817 (1965).

[5] H. D. Smith, Jr., T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

[6] H. D. Smith, Jr., C. O. Obenland, and S. Papetti, *ibid.*, **5**, 1013 (1966).

[7] H. D. Smith, Jr., M. A. Robinson, and S. Papetti, *ibid.*, **6**, 1014 (1967).

[8] T. L. Heying, J. W. Ayer, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

[9] For discussion of the interpretation of the ^{11}B spectrum of *o*-carborane see G. D. Vickers, *et al.*, *ibid.*, **5**, 693 (1966).

[10] L. I. Zakharkin, Yu. A. Chaponskii, V. A. Brattsev, and V. I. Stanko, *Zh. Obshch. Khim.*, **36**, 878 (1966).

[11] L. I. Zakharkin, V. A. Brattsev, and V. I. Stanko, *ibid.*, **36**, 886 (1966).

[12] C. R. Kutal, D. A. Owen, and L. J. Todd, *Inorg. Syn.*, **11**, 19 (1968).

TABLE I

INFRARED FREQUENCIES (CM^{-1}) OF ARSINOCARBORANES[a]

Compound	B–H		C–H		Other bands
	Str	Skeletal	Str	Bend	
$B_{10}H_{10}C_2[As(CH_3)_2]_2$	2610 s 2580 s 2570 s 2547 s	730 m 740 m	3020 w 3000 w	1419 m	800 m 835 m 840 m 850 s 900 m 930 w 970 w 1055 m, br 1072 m 1246 w 1262 m
$B_{10}H_{10}C_2[As(C_6H_5)_2]_2$	2680 s, db 2640 s, db 2600 s, db 2590 s		3098 m 3080 m 1490 s 1445 s, db	750 s, db 707 s	680 w 780 w 815 m 850 w 910 w 922 m 933 w 945 w, db 975 w 980 w 990 w 1005 m 1030 m 1050 w 1080 s 1085 m 1165 m 1190 m 1220 w 1280 w 1320 m 1345 w 1590 m
$B_{10}H_{10}C_2[As(C_6H_5)_2]_2PdCl_2$	2650 m, db 2640 m, db 2600 m, db 2585 m 2560 m		3075 w 1488 m 1450 s	744 s 690 s	800 w 830 w 870 vw 905 vw 934 vw 975 vw 1155 w 1165 w, db 1185 w 1275 vw 1310 w 1440 w 1580 w
$B_{10}H_{10}C_2[As(C_6H_5)_2]_2PdI_2$	2570 m 2590 m 2620 m		3060 w 1480 m 1437 s	740 s, db 685 m	775 vw 800 w 820 w 840 vw 865 vw 900 vw 910 vw 925 vw 935 vw 965 vw 1000 m 1020 w 1075 m 1158 w 1185 w 1308 w 1330 w 1580 vw

[a] Abbreviations: s, strong; m, medium; w, weak; vw, very weak; br, broad; db, doublet.

(a) **Propargyl Acetate.**—To 172 g (1.68 mol) of acetic anhydride was added 5 drops of concentrated HCl. After cooling to 0°, 94 g (1.68 mol) of propargyl alcohol was added dropwise at a moderate rate. The reaction mixture was allowed to warm to room temperature with stirring for 12 hr after which the solution was heated at 70° for 2 hr. The solution was then cooled to room temperature and poured into a stirred mixture of 100 g of Na_2CO_3, 125 g of $MgSO_4$, and 1 l. of hexane. The mixture was heated slightly while being stirred under a blanket of N_2 in order to ensure complete reaction. The solids were removed by filtration and the filtrate was distilled. The fraction boiling at 122–126° (1 atm) was collected and redistilled, yielding 79.2 g of propargyl acetate, bp 126°, 48.1% yield.

(b) **1-Acetoxymethyl-*o*-carborane.**—Bis(acetonitrile)decaborane was prepared by adding a solution of 41 g of acetonitrile in 100 ml of dry toluene to an 80° solution of 60.0 g of decaborane in 300 ml of dry toluene in a nitrogen atmosphere. After 2 hr at 80° a white solid precipitated. Propargyl acetate (50 g in 50 ml of toluene) was added to the mixture over a 20-min period while the temperature was maintained at 80°. The resulting clear yellow solution was heated at 80–90° for 12 hr, followed by 100° for 6 hr. The solvent was then removed at 80–90° (600–610 mm), leaving an orange syrup. Distillation of the crude product yielded 60 g of a white, crystalline solid, bp 120° (1 mm), mp 45–47°; yield, 55.5%.

(c) **1-Hydroxymethyl-*o*-carborane.**—1-Acetoxymethyl-*o*-carborane (0.1 mole) was dissolved in excess methanol containing 1 ml of concentrated HCl and the solution was heated to reflux. The volatile by-products and excess solvent were distilled out of the reaction flask over a 4–5-hr period. The residue was washed with hexane and dried under vacuum, mp 219–226°.

(d) ***o*-Carborane.**—A portion of the crude hydroxymethyl-*o*-carborane (24.0 g) was dissolved in 300 ml of acetone and a slurry of 47.0 g of $KMnO_4$ in 200 ml of acetone was added at once. After approximately 20 hr of stirring at room temperature, the mixture was filtered and the filtrate was evaporated to dryness, yielding a good grade of *o*-carborane (16.5 g, 79%).

1,2-Bis(dimethylarsino)-*o*-carborane.—To a dilithio-*o*-carborane suspension in diethyl ether[8] was added 2 equiv of dimethylbromoarsine. The solvent was removed by distillation and the white solid residue was refluxed in hexane. The hexane solution was filtered to remove the LiBr and then evaporated to dryness. The crude product was recrystallized from hot hexane and dried under vacuum, mp 111°. *Anal.* Calcd for $B_{10}H_{10}C_2[As(CH_3)_2]_2$: C, 20.46; H, 6.29; B, 30.69. Found: C, 20.28; H, 6.26; B, 31.15.

1,2-Bis(diphenylarsino)-*o*-carborane.—The procedure was the same as described above with the exception that the phenyl analog was insoluble in diethyl ether and hexane and was recrystallized from chloroform–hexane, mp 205°. *Anal.* Calcd for $B_{10}H_{10}C_2[As(C_6H_5)_2]_2$: C, 52.00; H, 5.03; B, 18.00. Found: C, 51.63; H, 4.81; B, 17.00.

$B_{10}H_{10}C_2[As(C_6H_5)_2]_2PdCl_2$.—1,2-Bis(diphenylarsino)-*o*-carborane (0.6 g, 0.01 mol) in $CHCl_3$ was added to 0.18 g of $(C_7H_5N)_2PdCl_2$ in refluxing $CHCl_3$. Concentration of the solution and addition of hexane precipitated yellow crystals which were recrystallized from $CHCl_3$–hexane, mp 225° dec. *Anal.* Calcd for $B_{10}H_{10}C_2[As(C_6H_5)_2]_2PdCl_2$: C, 40.15; H, 3.88; Cl, 9.11. Found: C, 40.54; H, 4.06; Cl, 9.86.

$B_{10}H_{10}C_2[As(C_6H_5)_2]_2PdI_2$.—The $PdCl_2$ complex described above was dissolved in acetone and added to an excess of potassium iodide in acetone–water. Red crystals formed and were collected, washed with water, and recrystallized from $CHCl_3$, mp 329° dec.

Measurements.—Infrared spectra were measured using a Perkin-Elmer Model 237 grating spectrometer. The ^1H nmr spectrum was obtained with a Varian A-60 spectrometer, and the ^{11}B nmr spectrum was obtained with a Varian HA-100 spectrometer operating at 32 Mc/sec.

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The Preparation of Bis(dimethylarsino)-*o*-carborane and Related Compounds

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Recent syntheses of a variety of bis(phosphino)carborane–metal complexes[1–3] have prompted us to investigate analogous bis(arsino)carborane derivatives as possible complexing ligands. Such ligands should be structurally analogous to *o*-phenylenediarsines. Almost nothing is known about the steric and electronic effects of the carborane cage when present in such a ligand. It was hoped that the preparation of these ligands and their complexes would provide a source for bonding studies. It was also hoped that such a ligand, incorporating the carborane framework, would prove as versatile a complexing agent as *o*-phenylenebis(dimethylarsine).[4] The only reported arsino compound incorporating the *o*-carborane framework is $(o\text{-}C_6H_5\text{-}CB_{10}H_{10}C)_3As$.[5]

Experimental Section

All preparations were carried out under an atmosphere of nitrogen. All analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Hydrogen-1 nmr and infrared spectra were obtained as previously described.[6]

Boron nmr absorptions were obtained on a Varian Model HA 100 spectrometer with an operating frequency of 32 MHz. Trimethylboron was used as an external reference, by the tube-interchange technique.

Bis(dimethylarsino)-*o*-carborane.—The ligand $o\text{-}B_{10}C_2H_{10}[As(CH_3)_2]_2$[7] (bicars) was prepared in a manner analogous to that employed in the preparation of $o\text{-}B_{10}C_2H_{10}[PR_2]_2$,[8] but employing $(CH_3)_2AsBr$.[9]

Separation of the pure white crystalline product was effected by immediate precipitation upon the addition of 50 ml of water to a saturated solution of the reaction products in ethyl ether.

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(4) For a summary of many of these complexes see F. P. Dwyer and D. P., Mellor, Ed., "Chelating Agents and Metal Chelates," Academic Press Inc., New York, N. Y., 1964, Chapter 3.

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