THE CHEMISTRY OF ARSINO - 1, 2 - DICARBA - CLOSO - DODECABORANE (12) DERIVATIVES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
ROBERT BERNARD ZABOROWSKI
1969

ABSTRACT

THE CHEMISTRY OF ARSINO-1,2-DICARBA-CLOSO-DODECABORANE(12) DERIVATIVES

by Robert Bernard Zaborowski

The compounds 1,2-bis(dimethylarsino)-1,2-dicarba-closo-dodecaborane(12), dimeric methylarsino(III)-1,2-dicarba-closo-dodecaborane(12) and the complexes formed by replacing two carbonyl groups in nickel carbonyl, iron pentacarbonyl and molybdenum hexacarbonyl with the ligand, 1,2-bis(dimethylarsino)-1,2-dicarba-closo-dodecaborane(12) were prepared. These new compounds were characterized by analysis, nmr and infrared data. Mössbauer data obtained on the iron complex suggests that the ligand is a potent electron donor, while infrared arguments suggest that the ligand may also function as an electron acceptor. Additional data on other attempted preparations is also discussed.

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By

Robert Bernard Zaborowski

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1969

To my wife, Paula,

Mom and Dad.

ACKNOWLEDGEMENTS

The author is deeply indebted to Dr. Kim Cohn for his guidance and personal interest throughout the course of this research.

The author is grateful to Dr. P. G. Rasmussen of the University of Michigan, Ann Arbor, for obtaining the Mössbauer data, and to Mr. F. Parker and Dr. R. W. Parry of the University of Michigan, Ann Arbor, for the B^{11} nmr data.

The author wishes to express his gratitude to the Department of Chemistry, Michigan State University, especially the Inorganic Division faculty members for their patient tutelage and effort and for the financial aid and experience gained as a Graduate Teaching Assistant.

The author also wishes to express his deepest appreciation to his wife for her help in the final preparation of this manuscript and her devoted encouragement throughout.

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NOMENCLATURE

The rapid development of research in the area of cage boron compounds was in part responsible for the recent development of a complete set of rules governing the nomenclature of such systems (1, 2). This nomenclature will be employed in naming all compounds in this manuscript with the exception of references to compounds which have been previously reported by other authors. These references will retain the nomenclature used in the original publication. In all work contained in the experimental section of this manuscript, the $B_{10}C_2H_{10}$ unit will be referred to as 1,2-dicarba-closo-dodecaborane(12) rather than the common name carborane.

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[1] R. Adams, Inorg. Chem., 2, 1087 (1962).

[2] Inorg. Chem., 7, 1945 (1968).

INTRODUCTION

During the era from 1912 to 1936, Alfred Stock and his co-workers prepared and chemically characterized a number of the more common boron hydrides. Within the past decade the boron hydrides have received considerable attention as a result of the demands for new high energy fuels by the Defense Department (1). While all attempts to prepare useful fuels have proved futile, industrial chemists had uncovered a new class of stable polyhedral boranes.

The polyhedral boranes encompass molecules or ions in which boron atoms alone or in combination with other atoms, describe a closed polyhedron ranging from the tetrahedron to the icosahedron (2). Investigation of these polyhedral boranes revealed an aromatic character manifest not only in an extraordinary thermal stability, but also in a substitution chemistry centered on the exopolyhedral boron-hydrogen or carbon-hydrogen bonds. The low toxicity (3) of these polyhedral boranes and their high stability toward acids and bases is surprising when compared with the toxicity and stability of other boron hydrides (4). The icosahedral carboranes share this stability, but are less stable to basic degradation than $B_{12}H_{12}^{2-}$.

The discovery of this new class of compounds, "aromatic" polyhedral boranes, has opened up broad areas of research with a variety of specific synthetic and theoretical problems. Recent reports have suggested that the derivative chemistry of this class of compounds will rival that of aromatic hydrocarbons. Several reviews on the chemistry of some of these materials, particularly $B_nH_n^{2-}$ and $B_{n-2}C_2H_n$, are available (5-11).

One smaller area of interest developed when the synthesis of 1,2-Dicarba-closo-dodecaborane(12) (11) provided a new, presumably aromatic, structure. This synthesis, in turn, has led to extensive synthetic investigations of the derivative chemistry which is based on substitution at the two carbon atoms (12). In general, groups which are so substituted act as if they were attached to a very bulky, electron withdrawing moiety (7, 9). If appropriate groups are substituted at these two carbon atoms, it is possible to prepare a potential bifunctional ligand. Almost nothing is known of the steric and electronic properties of the carborane cage when present in such a ligand. In fact, only five reports have appeared which are concerned with complexes which contain ligands of this type.

H. D. Smith (13) has reported that the reaction of nickel(II) chloride 6-hydrate with 1,2-bis(diphenylphosphino)-o-carborane, as well as with the corresponding derivatives containing one, two and three bromine atoms attached to the carborane nucleus, produced complexes containing two molecules of the bisphosphino ligand and one of nickel(II) chloride. In addition, he obtained ligand-exchange data which suggested that the order of stability of the series described was $[((C_6H_5)_2P)_2B_{10}H_{10}C_2]NiCl_2<[((C_6H_5)_2P)_2B_{10}H_{10}C_2]_2NiCl_2<[((C_6H_5)_2P)_2B_{10}H_9C_2]_2NiCl_2<[((C_6H_5)_2P)B_{10}H_8Br_2C_2]_2NiCl_2<[((C_6H_5)_2P)_2B_{10}H_7Br_3C_2]NiCl_2$. Other complexes containing the ligand and Cu(II), Pt(II) and Pd(II) were prepared but not characterized.

R. H. Holm and F. Rohrscheid (14) have reported that similar bisphosphino ligands will replace CO from $Ni(CO)_4$. On the basis of carbonyl absorptions they suggested that the bisphosphino-*o*-carborane group may accept electron density to a greater extent than conventional diphosphine ligands.

Russian workers (15) have also reported that bisphosphino-*o*-carborane ligands will displace CO from $Ni(CO)_5$ and $Fe(CO)_5$ and will form complexes with NiI_2 and $PdCl_2$. No spectral data were reported for these complexes.

In a recent article Smith, Robinson and Papetti (16) reported that nickel(II) and cobalt(II) salts react with 1,2-bis(mercapto)-*o*-carborane to yield square-planar MS_2P_2 and MS_4^{2-} complexes. On the basis of an empirical comparison of the electronic spectrum with previously reported spectra, they report that the carborane nucleus does not provide an effective network for π-delocalization. To some extent, their conclusion is supported by an investigation on *m*- and p-[α-carbonyl] benzoic acids by Hawthorne, Berry and Wegner (17). This study also suggested that the interaction of the *o*-carborane group with the aryl group does *not* allow electronic delocalization.

In apparent contradiction to the conclusions of Smith and co-workers as well as Hawthorne and co-workers, Longuet-Higgins and Roberts (18) have proposed that back-bonding by π substituents on the isoelectronic $B_{12}H_{12}^{2-}$ ion is possible.

The controversy surrounding the electronic interaction of these bifunctional carborane ligands and their complexes prompted investigation into the synthetic possibilities of bisarsino-1,2-dicarba-closo-dodecaborane(12) derivatives and their subsequent use as complexing agents. Such ligands should be structurally analogous to o-phenylenediphosphines and -diarsines and should provide a source for detailed ligand-metal bonding studies. It was also hoped that such a ligand system, incorporating the carborane framework, would prove as versatile a complexing agent as o-phenylenebis-dimethylarsine (19). The only previously reported arsino compound incorporating the carborane framework is $(o\text{-PhCB}_{10}H_{10}C)_3As$ (20).

EXPERIMENTAL

Experimental Methods

A Perkin-Elmer 237B grating spectrophotometer was employed for obtaining all infrared spectra. Solid spectra were run either as nujol or as fluorolube mulls. Solution spectra were run in either chloroform or methylene chloride.

Proton nmr spectra were observed on a Varian Model A-60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Tetramethylsilane was employed as an internal standard. 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.

Index of refraction measurements were obtained on a Bausch & Lomb Abbe Refractometer. A constant temperature bath was utilized for the water-cooling system.

The Mössbauer data were obtained in cooperation with the Chemistry Department of the University of Michigan. The instrument used employs an electromechanical tranducer for the drive operated in conjunction with a multichannel analyzer as previously described (21). The standard employed in the work was $Na_2Fe(CN)_5NO \cdot 2H_2O$.

All preparations were carried out under an atmosphere of nitrogen. Iron analyses were performed volumetrically employing potassium permanganate as titrant. The samples were dissolved in concentrated nitric acid and reduced to the ferrous state with stannous chloride solution (22). All other analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. All melting points were recorded on a Thomas-Hoover Capillary Melting Point Apparatus.

Primary Starting Material

Primary starting material 1,2-dicarba-closo-dodecaborane(12), more commonly *o*-carborane, was prepared directly from purified acetylene (Matheson) and decaborane (U.S. Department of the Air Force) (11,23, 24). The synthetic method of Hawthorne *et al.* (23), was modified in the following manner. First, the number of sulfuric acid containing traps, as well as, the number of empty-safety traps in the purification train was increased. Second, the fluffy, cream colored $B_{10}C_2H_{12}$ was dried *in vacuo* instead of over P_2O_5. Third, the final purification of the pure white solid, $B_{10}C_2H_{12}$, was accomplished by filtration and dried *in vacuo*. The identity of the product was confirmed by the recorded melting point of $297 \pm 2^{\circ}$ (literature value 298° (11)) and comparison of the infrared spectrum with the previously reported spectrum (25). The ^{1}H nmr spectrum of the product dissolved in chloroform displayed a broad CH resonance at -3.52 ppm from TMS (literature value 3.54 ppm (23)). The pure $B_{10}C_2H_{12}$ was stored in an evacuated dessicator over P_2O_5 prior to use.

Synthesis

1,2-Bis(dimethylarsino)-1,2-dicarba-closo-dodecaborane(12)

The ligand $B_{10}C_2H_{10}[As(CH_3)_2]_2$, which we will call Bicars (26), was prepared in a manner analogous to that employed in the preparation of $B_{10}C_2H_{10}[PR_2]_2$ (25), but employing $(CH_3)_2AsBr$ (27, 28), instead of $(CH_3)_2PCl$.

Dimethylbromoarsine was prepared according to the method of Maier et al. (27). The method was modified slightly by elimination of the second trap which was to be cooled to -80° (27). The mixture of $(CH_3)_2AsBr$ and CH_3AsBr_2 was effectively separated by distillation at 42 ± 1 mm pressure to yield the pure $(CH_3)_2AsBr$. The ^1H nmr of the $(CH_3)_2AsBr$ fraction run neat exhibited a single resonance at -1.51 ppm which suggested complete separation. The compound was identified by its refractive index, n_D^{21} 1.5684 (literature value n_D^{20} 1.5713 (28)) and boiling point of 50 ± 2° at 42 mm (literature value 51° at 42 mm (28)).

A slurry of dilithiocarborane (12), $B_{10}C_2H_{10}Li_2$, was freshly prepared by charging a nitrogen purged 100 ml. three-necked flask with a solution of n-butyllithium (0.055 mole) in 50 ml. dry ethyl ether. The flask was fitted with a magnetic stirrer, nitrogen inlet and an addition funnel with nitrogen outlet. This flask was then cooled to 0°. A solution of o-carborane (0.026 mole) in 20 ml. of dry ethyl ether was added and the mixture was stirred for ten minutes while it was maintained at 0°. After addition, the stirring was continued for another 45 minutes while the mixture was maintained at 0°.

A solution of $(CH_3)_2AsBr$ (0.055 mole) in 20 ml. of dry ethyl ether was then added to the cooled $B_{10}C_2H_{10}Li_2$ slurry over a period of 25 minutes. Reaction appeared to be immediate as indicated by diappearance of the white $B_{10}H_{10}C_2Li_2$ slurry. The slight yellow mixture was allowed to warm to 20^o and stirred for an additional 30 minutes. It was then refluxed for 1 hour. The solvents were removed by evaporation which was accomplished by the continued passage of nitrogen throught the system for 24 hours at 23^o.

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. This procedure hydrolyzed the LiBr formed in the reaction and effected a quantitative separation of the desired product. The product was then collected by filtration. The product was purified by dissolution in ethyl ether and recrystallization upon addition of water. It was then dried in vacuo to remove all traces of water. The product may also be purified by recrystallization from a minimum amount of hot n-hexane.

The formula, $B_{10}C_2H_{10}[As(CH_3)_2]_2$, is supported by all spectral data. The ^1H nmr spectrum of the ligand 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 B^{11} nmr spectra of the ligand (29), as shown in Figure 1, 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.

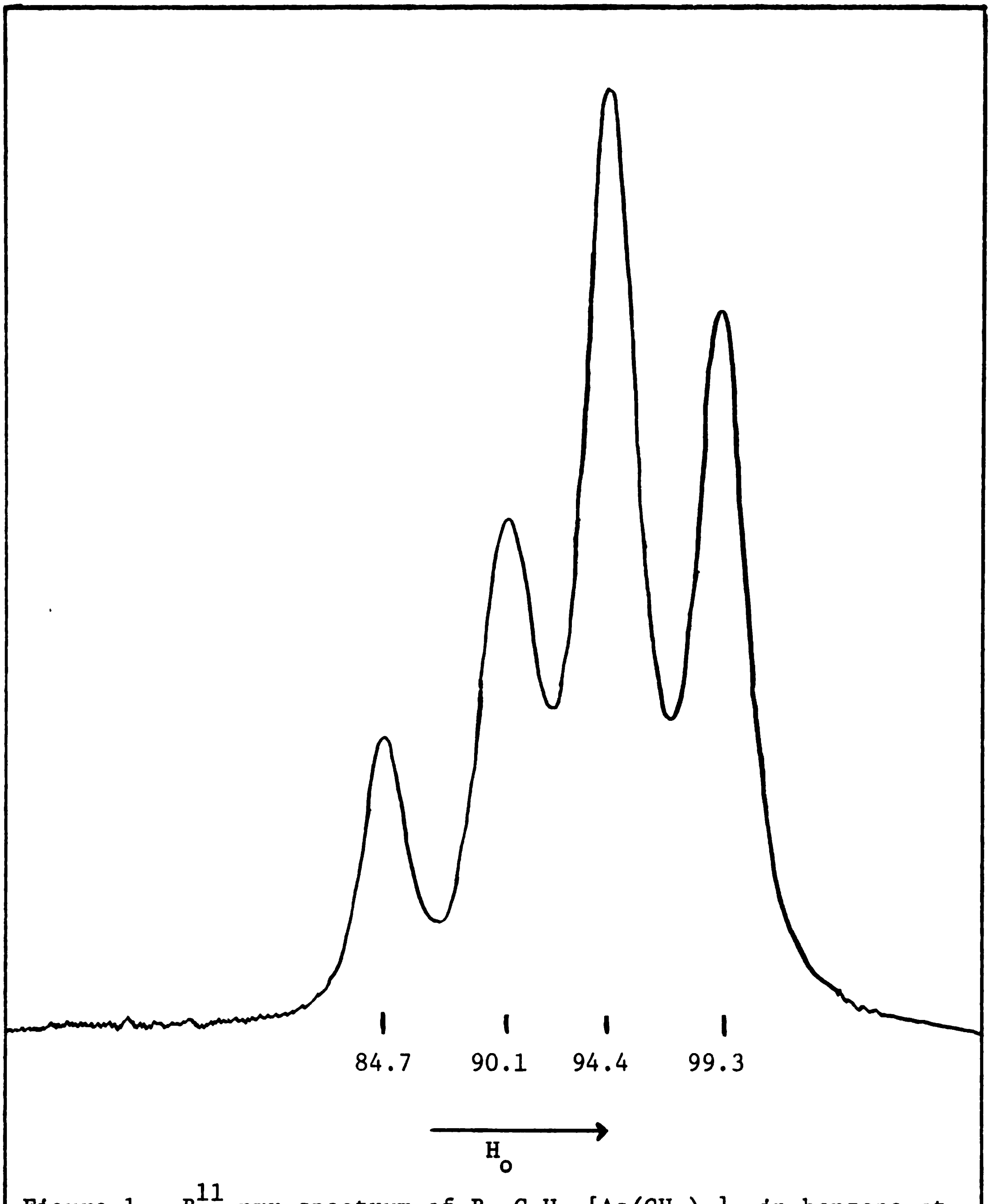


Figure 1. B^{11} nmr spectrum of $B_{10}C_2H_{10}[As(CH_3)_2]_2$ in benzene at an operating frequency of 32.1 MHz. $(CH_3)_3B$ was used as an external reference.

The infrared spectrum is shown in Figure 2. The spectrum exhibits characteristic absorptions at 724(s) and 2570(s) cm^{-1}. The absorption at 724(s) cm^{-1} is attributed to the B-H cage structure and the one at 2570(s) cm^{-1} ascribed to the B-H stretching mode. Other absorptions appear at 862, 902(m), 982(w), 1080(m) and 1262(w) cm^{-1}.

Analysis: Calculated 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. Molecular weight determined cryoscopically in benzene is 344 g/mole (theoretical 353 g/mole). The melting point is $111 \pm 2^{\circ}$ which compares favorably with the melting point of 111° obtained in separate work by H. D. Smith (30). 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.

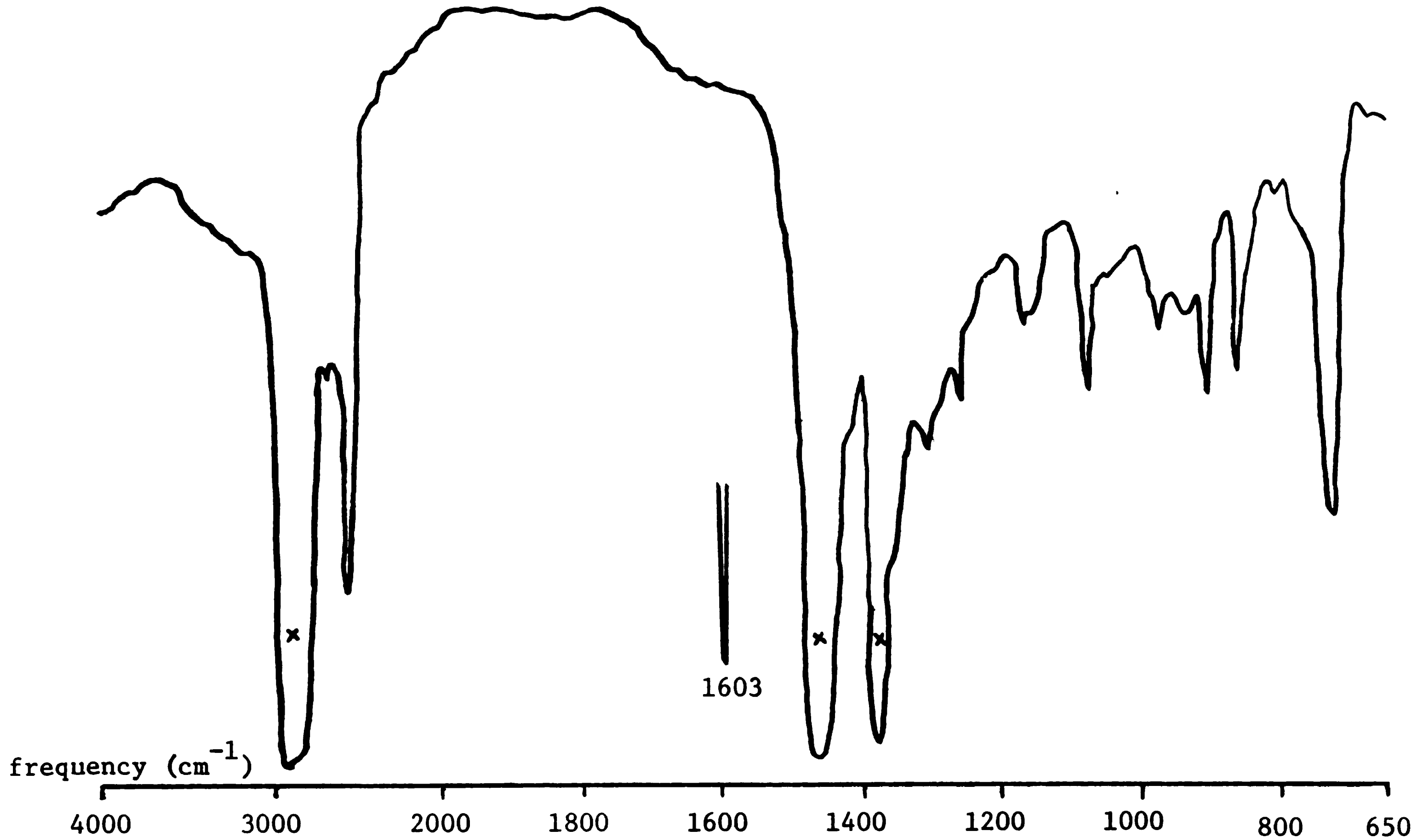


Figure 2. Infrared spectrum of $B_{10}C_2H_{10}[As(CH_3)_2]_2$ run as a nujol mull where x denotes the absorption due to nujol.

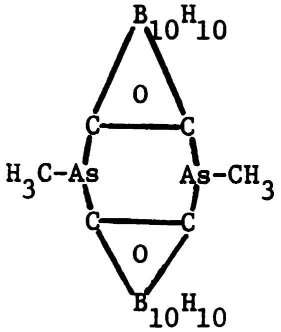
Dimeric Methylarsino(III)-1,2-dicarba-closo-dodecaborane(12)

This preparation was carried out in a manner analogous to that used in the preparation of $[B_{10}C_2H_{10}]_2$ (25) but which employed CH_3AsBr_2 instead of CH_3PCl_2. Methyldibromoarsine was prepared by the method of Maier _et al._ (27) as previously indicated on page 8 of this manuscript. The identity of the oily pale yellow liquid was established by a boiling point of 87 ± 1° at 41 mm (literature value 88° at 41 mm (28)).

A 0.021 mole sample of $B_{10}C_2H_{12}$ was used to prepare a slurry of $B_{10}C_2H_{10}Li_2$ in 10 ml. dry ethyl ether as previously described. The slurry was cooled to 0° and a solution of CH_3AsBr_2 (0.022 mole) in 15 ml. dry ethyl ether was added over a 25 minute period while the solution was stirred. The mixture was stirred for 45 minutes at 23°; then allowed to reflux for four hours.

The volatile components of the reaction mixture were removed by distillation _in vacuo_. The white residue was then dissolved in ethanol and the desired product collected by filtration. The filtrate was purified by recrystallization from a minimum of dry ethyl ether to yield the pure white microcrystalline product, $[B_{10}C_2H_{10}AsCH_3]_2$.

The formula is supported by all spectral data.



The ^{1}H nmr spectrum of the material dissolved in benzene exhibits a single absorption at -0.95 ppm due to the methyl protons. The infrared spectrum is shown in Figure 3. The spectrum displays the characteristic cage absorption at 730(vs) cm^{-1} and the B-H stretching absorption at 2565(s) cm^{-1}. Other absorptions occur at 770(w), 802(m), 827(w), 854(s), 902(vw), 925, 970(m, br), 1076(s), 1257(s), and 1625(m,br) cm^{-1}.

Analysis: Calculated 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. Molecular weight determined cryoscopically in benzene is 460 g/mole (theoretical, 474 g/mole). The melting point is 218 ± 3°.

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

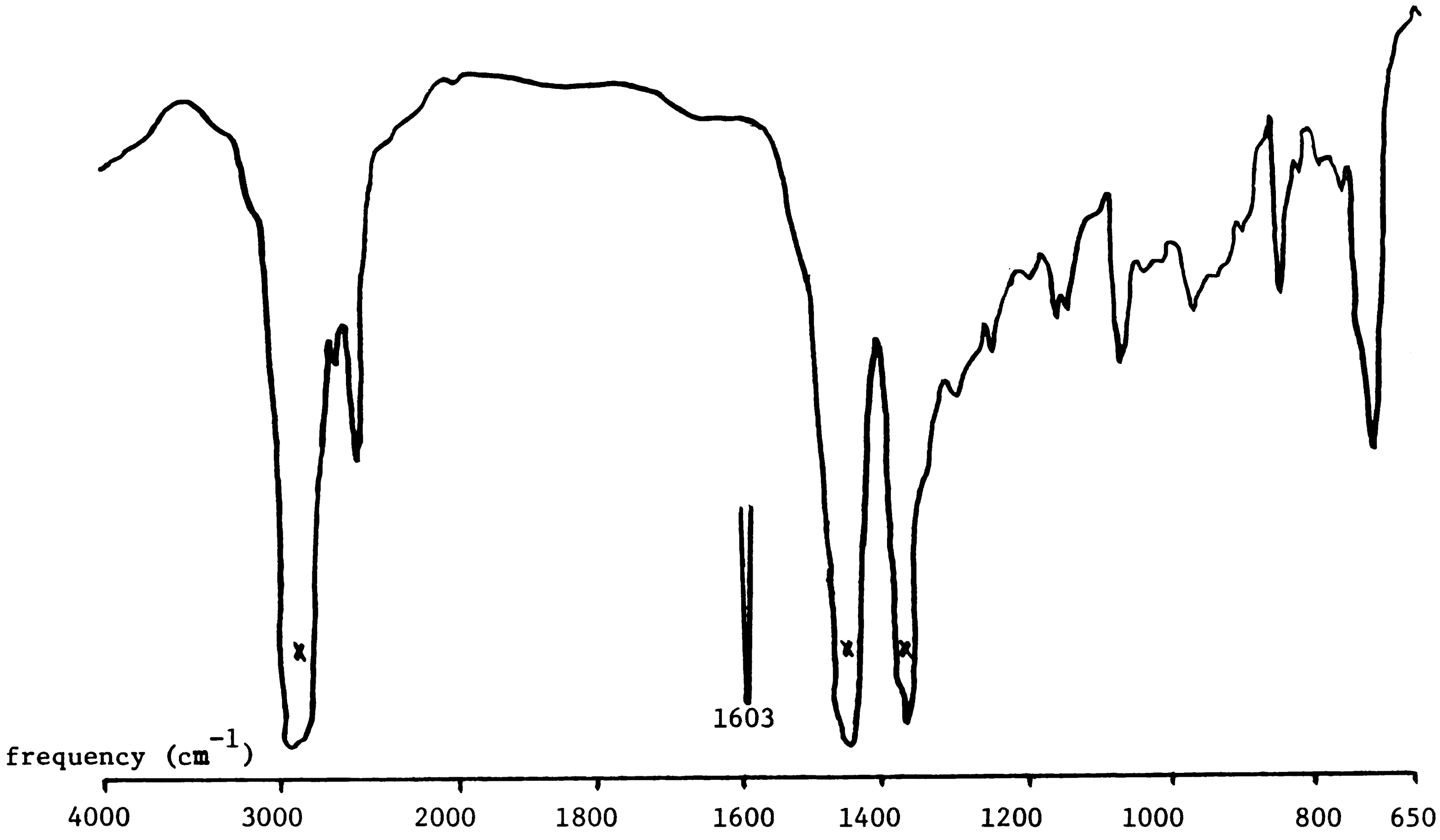


Figure 3. Infrared spectrum of $[B_{10}C_2H_{10}AsCH_3]_2$ run as a nujol mull where x denotes the absorptions due to nujol.

1,2-Bis(dimethylarsino)-1,2-dicarba-closo-dodecaborane nickel dicarbonyl

The reaction between nickel carbonyl and 1,2-bis(dimethylarsino)-1,2-dicarba-closo-dodecaborane(12) was carried out using standard vacuum techniques. A 2.31 mmole sample of the ligand, Bicars, was transferred to a 50 ml. single-neck flask. About 15 ml. of dry n-hexane was condensed *in vacuo* into the reaction flask at -196°. A 7.32 mmole sample of $Ni(CO)_4$ (Matheson) was then condensed at -196° into the reaction tube. The reaction mixture was allowed to warm to 0° and the rate of reaction observed by evolution of carbon monoxide. Upon completion of reaction, about two hours, all volatile materials were recovered by distillation *in vacuo* leaving behind a creamy white powdery product. The product was purified by recrystallization from petroleum ether.

The ^1H nmr spectrum of the complex dissolved in benzene exhibited a single resonance absorption at -0.96 ppm from TMS. The infrared spectrum of the complex is shown in Figure 4. The characteristic absorptions due to the cage structure and B-H stretch are exhibited at 726(s) and 2600(br) cm^{-1}, respectively. As expected for the carbonyl complex two absorptions are found at 1968(vs) and 2027(s) cm^{-1}. Other absorptions are found at 804(br), 868(s), 901(s), 932(w), 1020(w), 1070(m) and 1252(s) cm^{-1}.

Analysis: Calculated 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. Molecular weight determined cryoscopically in benzene is 475 g/mole (theoretical, 467 g/mole).

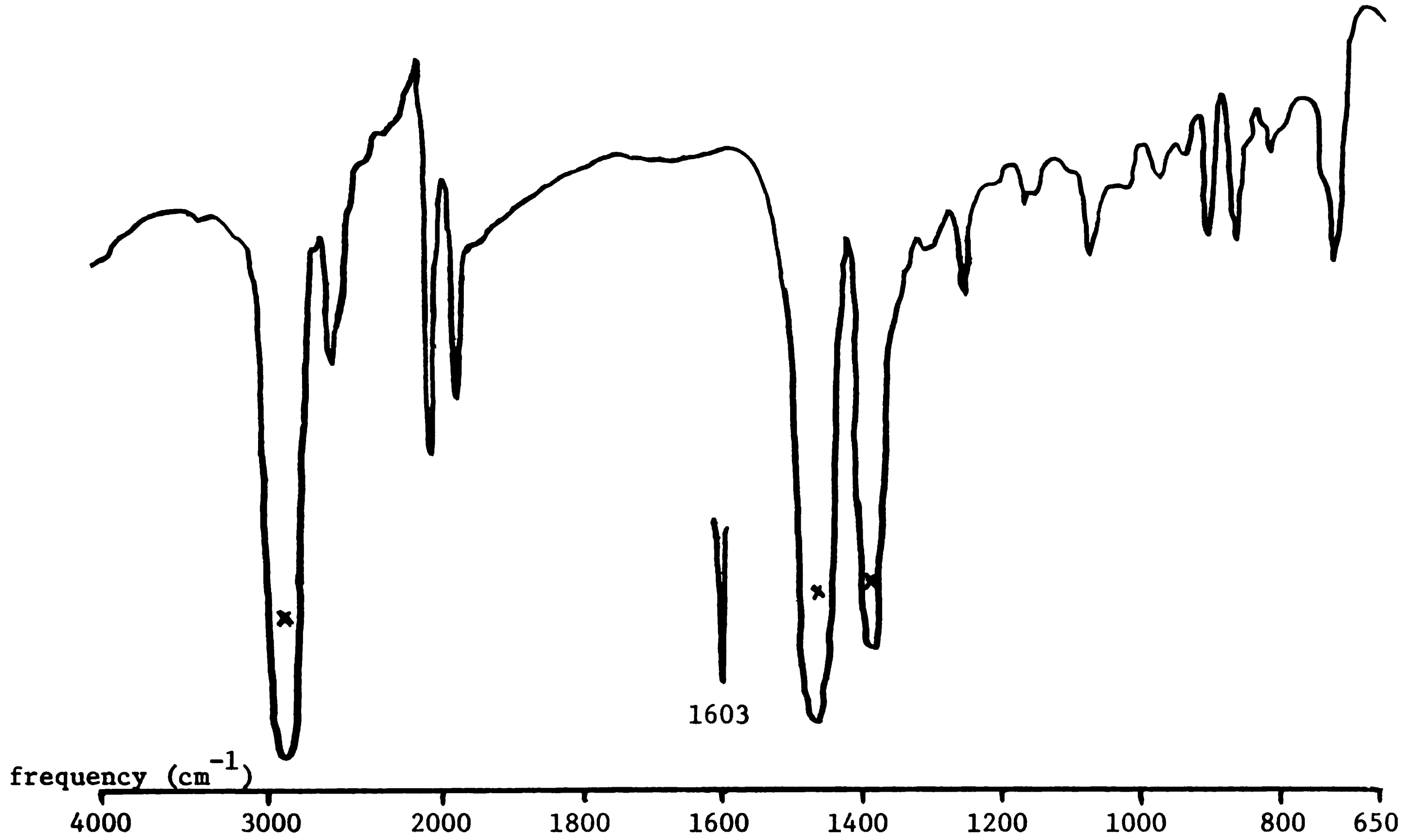


Figure 4. Infrared spectrum of (Bicars)Ni$(CO)_2$ run as a nujol mull where x denotes the absorptions due to nujol.

1,2-Bis(dimethylarsino)-1,2-dicarba-closo-dodecaborane(12) iron tricarbonyl

The mustard yellow crystalline complex was prepared in a manner similar to (Diars)$Fe(CO)_3$ (31). $Fe(CO)_5$ was fractionally distilled under a nitrogen atmosphere to yield the pure yellow oily liquid boiling at 102° at 760 mm (literature value 102° (32)). An excess of the freshly distilled $Fe(CO)_5$ (6.5 mmole) was added to a 12 mm thick-walled tube containing a 1.14 mmole sample of $B_{10}C_2H_{10}[As(CH_3)_2]_2$. The tube and contents were cooled to -196°, evacuated and sealed.

The reaction mixture was then heated to 140° ± 10° in a combustion furnace for four hours. The tube and contents were first allowed to cool to 23°, then were cooled to -196° and opened. The excess $Fe(CO)_5$ was then removed by distillation *in vacuo*.. The product was purified by recrystallization from benzene. The complex decomposes over a two month period in air and light from the mustard yellow crystals to a light brown powder.

The ^1H nmr spectrum of the complex dissolved in benzene exhibits a single resonance absorption at -1.22 ppm from TMS. The infrared spectrum is shown in Figure 5. The characteristic cage and B-H stretching absorptions are apparent at 724(s) and 2585(br) cm^{-1}, respectively. Five absorptions attributed to carbonyl stretching modes are exhibited at 1898(w), 1926(s), 1947(s), 1997(vw) and 2002(vs) cm^{-1}. Other absorptions occur at 823(m), 855(w), 876(s), 912(s), 972(br), 1074(s), 1256(m) and 1270(w) cm^{-1}.

The Mössbauer spectrum (33) of the complex gave an isometric shift, δ, of +0.18 mm/sec. relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$. Due to the

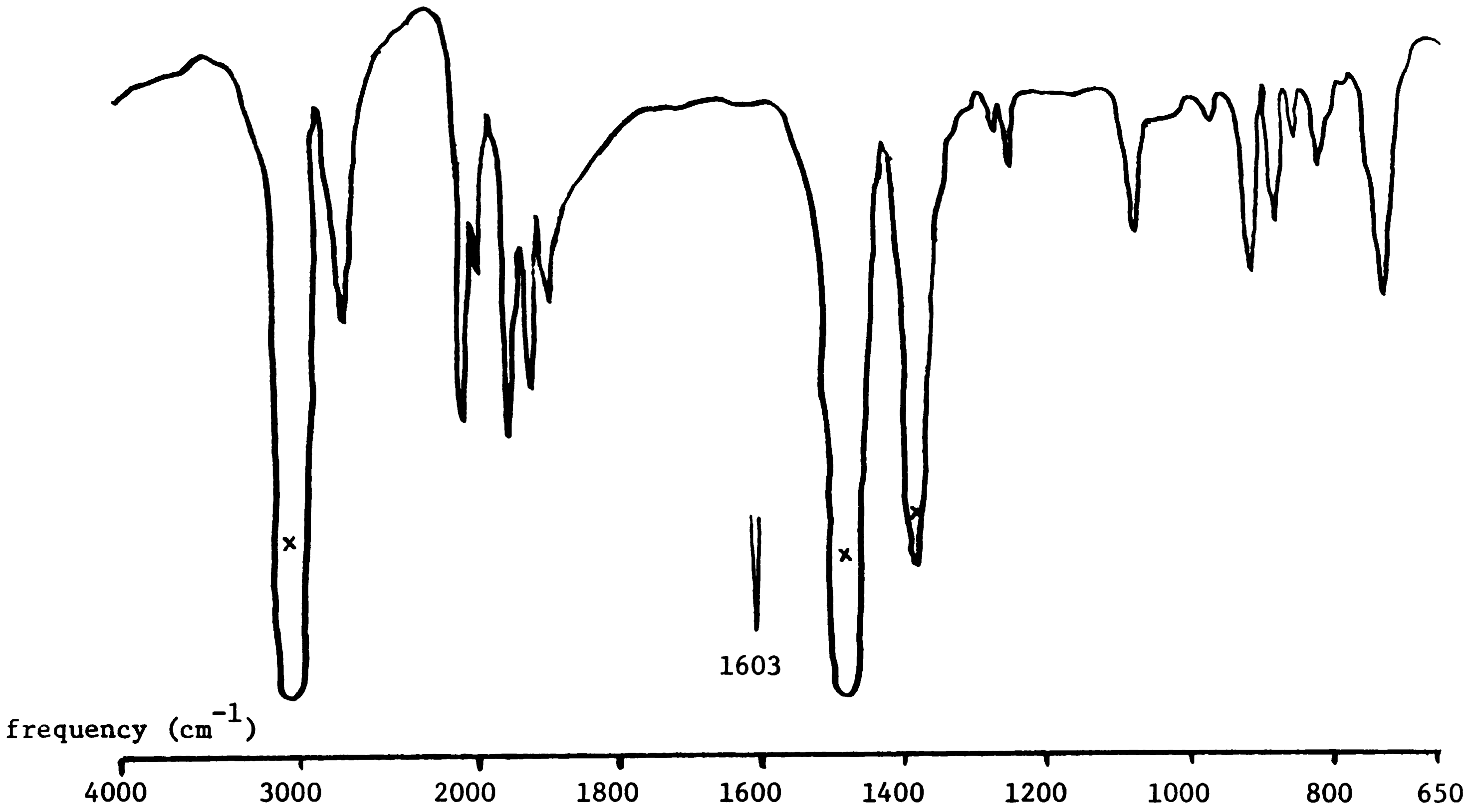


Figure 5. Infrared spectrum of (Bicars)Fe$(CO)_3$ run as a nujol mull where x denotes the absorption due to nujol.

assymetry 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.

Analysis: Calculated 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. Molecular weight determined cryoscopically in benzene is 480 g/mole (theoretical 492 g/mole). The melting point is 140 ± 2° (with decomposition).

1,2-Bis(dimethylarsino)-1,2-dicarba-closo-decaborane(12) molybdenum tetracarbonyl

A 1.1 mmole sample of $B_{10}C_2H_{10}[As(CH_3)_2]_2$ was transferred to a 12 mm thick-walled reaction tube about 12 inches in length. An excess of freshly sublimed $Mo(CO)_6$ (3.2 mmole) was then introduced followed by 3-4 ml. of xylene previously dried over calcium hydride. The reaction tube and contents were then cooled to -196^{o}, evacuated and sealed.

The reaction mixture was then heated to $140^{o} \pm 10^{o}$ for four hours in a combustion furnance. The tube was allowed to cool slowly to 23^{o} and was then cooled to -196^{o} and opened. The excess $Mo(CO)_6$ and solvent were removed by distillation in vacuo. The pure white crystalline product was purified by recrystallization from a minimum of benzene.

The ^{1}H nmr of the pure white powdery complex dissolved in benzene exhibits a single resonance at -1.03 ppm from TMS. The infrared spectrum of the complex is shown in Figure 6. The characteristic absorptions due to the cage structure and B-H stretching are found at 725(s) and 2610(br) cm^{-1}, respectively. The complex shows seven carbonyl absorptions at 1875(br), 1940(bs), 1946(w), 1953(vw), 1994(s), 2015(vw) and 2020(s) cm^{-1}. Other absorptions are exhibited at 824(m), 874(s), 904(m), 935(w), 1075(m), 1254(m) and 2560(br) cm^{-1}.

Analysis: Calculated 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. Molecular weight determined cryoscopically in benzene is 566 g/mole (theoretical, 560 g/mole). The melting point is 191 ± 2^{o} (with decomposition).

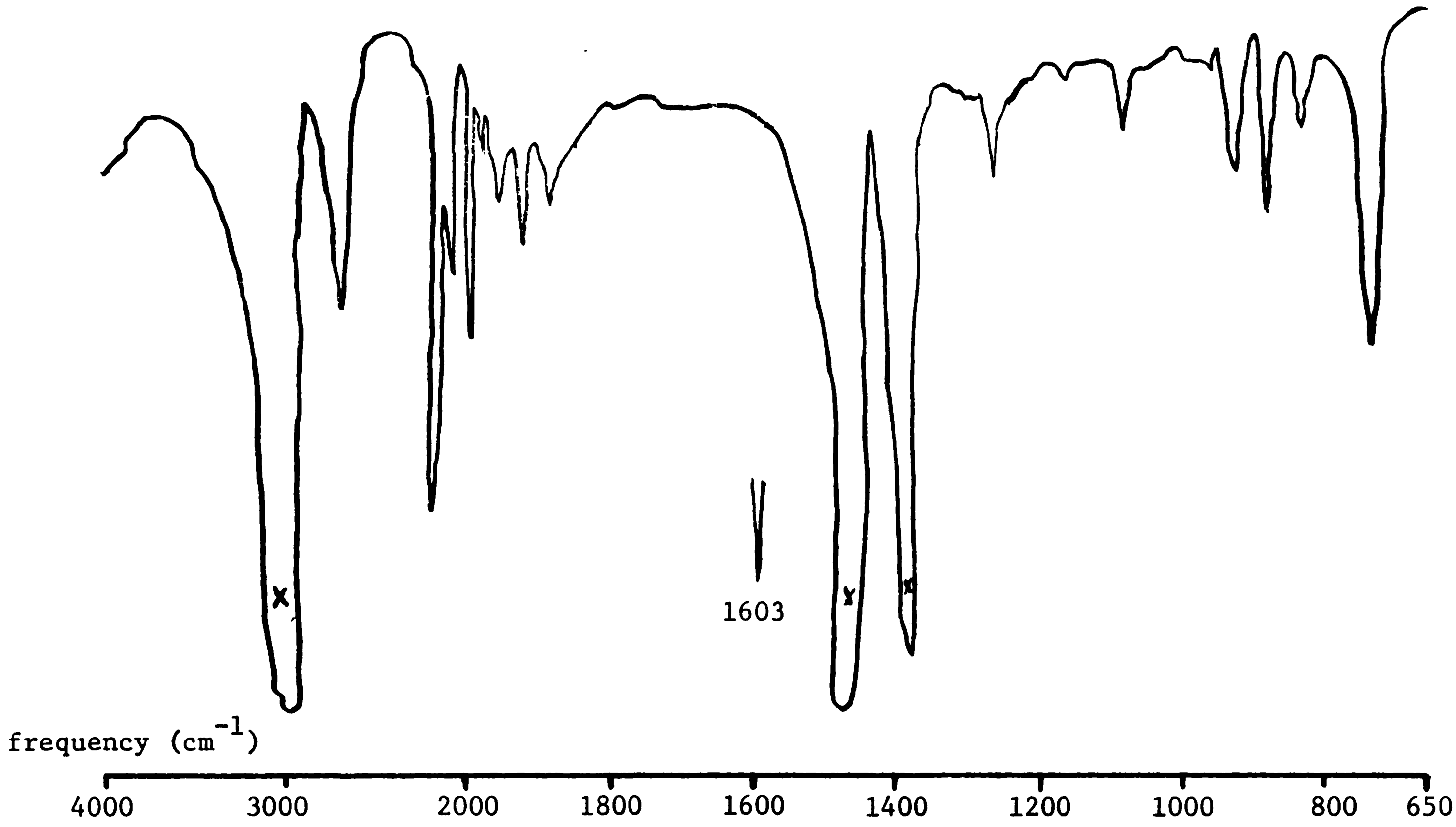


Figure 6. Infrared spectrum of (Bicars)Mo$(CO)_4$ run as a nujol mull where x denotes the absorptions due to nujol.

Attempted Synthesis

Dimeric Methylarsino(III)-1,2-dicarba-closo-dodecaborane(12) nickel dicarbonyl (33)

The preparation was attempted analogous to the preparation of (Bicars)Ni$(CO)_2$ as described on page 16 of this manuscript. A 1.65 mmole sample of the ligand, Bicars, about 15 ml. of dry n-hexane and an excess of $Ni(CO)_4$ (6.45 mmole) were employed. The reaction was allowed to proceed for some 12 hours until the $Ni(CO)_4$ began to decompose in the reaction system as evidenced by formation of a nickel(0) deposit.

After removing all volatile materials by distillation in vacuo, a white product remained. The product was purified by recrystallization from benzene. All spectral evidence suggests no reaction occurred between the $[B_{10}C_2H_{10}AsCH_3]_2$ and $Ni(CO)_4$. The infrared spectrum of the white product failed to exhibit any absorptions in the carbonyl stretching region. The ^1H nmr of the material in benzene was identical with the observed spectrum of the starting material $[B_{10}C_2H_{10}AsCH_3]_2$.

Dimeric Methylarsino(III)-1,2-dicarba-closo-dodecaborane(12) iron tricarbonyl

The preparation was attempted in a manner analogous to the preparation of (Bicars)Fe$(CO)_3$ as described on page 18 of this manuscript. An excess of freshly distilled Fe$(CO)_5$ (4.6 mmole) and a 1.2 mmole sample of $[B_{10}C_2H_{10}AsCH_3]_2$ were employed in the reaction mixture. The mixture was heated to 150 ± 10^o for 5 hours in the combustion furnace.

After removal of the unreacted Fe$(CO)_5$ by distillation *in vacuo* a dark residue remained.

All spectral data suggest no reaction occurred between the Fe$(CO)_5$ and $[B_{10}C_2H_{10}AsCH_3]_2$. The ^1H nmr spectrum of the dark residue dissolved in benzene was identical with the observed spectrum of the starting material $[B_{10}C_2H_{10}As(CH_3)]_2$.

Dichlorodi-1,2-dicarba-closo-dodecaborane(12) iron(III) Tetrachloroferrate

The product was prepared using Bicars and $FeFl_3$ in a manner similar to that employed in the preparation of $(Diars)_2FeCl_2FeCl_4$ (35). A 3.05 mmole sample of freshly prepared anhydrous $FeCl_3$ (36) was transferred under nitrogen atmosphere to a 50 ml. flask. About 40 ml. of dry ethyl ether was added to the flask and the solution was filtered to remove insoluble impurities. The filtered solution was then transferred to an addition funnel.

A 3.02 mmole sample of the ligand, was introduced into a 250 ml. single-neck flask equipped with a side-arm for nitrogen inlet. About 40 ml. of dry ethyl ether was added to the flask and the solution stirred with a magnetic stirrer. The addition funnel containing the $FeCl_3$ solution was attached to the flask and the entire system purged with nitrogen. The $FeCl_3$ solution was added over a period of 10 minutes. The dark mixture was stirred for an additional 15 minutes at 20^o. The reaction was then allowed to reflux for an additional 30 minutes.

As the solvent evaporated during refluxing a deep red crust formed on the side of the reaction vessel. The remaining solvent was then removed by distillation in vacuo to yield the deep blood-red product. The product was purified by thoroughly washing it with benzene to remove any unreacted starting materials. Final purification consisted of recrystallization from a small amount of warm benzene.

The infrared spectrum of the product as shown in Figure 7 suggests formation of a complex containing the ligand Bicars. Present in the

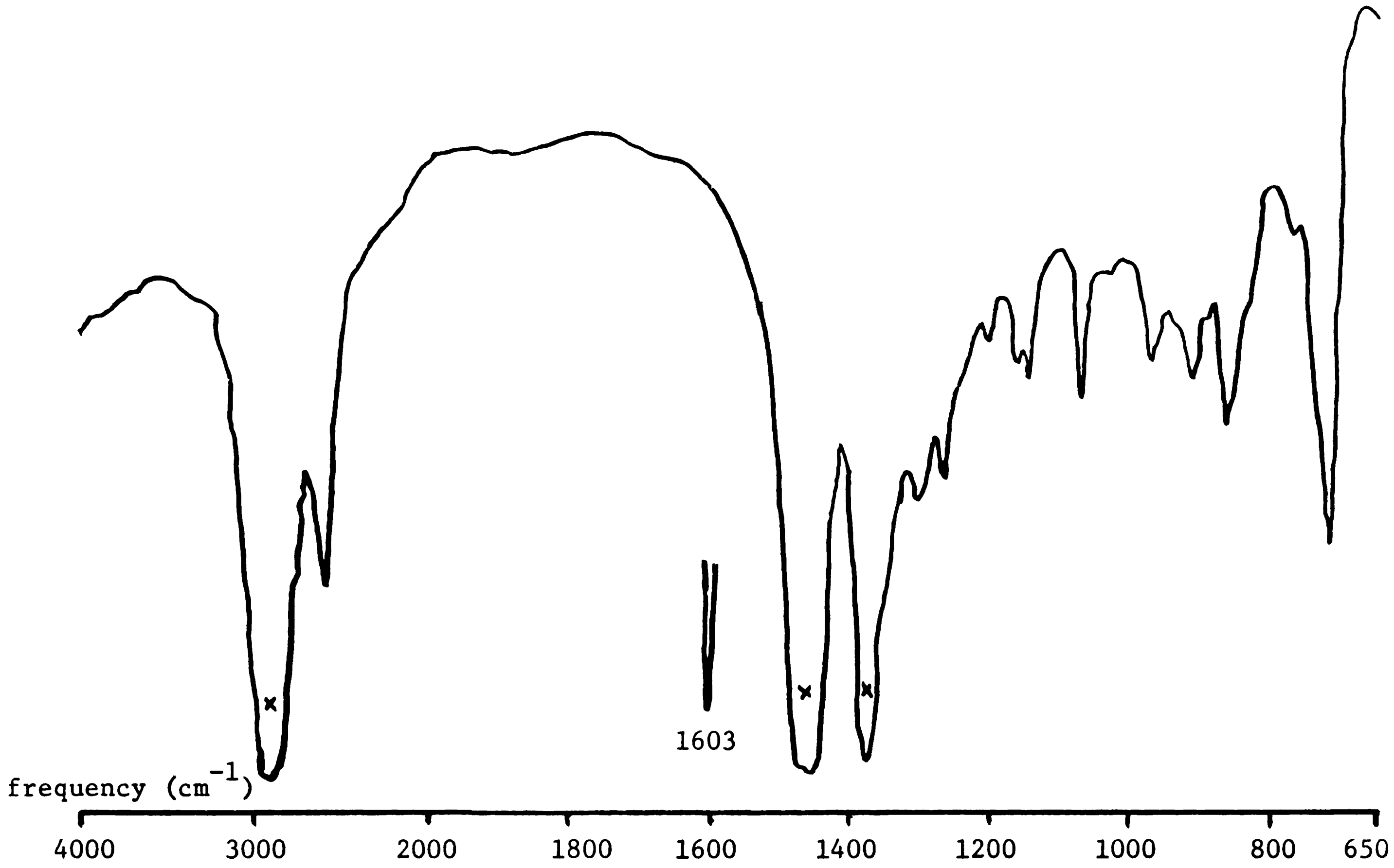


Figure 7. Infrared spectrum of $(Bicars)_2FeCl_2FeCl_4$ run as a nujol mull where x denotes the absorptions due to nujol.

spectrum are the characteristic B-H stretching and cage absorptions at 1265(br) and 726(s) cm^{-1} respectively.

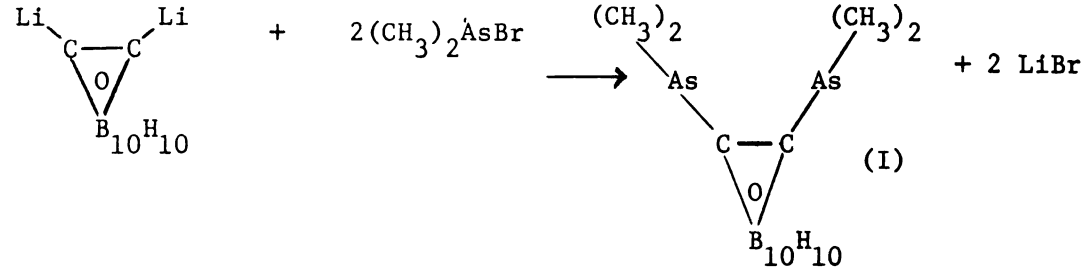
Analysis: Calculated for $C_{12}H_{44}As_4B_{20}Fe_2$: C, 14.01; H, 4.31; Fe, 10.86. Found: C, 12.88, H, 3.95; Fe, 10.94.

The deep blood-red product appears to be destroyed by allowing it to react with water. A white residue is obtained after this treatment. The infrared spectrum of the white residue is identical to the observed spectrum of the ligand, Bicars.

DISCUSSION

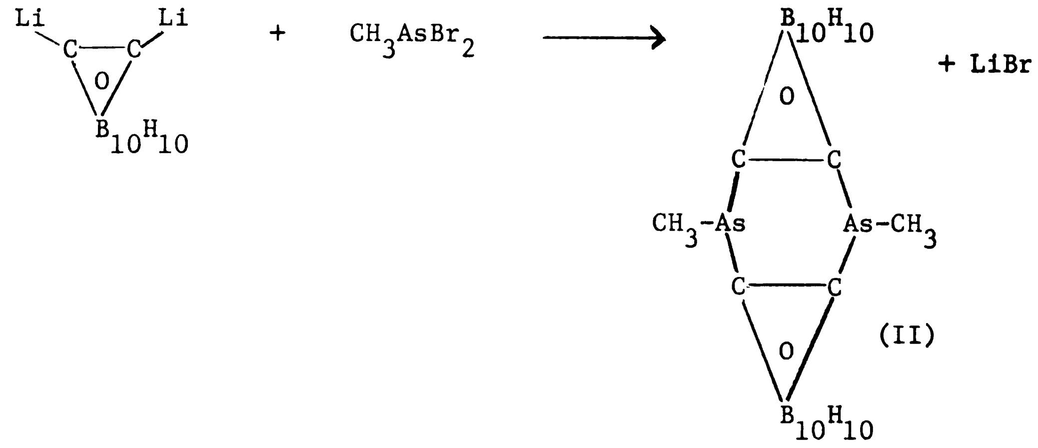
The possibility of preparing bisarsinocarborane derivatives was established with the following examples.

1.



(I)

2.

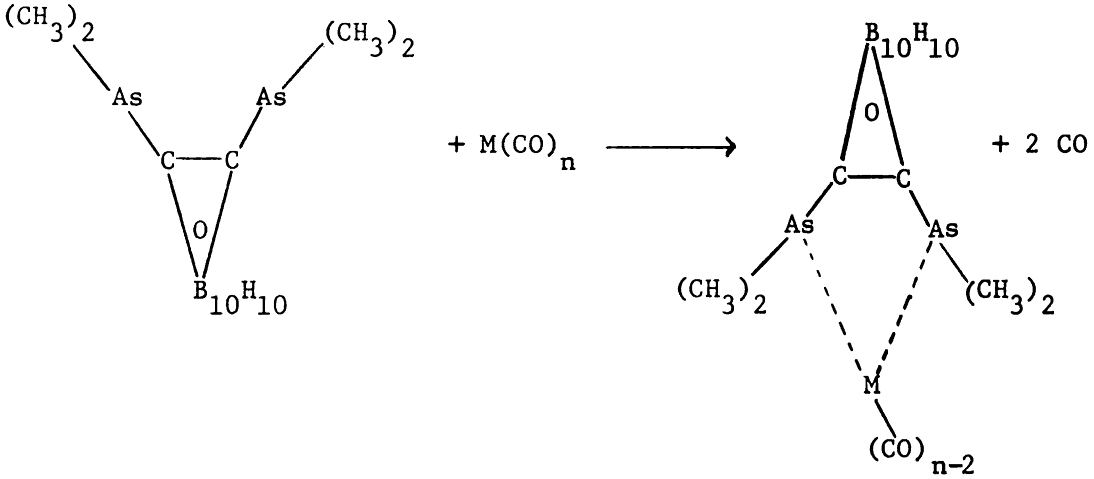


(II)

Both species (I and II) display stability toward air oxidation and hydrolysis in contrast to the behavior of Diarsine (o-phenylenebisdimethylarsine).

The possibility of employing the new bisarsino-1,2-dicarba-closo-dodecaborane(12) derivatives as ligands was then investigated. A series of reactions was conducted which established that

$B_{10}C_2H_{10}[As(CH_3)_2]_2$, 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 the following equation:

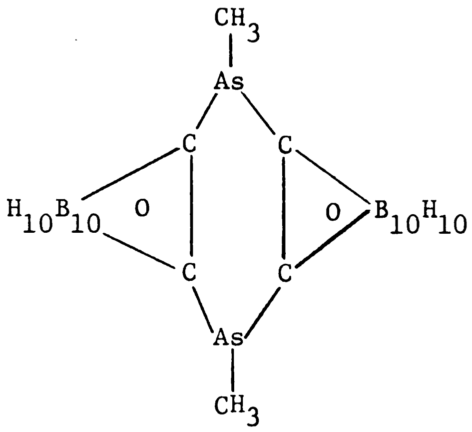


where: M=Ni n=4

M=Fe n=5

M=Mo n=6

All attempts to prepare the analogous Ni (34) and Fe complexes with dimeric methylarsino(III)-1,2-dicarba-closo-dodecaborane(12) (species II) failed. This may be a result of the steric hinderance due to the large $B_{10}C_2H_{10}$ cage units. Such a hypothesis is supported by the preliminary x-ray data on the ligand Bicars (37) which shows extremely short As-C bond distances. As short and possibly shorter As-C bond distances in the system:



would bring the two large $B_{10}C_2H_{10}$ cage units even closer together making it nearly impossible to get a metal atom close enough for bonding through the arsenic atoms. In addition, the position of the two methyl groups would pose further steric problems.

The difficulties encountered in the attempted preparation of the complex $(Bicars)_2FeCl_2FeCl_4$ may be a reflection of the ease with which the compound hydrolyzes. Both iron analysis and infrared data suggest the presence of the desired product. The carbon-hydrogen data may be explained by possible hydrolysis of the product during shipping and handling.

The Mössbauer spectrum of the iron complex, $(Bicars)Fe(CO)_3$, 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 is reflected in the negative shift compared to $Fe(CO)_5$ (literature value of -.282 mm/sec. (38) corrected for difference in standard and temperature to +.201 mm/sec.). If one agrees with the idea of $d\pi$-$p\pi$ back-bonding, it may be concluded from this evidence that forward coordination dominates over back donation. This idea is supported by Collins and Pettit (39) in a Mössbauer study of the $(\Phi_3P)_2Fe(CO)_3$ system. The isomer shift for the complex of +0.16 mm/sec. (39) (cited value corrected for difference in standard employed) compares favorably with that of the (Bicars) $Fe(CO)_3$ system, suggesting a similarity in bonding properties of the two ligands.

Table 1 shows the infrared absorptions attributed to carbonyl stretching modes for various $(L)Ni(CO)_2$ systems where L is a variety of bisphosphino and arsino ligands. The complex $(Bicars)Ni(CO)_2$ exhibits two strong infrared absorptions which may be easily attributed to the carbonyl stretching modes at 2027 and 1968 cm^{-1}. The lower frequencies compared with $Ni(CO)_4$ (literature value 2057 cm^{-1} (40)) suggest that the ligand Bicars, is a weaker π-acceptor than the carbonyl group in line with other phosphino and arsino derivatives. Further, these frequencies are about 20 to 30 cm^{-1} higher than those for the comparable complex containing Diarsine as a ligand, $Ni(CO)_2[\underline{o}-C_6H_4(AsMe_2)_2]$. This suggests that the ligand, Bicars incorporating the carborane framework, may back accept electron density to a greater extent than the more conventional arsine ligand. A similar observation regarding the phosphinocarborane ligands shown in Table 1, whose carbonyl absorptions compare favorably with those of the ligand Bicars, has also been mentioned by Rohrscheid and Holm (14).

It is interesting to note that the Mössbauer and IR data confirm the fact that o-carborane possesses the ability to serve

Table 1. Infrared carbonyl absorptions for various (L)Ni(CO)$_2$ systems. All spectra run as solution spectra in dichloromethane.

Ligand	Absorptions in cm^{-1}	
$C_6H_4[As(CH_3)_2]_2$	2001 1934	(41)
$B_{10}C_2H_{10}[As(CH_3)_2]_2$	2027 1968	
$B_{10}C_2H_{10}[P(CH_3)_2]_2$	2013 1955	(14)
$B_{10}C_2H_{10}[P(C_6H_5)_2]_2$	2021 1966	(14)

as both electron donor and acceptor, already chemically established (42).

The B^{11} nmr spectra of the ligand, Bicars, as displayed in Figure 1 may be explained in the following manner. Assuming a nearly icosahedral structure for the $B_{10}C_2H_{10}$ unit as in o-carborane (42); one readily recognizes the existance of four different types of boron atoms, namely, 3(6), 8(10), 9(12) and 4(5, 7, 11). This would give rise to four singlets. The absorptions, however are further split by spin-spin coupling due to the protons attached to the borons to give a predicted spectrum of four doublets of relative integral intensities, 2:2:2:4. Such a spectrum has been reported for the B^{11} of o-carborane at 60 MHz (43, 44). It has been found that at a lower frequency the spectrum obtained may be explained in terms of selective overlapping of the expected doublets (43).

The predicted spectrum consisting of four doublets is shown schematicly in Figure 8a. With a reduction in resolution, doublets a & b coalesce so that the high-field member of a and the low-field member of b are nearly superimposed. At the lower frequency, the doublet b is nearly centered on the low-field member of c and the doublets c and d are so closely overlapped as to be indistinguishable. This behavior is represented in Figure 8b. The resultant spectrum consists of four singlets of relative intensity 1:2:4:3 as shown. This corresponds exactly to the observed B^{11} nmr spectrum of Bicars, Figure 1. The higher degree of resolution in the B^{11} of Bicars over that of o-carborane (45) suggests an increased

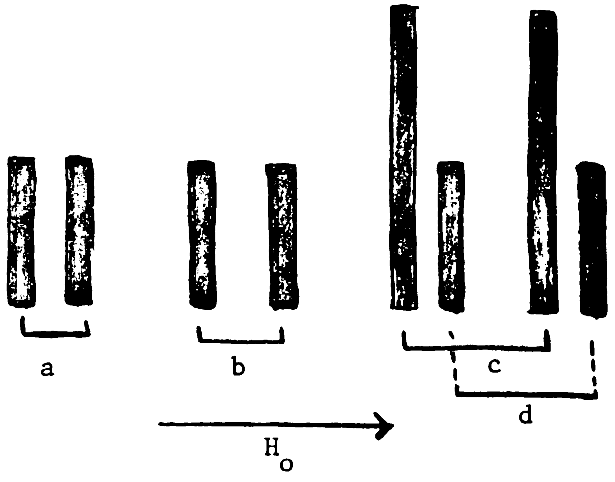


Figure 8a. Schematic representation of predicted spectrum for $B_{10}C_2H_{10}$ unit.

Figure 8b. Schematic representation of spectrum resulting from selective overlapping.

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.

SUGGESTIONS FOR FUTURE RESEARCH

Further research should be directed toward the preparation of a compound suitable for epr studies. Such studies should provide information regarding spin density transmission in the Bicars-metal system. For example, the complex (Bicars)Fe$(CO)_2Cl$ may be prepared by reaction of (Bicars)Fe$(CO)_3$ in HCl solution followed by air oxidation and the complex $(Bicars)_2FeCl_2 \cdot B\Phi_4$ by replacement of the $FeCl_4^-$ of $(Bicars)_2FeCl_2 \cdot FeCl_4$ with $B\Phi_4^-$. Such systems would be useful for epr studies because they should contain Fe d^1 systems and in addition they possess a high degree of symmetry which simplifies interpretation of the epr measurements results. Mössbauer studies of these systems would provide additional information concerning the nature of the Fe-ligand bonding. The chemical shift is a direct indication of the Fe s-electron density. Interpretation of this information in terms of the Fe d-electrons would provide an indication of the donor-acceptor properties of the ligand, Bicars.

Single crystal x-ray diffraction studies of the compound, dimeric methylarsino(III)-1,2-dicarba-closo-dodecaborane(12) should be initiated. Structural information for this compound should help clarify the reasons underlying its inability to displace CO from either $Fe(CO)_5$ or $Ni(CO)_4$. This inability may be a consequence of steric hinderance arising from extremely short C-As bond distances. Such short bond distances could result from resonance stabilization requiring the $B_{10}C_2H_{10}$ unit to accept a partial negative charge. Such behavior is consistant with the established donor-acceptor properties of the $B_{10}C_2H_{10}$ nucleus (17, 26).

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