(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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The product was purified by dissolution in ethyl ether and recrystallization upon addition of water. The bicars was then dried *in vacuo* to remove all traces of water.

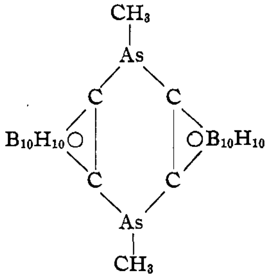
The formula $o\text{-}B_{10}C_2H_{10}[As(CH_3)_2]_2$ is supported by all spectral data. The ^1H nmr spectrum of bicars dissolved in carbon tetrachloride and carbon disulfide exhibits a single resonance absorption at −1.22 ppm from TMS due to the methyl groups attached to the arsenic atoms. A chemical shift of −0.86 ppm from TMS is recorded when the ligand bicars is dissolved in benzene. The ^{11}B nmr spectra of the ligand consists of a set of four distinct absorptions of relative intensity 1:2:4:3 at 84.7, 90.1, 94.4, and 99.3 ppm from $(CH_3)_3B$ respectively.

The ir spectrum exhibits a B–H cage absorption at 724 (s) cm^{-1}. Other absorptions appear at 862, 902 (m), 982 (w), 1080 (m), 1262 (w), and 2570 (s) cm^{-1}.

Anal. Calcd for $C_6H_{22}As_2B_{10}$: C, 20.46; H, 6.30; As, 42.02; B, 30.72. Found: C, 20.66; H, 6.46; As, 41.79; B, 31.09. The molecular weight determined cryoscopically in benzene is 344 (theoretical 353). The melting point is 111 ± 2°.

The compound was found to be readily soluble in acetone, benzene, and ethyl ether. It is extremely insoluble in water. The compound appears to be quite stable in air and is not decomposed in boiling water.

Dimeric Methylarsino(III)carborane.—This preparation was carried out analogous to that of $[o\text{-}B_{10}C_2H_{10}PR]_2$[8] employing CH_3AsBr_2.[9] The pure white microcrystalline product was purified by recrystallization from ethyl ether. As in the previous case, the formula is supported by all spectral data. The ^1H nmr spectrum of the material dissolved in benzene exhibits an absorption at −0.95 ppm due to the methyl protons. The ir spectrum exhibits absorptions at 730 (vs), 770 (w), 802 (m), 827 (w), 854 (s), 902 (vw), 925, 970 (m, br), 1076 (s), 1257 (s), 1625 (m, br), and 2565 (s) cm^{-1}.



Anal. Calcd for $C_6H_{26}B_{20}As_2$: C, 15.19; H, 5.52; B, 45.61; As, 33.68. Found: C, 14.99; H, 5.49; B, 45.39; As, 33.58. The molecular weight was determined to be 460 (theoretical 474). The melting point is 218 ± 3°.

The compound appears to be quite stable toward air oxidation and hydrolysis by moisture in the air.

[Bis(dimethylarsino)-*o*-carborane]nickel Dicarbonyl.—The reaction between nickel carbonyl and bis(dimethylarsino)-*o*-carborane was carried out using standard vacuum techniques. A 2.31-mmol sample of ligand bicars was transferred to a 50-ml flask. About 15 ml of dry *n*-hexane was condensed *in vacuo* into the reaction tube at −196°. A 7.32-mmol sample of $Ni(CO)_4$ (Matheson) was then condensed into the reaction tube. The reaction mixture was allowed to warm to 0° and rate of reaction was observed by evolution of carbon monoxide. Upon completion of reaction, about 2 hr, all volatile materials were recovered by distillation *in vacuo* leaving behind a creamy white powdery product. The product was purified by recrystallization from pretroleum ether (bp 60–110°).

The ^1H nmr spectrum of the complex dissolved in benzene exhibited a single resonance absorption at −0.96 ppm from TMS. The ir spectrum run in Nujol and cyclohexane exhibits absorptions at 726 (s), 804 (br), 868 (s), 901 (s), 932 (w), 1020 (w), 1070 (m), 1252 (s), 1968 (vs), 2027 (s), and 2600 (br) cm^{-1}.

Anal. Calcd for $C_8H_{22}As_2B_{10}NiO_2$: C, 20.58; H, 4.75; As, 32.08; B, 23.17; Ni, 12.57. Found: C, 21.00; H, 4.93; As, 32.35; B, 24.06; Ni, 12.32. The molecular weight determined cryoscopically in benzene is 475 (theoretical 467). The complex was found to be diamagnetic.

[Bis(dimethylarsino)-*o*-carborane]iron Tricarbonyl.—The mustard yellow crystalline complex was prepared in analogous manner to $(diars)Fe(CO)_3$.[10] The product was purified by recrystallization from benzene. The complex decomposes over a 2-month period in air and light to a brown product.

The ^1H nmr spectrum of the complex dissolved in benzene exhibits a single resonance absorption at −1.22 ppm from TMS. The ir spectrum, obtained as a Nujol mull, shows absorptions at 724 (s), 823 (m), 855 (w), 876 (s), 912 (s), 972 (br), 1074 (s), 1256 (m), 1270 (w), 1898 (w), 1926 (s), 1997 (vw), 2002 (vs), and 2585 (br) cm^{-1}. The Mössbauer spectrum[11] of the complex gave an isometric shift, δ, of +0.18 mm/sec relative to $Na_2Fe(CN)_5NO\cdot 2H_2O$. Owing to the asymmetry of the system, a quadrupole splitting of 2.4 mm/sec was obtained. The spectrum appeared to be pure and contained only one "kind" of iron nuclei.

Anal. Calcd for $C_9H_{22}As_2B_{10}FeO_3$: C, 21.96; H, 4.50; As, 30.44; Fe, 11.34. Found: C, 21.87; H, 4.71; As, 30.09; Fe, 11.02. The molecular weight determined cryoscopically in benzene is 480 (theoretical 492). The complex was found to be diamagnetic.

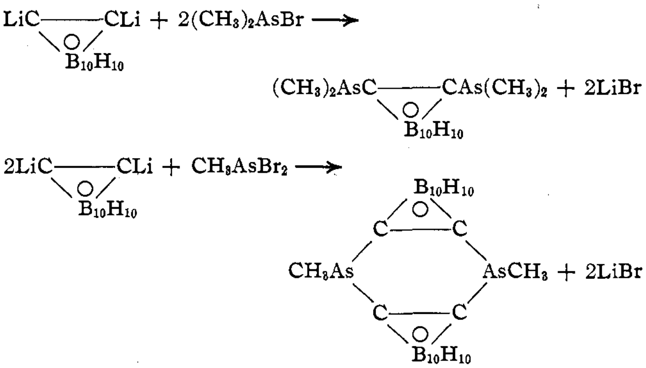
[Bis(dimethylarsino)-*o*-carboranel]molybdenum Tetracarbonyl.—The white crystalline complex was prepared as above employing 5 ml of dry xylene as solvent. The product was purified by recrystallization from benzene.

The ^1H nmr spectrum of the pure white powdery complex dissolved in benzene exhibits a single resonance at −1.03 ppm from TMS. The ir spectrum shows absorptions at 725 (s), 824 (m), 874 (s), 904 (m), 935 (w), 974 (w), 1075 (m), 1254 (m), 1875 (br), 1940 (vs), 1946 (w), 1953 (vw), 1994 (s), 2015 (vw), 2020 (s), 2560 (br), and 2610 (br) cm^{-1}.

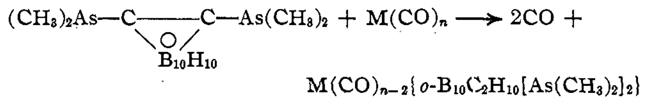
Anal. Calcd for $C_{10}H_{22}As_2B_{10}MoO_4$: C, 21.44; H, 3.96; As, 26.74; B, 19.31; Mo, 17.13. Found: C, 21.72; H, 3.74; As, 26.51; B, 19.07; Mo, 16.96. The molecular weight determined cryoscopically in benzene is 566 (theoretical 560).

Discussion

The possibility of preparing bis(arsino)carborane derivatives was established with the following examples.



Next a series of reactions was conducted in analogy to previous experiments[1-3] which established that $o\text{-}B_{10}C_2H_{10}[As(CH_3)_2]_2$, or bicars, was capable of replacing the carbonyl group in metal carbonyls and, in so doing, to form new 4-, 5-, and 6-coordinate complexes according to



$$(CH_3)_2As{-}\underset{B_{10}H_{10}}{\underbrace{C{-}C}}{-}As(CH_3)_2 + M(CO)_n \longrightarrow 2CO + M(CO)_{n-2}\{o\text{-}B_{10}C_2H_{10}[As(CH_3)_2]_2\}$$

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where M = Ni, $n = 4$; M = Fe, $n = 5$; M = Mo, $n = 6$.

The Mössbauer spectrum of the iron complex $Fe(CO)_3$(bicars) has provided some information about the electronic properties of this new ligand. The isomer shift of +0.18 mm/sec is typical of low-valent iron species. The strongly electron-donating properties of the ligand are reflected in the negative shift compared to $Fe(CO)_5$.[12] The isomer shift of $Fe(CO)_3$(bicars), +0.18 mm/sec, compares favorably with the value of +0.16 mm/sec[13] reported for $((C_6H_5)_3P)_2Fe(CO)_3$,[14] which suggests that these two ligands may be similar in their bonding properties.

The complex $Ni(CO)_2$(bicars) exhibits two strong infrared absorptions which may be easily attributed to the carbonyl stretching modes at 2027 and 1968 cm^{-1}. These frequencies are about 20–30 cm^{-1} higher than those for the comparable complex containing diarsine as a ligand, $Ni(CO)_2[o\text{-}C_6H_4(As(CH_3)_2)_2]$. This suggests that the ligand containing the carborane framework may back-accept electron density to a greater extent that the more conventional arsine ligand. A similar observation about phosphine ligands has also been mentioned by Rohrscheid and Holm.[2]

It is interesting to note that the Mössbauer and ir data confirm the fact that *o*-carborane possesses the ability to serve as both electron donor and acceptor, already chemically established.[15]

The ^{11}B nmr spectrum of the ligand bicars may be explained in terms of selective overlapping of the expected four doublets.[16,17] The higher degree of resolution in the ^{11}B spectrum of bicars over that of *o*-carborane[18] suggests an increased differentiation in the types of borons in the molecule. This change in environment about the carbon atoms may be due to the presence of the $As(CH_3)_2$ groups.

In addition to the position of carbonyl absorptions, the number of absorptions also adumbrates steric properties of the ligand bicars. Group theory suggests that the C_{2v} octahedral complex containing four carbonyl groups and a bidentate ligand, for example, $Mo(CO)_4[o\text{-}C_6H_4(AsCH_3)_2]$, should exhibit four infrared-active carbonyl vibrations. This has been observed by Nyholm.[19] If the ligand would cause the octahedral complex to be distorted to C_{4v} symmetry with the four carbonyl groups occupying the same plane, four carbonyl absorptions would still be expected. If the distortion were less than above, but still significant, the distorted octahedron thus produced would show seven infrared-active absorptions ($3A_1 + 2B_1 + 2B_2$). The complex $Mo(CO)_4$(bicars) does indeed show seven bands attributable to carbonyl absorptions at 2020, 2015 (sh), 1994, 1953, 1946, 1940, and 1875 cm^{-1}, suggesting that a distortion of this type may occur. The complex $Fe(CO)_3$(bicars) also exhibits five rather than the four infrared bands expected in the carbonyl region for C_{3v} symmetry ($2A_1 + 2E$). This increase in the number of bands may also reflect a distortion of some type which lowers the symmetry of the complex.

We are currently employing epr data in conjunction with Mössbauer information in order to elucidate more fully the nature of the electronic properties of the ligand in some selected iron complexes. The results of this work will be published in the future.

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Thermodynamics of Ion Association. XVIII. Copper Complexes of Tetraglycine[1]

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Recently,[2] a potentiometric and calorimetric study was made of copper diglycine and triglycine complexes, systems of particular interest because of their biological importance in enzyme reactions.

In solutions of higher pH, evidence for multichelated structures similar to those in the solid state[3–6] has usually been based upon the results of potentiometric, kinetic, and spectral measurements.[7–12] At lower pH

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(1) Supported by National Science Foundation Grant No. GP-6042.

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