bonded organometallic compounds and which may contain a single Fe^{II-III} simultaneously bonded to the open faces of two $B_9C_2H_{11}^{-2}$ icosahedral fragments. Compounds of this type present a novel marriage of carboranes with transition metal derivatives.

The synthesis of $Fe(B_9C_2H_{11})^{-2}$ (I) and $Fe(B_9C_2 H_{11}$)₂⁻¹ (II) was implemented by the preparation of a new ion, $B_9C_2H_{11}^{-2}$ (III). C-Substituted derivatives were obtained from the corresponding derivatives of III. The $B_9C_2H_{12}^-$ ion¹ (IV), which appears to have the geometry of an eleven-particle icosahedral fragment, was readily converted to III by the abstraction of a proton with sodium metal or sodium hydride in tetrahydrofuran. Hydrolysis of III regenerated IV in quantitative yield. The hypothetical $B_{11}H_{11}^{-4}$ ion, isoelectronic with III, may be formally generated from icosahedral $B_{12}H_{12}^{-2}$ by the removal of a BH^{+2} unit. This delocalized model of $B_{11}H_{11}^{-4}$ would resemble the $C_{5}H_{5}^{-}$ ion in that the five equivalent atomic orbitals directed toward the empty apex would form a set of three bonding molecular orbitals which contain a total of six electrons.

The reaction of FeCl₂ with III and its C-substituted derivatives produced the corresponding I derivative. Air oxidation of the reaction mixture allowed the isolation of II and its C-substituted derivatives in yields as high as 85%. The salts of unsubstituted II are red $[\lambda_{max} (\epsilon): 272 (21,200), 296 (18,000), 444 (585), and sh.$ 520 (400)] and stable to acids, bases, and high temperatures (>300°). Anal. Calcd. for $Fe(B_9C_2H_{11})_2$ -N(CH₃)₄: C, 24.40; B, 49.30; H, 8.64; N, 3.56; Fe, 14.18; equiv. wt., 394; mol. wt., 394. Found: C, 24.56; B, 49.00; H, 8.73; N, 3.65; Fe, 14.39; equiv. wt., 406; mol. wt., 402. Degradation of C,C'-dimethyl II with aqueous hydroxide ion at the reflux temperature produces C,C'-dimethyl IV (95%) and 97.5% of the theoretical Fe as hydrous oxide. I is diamagnetic and II is paramagnetic. Polarography of II gives a one-electron reduction to produce I. Reduction of II with sodium amalgam in aqueous acetonitrile produces I in quantitative yield. The ¹H n.m.r. spectrum of I [bis N⁺(CH₃)₄ salt] contained a carborane proton resonance (intensity 1) at τ 6.52 and a methyl proton resonance (intensity 6) at τ 6.83. The ¹¹B n.m.r. spectrum of I extended over 30 p.p.m. and exhibited structure which could not be conclusively interpreted. Since II is paramagnetic, no useful ¹H n.m.r. spectra could be obtained. The ¹¹B n.m.r. spectrum of II was unique when compared with the spectra of known compounds since it extended over approximately 560 p.p.m., was well resolved, and gave no evidence of ${}^{11}B-{}^{1}H$ coupling.² A broad singlet (intensity 2) was observed at highest field with II, but separated into two singlets in the case of C-phenyl II. This may be taken as evidence that the two boron atoms responsible for this resonance are at the same time very near iron and the two carbon atoms. The remainder of the spectrum consisted of two welldefined peaks (intensity 1) and an unresolved set of at least two and more likely three resonances of total intensity 5. A true "sandwich" structure would require a third boron atom to be in close proximity to

iron, but the ¹¹B n.m.r. resonance associated with this boron atom has not been clearly observed although it may reside amidst the unresolved array of intensity 5. The chemical evidence now available suggests that each $B_9C_2H_{11}^{-2}$ unit contributes six electrons for bonding to Fe^{+2} in I, and the two $B_9C_2H_{11}^{-2}$ units thus complete the krypton shell about iron. The novel "sandwich" structure which would allow a single iron atom to complete two carborane icosahedra cannot be ruled out with the evidence now at hand. Further synthetic and structural studies are in progress.

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(3) Alfred P. Sloan Research Fellow.

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Azodicarbonitrile

Sir:

We have prepared the elusive azodicarbonitrile $(1)^1$ in 54% yield by the pyrolysis of cyanogen azide.² At 200° in the vapor phase the synthesis is believed to involve cyanonitrene (2) as an intermediate.³

$$N_{3}CN \xrightarrow{200^{\circ}} NCN + N_{2}$$

$$2$$

$$N_{4}CN + NCN \longrightarrow NCN = NCN + N_{2}$$

$$1$$

Azodicarbonitrile is a crystalline, orange-red, volatile solid, m.p. $35.5-37^{\circ}$. Anal. Calcd. for 1: N, 70.0. Found: N, 69.5, 70.2, 69.5; mol. wt., 80 (mass spectrometer); $\lambda_{max}^{CH_{2}CN}$ 240 (ϵ 7830), 445 m μ (ϵ 18); λ_{max} 4.51 μ . Vapor pressure measurements and gas-liquid chromatography indicate both *cis* and *trans* isomers are present; however, they have not been separated. Vapor phase decomposition of 1 at 100° is slow; however, crystalline 1 detonates when mechanically shocked or heated in a closed vessel. Because of the hazardous nature of pure cyanogen azide, 1 has been synthesized on a limited scale. Azodicarbonitrile is soluble without reaction in benzene, acetonitrile, ethyl acetate, 1,1,2trichloro-1,2,2-trifluoroethane, and nitromethane. It is decomposed by methanol, water, or ether.

Azodicarbonitrile reacts instantly as a dienophile with 2,3-dimethylbutadiene to give 1,2-dimethyl-4,5dicyano-4,5-diazacyclohexene (3), m.p. 79° (*Anal.* Calcd. for 3: C, 59.2; H, 6.2; N, 34.6. Found: C, 59.0; H, 6.3; N, 34.5), and with cyclopentadiene to give 5,6-dicyano-5,6-diazabicyclo[2.2.1]heptene (4), m.p. 68-69° (*Anal.* Calcd. for 4: C, 57.5; H, 4.1; N, 38.4. Found: C, 57.2, 57.7; H, 4.2, 4.3; N, 37.3). The anthracene adduct, 1,2,3,4-tetrahydro-1,4-o-benzenophthalazine-2,3-dicarbonitrile (5), m.p. 180-181.5°.

⁽¹⁾ R. A. Wiesboeck and M. F. Hawthorne, J. Am. Chem. Soc., 86, 1642 (1964).

⁽²⁾ W. N. Lipscomb and A. Kaczmarczyk, *Proc. Natl. Acad. Sci.* U. S., 47, 1796 (1961), have observed the loss of ${}^{\pm1}B{}^{\pm1}H$ coupling in ${}^{\pm1}B$ n.m.r. spectra obtained in the presence of Fe¹¹¹.

^{(1) (}a) H. Wieland and H. Hess, *Ber.*, 42, 4175 (1909), attempted dehydration of NH₂CON=NCN=NOH without positive results; (b) O. Diels and M. Parguin, *ibid.*, 46, 2000 (1913), dehydrated azodicarbonamide with P_2O_5 and obtained H_2O , N_2 , HOCN, and HCN.

⁽²⁾ F. D. Marsh and M. E. Hermes, J. Am. Chem. Soc., 86, 4506 (1964).

^{(3) (}a) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *ibid.*, 87, in press; (b) F. D. Marsh, *ibid.*, 87, in press; (c) G. J. Pontrelli and A. G. Anastassiou, J. Chem. Phys., 41, in press.

is formed in 3 days at room temperature (*Anal.* Calcd. for **5**: C, 74.4; H, 3.9; N, 21.7. Found: C, 75.2;



H, 4.1; N, 20.9). On heating at 120° , 5 reverts to 1 and anthracene.⁴

Azodicarbonitrile is reduced chemically or electrolytically to a stable anion radical. Sodium azodicarbonitrilide (6), prepared in 94% yield from 1 and sodium iodide in acetonitrile, is a bronze, explosive powder,

$$2NCN = NCN + 2NaI \longrightarrow 2Na^+NCN = NCN \div + I_2$$

soluble and stable in water, methanol, and dilute base. Anal. Calcd. for **6**: C, 23.3; N, 54.4. Found: C, 23.2; N, 52.5; $\lambda_{\text{max}}^{\text{CH}_{6}\text{CN}}$ 222 (ϵ 5270), 372 (ϵ 4560), 525 m μ (ϵ 120); $\lambda_{\text{max}}^{\text{KB}_{7}}$ 4.62 μ . Polarographic reduction of **1** to **6** is a reversible, one-electron process at $E_{1/2}$ +0.40 v. vs. s.c.e., *i.e.*, more facile than the reduction of tetracyanoethylene (+0.152 v.) or of tetracyanoquinodimethane (+0.127 v.).³ Molecular orbital calculations on **1** indicate an unfilled bonding orbital is present at +0.42 β . Electron spin resonance of **6** in acetonitrile shows 5 lines, each split to 5 lines, thus indicating two equivalent pairs of nitrogen atoms.

(4) J. Harley-Mason and J. C. W. Tims, *Proc. Chem. Soc.*, 345 (1963), report an analogous reaction, the formation of ethyl cyanoazoformate from its anthracene adduct.

(5) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, J. Am. Chem. Soc., 84, 3374 (1962).

F. D. Marsh, M. E. Hermes

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Diazotetracyanocyclopentadiene and Its Conversion to Tetracyanocyclopentadienide and Pentacyanocyclopentadienide

Sir:

We have synthesized diazotetracyanocyclopentadiene (4) from hexacyanobutenediide¹ (1) and used this "diazonium" compound to make the very stable tetraand pentacyanocylopentadienide anions 5 and 6. Because of the marked stabilizing effect of the four cyano groups, the chemical properties of the "diazonium" group in diazotetracyanocyclopentadiene and the carbon-hydrogen bond in tetracyanocyclopentadienide parallel those of a benzene diazonium group and benzene carbon-hydrogen bonds. Thus, the aromaticity of the cyclopentadienide system can now be examined by classical chemical means.

In dilute aqueous acid, disodium hexacyanobutenediide cyclizes to 1-amino-2,3,4,5,5-pentacyanocyclopentadiene² (2), a bright yellow unstable solid, $\lambda_{\text{max}}^{\text{cHaCN}}$ 413 m μ (ϵ 7000). One of the cyano groups at the 5-position in 2 is hydrolyzed by concentrated hydrochloric acid at 15° , and the resulting carboxylic acid group spontaneously loses carbon dioxide to generate aminotetracyanocyclopentadienide (3), m.p. (tetraethylammonium salt) $126-127^{\circ}$. Its aqueous solutions are neutral, which indicates the tetracyanocyclopentadienidyl portion of the ion is withdrawing electrons from the amino group.



Diazotetracyanocyclopentadiene (4) results when aminotetracyanocyclopentadienide is diazotized under conditions ordinarily used to prepare aromatic diazonium compounds. Diazotetracyanocyclopentadiene, recrystallized from acetonitrile, is a light-yellow, waterinsoluble solid which decomposes at $\sim 200^{\circ}$. It does not appear to be shock sensitive. In view of its high dipole moment, 11.44 D., and chemical properties, which parallel aromatic diazonium compounds, a zwitterion structure is preferred.

Diazotetracyanocyclopentadiene reacts with cuprous cyanide to give pentacyanocyclopentadienide (6) and azotetracyanocyclopentadienide (7). Pentacyanocyclopentadienide salts are remarkably stable. For instance, the potassium salt can be heated at 400° in air without decomposition. Spectrophotometrically, we could not detect any protonation of the anion by perchloric acid in acetonitrile. The pK_a of pentacyanocyclopentadiene in this solvent is therefore less than $-2.^3$ For comparison, the pK_a of sulfuric acid in acetonitrile is $+7.25.^4$

Diazotetracyanocyclopentadiene is reduced by ethanol in the presence of copper powder to tetracyanocyclopentadienide (5), isolated as the tetraethylammonium salt, m.p. $130-132^{\circ}$. Its p K_a in acetonitrile

⁽¹⁾ O. W. Webster, J. Am. Chem. Soc., 86, 2898 (1964).

⁽²⁾ Satisfactory analytical results were obtained on all compounds.

⁽³⁾ The pK_n measurements were made by Dr. J. Fok.

⁽⁴⁾ I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., J. Am. Chem. Soc., 83, 3927 (1961).