A New Boron Hydride, $B_{20}H_{16}$

Sir:

We wish to report the synthesis and characterization of a new boron hydride, $B_{20}H_{16}$, which is the first example of a volatile borane that has fewer hydrogen than boron atoms.[1] Preparation was effected by catalytic pyrolysis of decaborane-14 at 350° (<1 mm.). With methylaminodimethylborane as the catalyst, yields of $B_{20}H_{16}$ averaged about 10%. The product was purified by repeated vacuum sublimation. The new hydride is a white, hygroscopic crystalline solid that melts at 196–199°, sublimes at 100–120° (<1 mm.), and is soluble in most common organic solvents.
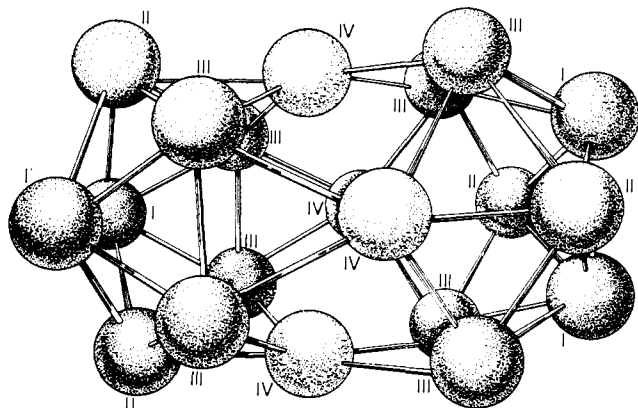

Fig. 1.—Proposed boron atom arrangement in $B_{20}H_{16}$. The unique boron atoms not directly bonded to hydrogen atoms are the central four atoms labeled IV.

Characterization is based on a thrice-sublimed sample of $B_{20}H_{16}$ which showed only one peak of any significance on gas chromatographic analysis using a 1 m. apiezon-on-firebrick column.

Anal. Calcd. for $B_{20}H_{16}$: B, 93.1; H, 6.9; C, 0.0; mol. wt., 232.5. Found: B, 92.9; H, 7.1; C, 0.3.

These data establish a hydrogen deficiency; the B–H ratio is about 20:16.3. Isopiestic molecular weight determinations in *n*-pentane gave values of 235 and 239 using as standards $B_{10}C_2H_{12}$ and azobenzene, respectively. The mass spectrum showed positive ions of every mass up to 236, and those clustered around the 100% peak at 232 were by far the most abundant. The highest mass of any significance is 236 which corresponds to $^{11}B_{20}H_{16}$. Additional molecular weight data were obtained from a preliminary single crystal X-ray study (*vide infra*). With a measured density of 1.13 g./cc., the X-ray molecular weight is 231.

With the number of boron atoms determined by molecular weight and elemental analysis data, the hydrogen atom number was confirmed as 16 by aqueous acid hydrolysis. Values of 163.9 ± 0.8 and 164.4 ± 0.8 check with that of 163.4 mmoles of H_2/g. required for $B_{20}H_{16}$. Since $B_{20}H_{16}$ is diamagnetic, odd hydrogen atom numbers are excluded. Formulations as $B_{20}H_{14}$ and $B_{20}H_{18}$ fall well outside the precision and accuracy of the acid hydrolysis experiment; respective hydrolysis values would be 160.5 and 166.2 mmoles of H_2/g. Thus the $B_{20}H_{16}$ composition is fully established.

The infrared spectrum of $B_{20}H_{16}$ shows no evidence of a bridge hydrogen stretching absorption. In the spectrum of the solid (Nujol mull), the B–H stretch at

(1) L. F. Friedman, R. D. Dobrott, and W. N. Lipscomb, have independently found and characterized $B_{20}H_{16}$, *J. Am. Chem. Soc.*, **85**, 3505 (1963). This information was kindly given to us before publication by W. N. Lipscomb.

2600 cm.$^{-1}$ has just discernible fine structure. This splitting must be a crystalline lattice effect, since it is absent in solution spectra. No ultraviolet absorption maxima were detected in cyclohexane solution.

The B^{11} n.m.r. spectrum at 19.2 Mc. in CCl_4 solution consists of three peaks of unequal intensity at +7.8, +18.5, and +27.4 p.p.m.[2] On irradiation of the hydrogen nuclei at 60 Mc., the peak at +7.8 p.p.m. was not significantly altered, indicating these boron atoms are not directly bonded to hydrogen. On sweeping with the saturating proton field, two other boron resonances are detected at +15.6 and +22.4 p.p.m. Relative intensities in the decoupled B^{11} spectra are ∼4, 4, and 12 for the 7.8, 15.6, and 22.4 resonances, respectively.

X-Ray studies have shown the crystals to be tetragonal with the cell dimensions of $a = 9.60 ± 0.05$ Å. and $c = 29.4 ± 0.1$ Å. and space group I4$_1$/acd. There are eight molecules per unit cell and the required molecular symmetry is $\bar{4}$ or 222.

The X-ray and n.m.r. data indicate a model of D_{2d} symmetry formed by joining two decaborane cages so that the 6 and 9 boron atoms of each decaborane cage contact the 5,10 and 7,8 boron atoms of the other cage (Fig. 1). Four boron atoms in the center plane are not bonded to hydrogen in agreement with analysis of the B^{11} n.m.r. spectrum.[3]

The chemistry of this novel boron hydride is under study. We have established that $B_{20}H_{16}$ dissolves with reaction in water. No hydrogen is evolved and a strongly acidic solution is generated. The titration curve of the aqueous solution is typical of that of a strong acid. Equivalent weight determined by titration was 116 ± 2 indicating that the species in solution is a diprotic acid.

Acknowledgments.—We wish to thank Dr. John Whitney for the X-ray data, and Mr. W. B. Askew and Mr. R. J. Berndt for the mass spectral information.

CONTRIBUTION No. 922   N. E. MILLER
CENTRAL RESEARCH DEPARTMENT   E. L. MUETTERTIES
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON 98, DELAWARE
                    RECEIVED OCTOBER 2, 1963

Reactions of Unsaturated Free Radicals with Nitric Oxide. Radical-Induced Scission of Carbon–Carbon Triple Bonds

Sir:

We have recently examined the gas phase reactions, at room temperature, of nitric oxide with vinyl and substituted vinyl radicals, where the radicals were formed *in situ* by the addition of an inducer radical (Y·) to an alkyne (X—C≡C—Z). The results suggest a new family of free-radical reactions involving degradation, at the triple bond, of the parent alkynyl structure. The general reaction to be exemplified may be written
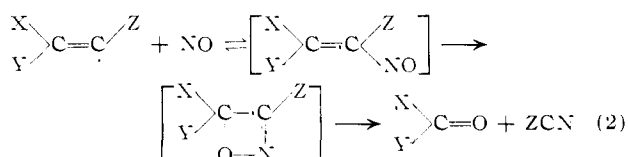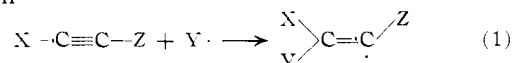
$$X-C{\equiv}C-Z + Y\cdot \longrightarrow \underset{Y}{\overset{X}{>}}C{=}C\overset{Z}{\underset{\cdot}{<}} \qquad (1)$$

$$\underset{Y}{\overset{X}{>}}C{=}C\overset{Z}{\underset{\cdot}{<}} + NO \rightleftharpoons \left[\underset{Y}{\overset{X}{>}}C{=}C\overset{Z}{\underset{NO}{<}}\right] \longrightarrow$$

$$\left[\underset{Y}{\overset{X}{>}}C{-}C\overset{Z}{\underset{O-N}{<}}\right] \longrightarrow \underset{Y}{\overset{X}{>}}C{=}O + ZCN \qquad (2)$$

TABLE I

PRODUCTS OF THE RADICAL-INDUCED REACTIONS OF ALKYNES WITH NITRIC OXIDE

Series	Alkyne	Inducer (Y·)	System	Products
I	C_2H_2	H· from $H_2S + h\nu$	a	HCN, CH_2O
II	C_2H_2	Cl· from $COCl_2 + h\nu$	b	HCN, CO, HCl
III	C_2H_2	C_2H· and H· from $C_2H_2 + Hg·6(^3P_1)$	c	HCN, C_2HCHO (propynal), CH_2O
IV	C_2HCl	Cl· from $COCl_2 + h\nu$	d	CNCl, CO, HCl
V	C_2H_2	Cl· and C_2H· from $C_2HCl + h\nu$	e	HCN, CO, HCl, C_4H_2, smaller amounts of CNCl and C_2HCHO
VI	CH_3–C_2H	Cl· from $COCl_2 + h\nu$	f	CH_3CN, CO, HCl
VII	C_2HCl	Cl· and C_2H· from $C_2HCl + h\nu$	g	CNCl, CO, HCl, C_4H_2

^{a} Static photolysis, without Vycor 7910 filter, $P(C_2H_2) = 110$ mm., $P(H_2S) = 17$, $P(NO) = 2.1$. ^{b} Static photolysis, 6-mm. thick Vycor 7910 filter, $P(C_2H_2) = 71$ mm., $P(COCl_2) = 20$, $P(NO) = 2.3$. ^{c} Flow photosensitization, $P(C_2H_2 + NO) = 8.5$ mm., mole % $(NO) = 0.3$–3.0, flow rate $= 0$–400 cm./sec. ^{d} Static photolysis, 6-mm. thick Vycor 7910 filter, $P(C_2HCl) = 69$ mm., $P(COCl_2) = 20$, $P(NO) = 3.1$. ^{e} Static photolysis, 2-mm. thick Vycor 7910 filter, $P(C_2H_2) = 430$ mm., $P(C_2HCl) = 21$, $P(NO) = 11.4$. ^{f} Static photolysis, 6-mm. thick Vycor 7910 filter, $P(CH_3C_2H) = 80$ mm., $P(COCl_2) = 23$, $P(NO) = 3.0$. ^{g} Static photolysis, without Vycor 7910 filter, $P(C_2HCl) = 39$ mm., $P(NO) = 1.6$.

where the cyclic structure in brackets represents a postulated intermediate yet unconfirmed.

The reactions were performed by generating the inducer radical, in the presence of the alkyne, containing 1–3 mole% NO, either by mercury-6($^3P_1$)-photosensitization, under flow conditions, of the alkyne itself, or by its static photolysis, or by the static photolysis of a radical source admixed with the alkyne. The flow-photosensitization equipment has been previously described.[1] For the static photolyses, cylindrical quartz cells were used, 10 cm. in length, and 5 cm. in diameter, with irradiation by a medium-pressure quartz mercury arc (Hanovia 30600) with the short wavelength cut-off controlled by Vycor 7910 filters. Analysis was by gas chromatography[2] and mass spectrometry excepting for CH_2O, where chromotropic acid was used.[3]

The results are summarized in Table I. Thus in the first series H-atoms from the H_2S photolysis form C_2H_3 radicals with the C_2H_2 present, and these in turn react with NO in the simplest example of eq. 2.
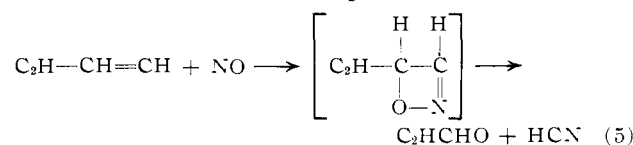
$$C_2H_3 + NO \longrightarrow \left[\begin{matrix} H & H \\ H-C-C \\ O-N \end{matrix} \right] \longrightarrow CH_2O + HCN \quad (3)$$
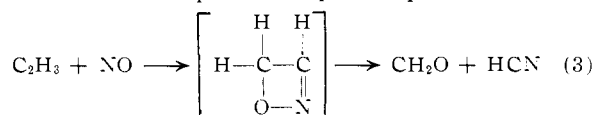
In series II, chlorovinyl radicals form and react with NO in another example of eq. 2.

$$C_2H_2Cl + NO \longrightarrow \left[\begin{matrix} Cl & H \\ H-C-C \\ O-N \end{matrix} \right] \longrightarrow HCN + (HClCO) \quad (4)$$
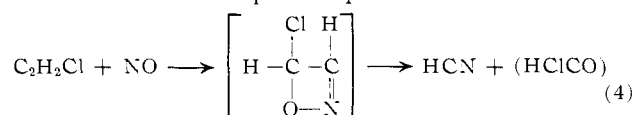
The HClCO is unstable and decomposes to the HCl and CO actually found.

By treating Hg-6($^3P_1$) atoms with C_2H_2,[4] C_2H and H were equivalently generated in C_2H_2 in series III. Flow conditions were used to avoid mercury depletion.[4] Both H and C_2H added to the substrate to form, respectively, C_2H_3 and C_4H_3 radicals, in equal numbers. No reaction between C_2H and NO was detected. The C_2H_3 species react with NO via eq. 3; while C_4H_3, which is a substituted vinyl radical, again follows the reaction scheme defined in eq. 2.

$$C_2H-CH=CH + NO \longrightarrow \left[\begin{matrix} H & H \\ C_2H-C-C \\ O-N \end{matrix} \right] \longrightarrow$$
$$C_2HCHO + HCN \quad (5)$$

The mechanism given predicts a yield ratio, HCN/C_2-HCHO, of 2. The ratio found was 1.7.

In series IV, the photolysis of $COCl_2$ is used as a source of Cl atoms,[5] which add to the chloroacetylene to form dichlorovinyl radicals: (a) $CCl_2=\dot{C}H$ and/or (b) $CHCl=\dot{C}Cl$. According to eq. 2, (a) would react with NO to form $COCl_2$ and HCN, while (b) would give CNCl, CO, and HCl—the products actually found (Table I), from which we conclude that the addition leads to (b).

$$CHCl=\dot{C}Cl + NO \longrightarrow \left[\begin{matrix} Cl & Cl \\ H-C-C \\ O-N \end{matrix} \right] \longrightarrow$$
$$CO + HCl + CNCl \quad (6)$$

In situ photolysis of C_2HCl itself, in C_2H_2 (series V), provides both Cl and C_2H for reaction with C_2H_2. The Cl atoms should react as in series II, to form HCN, CO, and HCl as observed (Table I). In addition reaction 6 should occur, but to a much smaller extent, since $P(C_2HCl)/P(C_2H_2)$ is only 0.05 in the reaction mixture. From Table I it can be seen that smaller amounts of CNCl were in fact found. As to the C_2H radicals, their major fate in this system is different than in pure C_2H_2 (series III). Thus in a separate study of the photolysis of C_2HCl[6] it has been shown that C_2H radicals undergo a displacement reaction with C_2HCl.

$$C_2H + C_2HCl \longrightarrow C_4H_2 + Cl \quad (7)$$

Step 7 is considerably faster than the addition of C_2H to C_2H_2 and hence in series V, C_4H_2 is a major product, and of course the additional Cl atoms formed in step 7 increase the yields of HCN, CO, and HCl via eq. 4. That some C_4H_3 radicals form in the series V system is evident from the small yield of propynal from step 5.

An interesting case of the general reaction 2 is found in the addition of Cl to CH_3–C_2H (series VI) in the presence of NO. Again here the vinyl radical can have two isomeric forms: (a) $CH_3CCl=\dot{C}H$ and (b) $CH_3\dot{C}=CHCl$. According to reaction 2, (a) would react with NO to form CH_3COCl and HCN, while (b) would give CH_3CN, CO, and HCl. Since the products predicted from reaction 2 for the (b) isomer were those found (Table I), and since neither CH_3COCl nor HCN was detected, it appears that the Cl atom adds exclusively at the H-substituted carbon of the methyl acetylene.

Finally, as noted under series V, the photolysis of C_2HCl with added NO (series VII) proceeds by eq. 6 to form CNCl, CO, and HCl, and C_2H reacts via eq. 7 to form C_4H_2, corresponding to the products found.

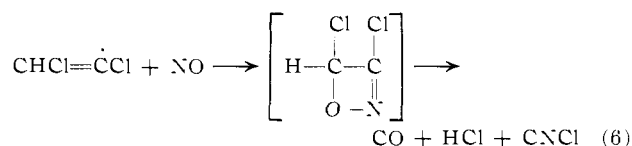(1) G. N. C. Woodall and H. E. Gunning, Bull. soc. chim. Belges, 71, 725 (1962).

(2) Gas chromatographic analysis, with molecular sieves column for products noncondensable at −196° and 6% 1,2,3-tris-(cyanoethoxy)-propane on firebrick for the condensable products. Eluted peaks were individually trapped for infrared and mass spectrometric characterization.

(3) A. Altshuller, D. Miller, and S. Sleva, Anal. Chem., 33, 621 (1961).

(4) A. G. Sherwood and H. E. Gunning, Can. J. Chem., 38, 466 (1960).

(5) M. H. J. Wijnen, J. Chem. Phys., 36, 1672 (1962).

(6) A. G. Sherwood and H. E. Gunning, to be published.

The seven examples cited here would seem to offer some convincing evidence in support of the mechanism given in eq. 2 for the reaction between NO and vinyl and substituted vinyl radicals at room temperature. Furthermore, starting with the alkyne, reactions 1 and 2 appear to define a new structurally specific route for the scission of carbon–carbon triple bonds.

Further work is in progress in this laboratory on the kinetics of the reactions herein described, on the applicability of the proposed mechanism to alkynyl and vinyl structures in general, and on the properties of the intermediate formed between the vinyl radical and nitric oxide.

Acknowledgment.—The authors express their deep appreciation to Dr. O. P. Strausz and Dr. A. J. Yarwood for many helpful discussions.

DEPARTMENT OF CHEMISTRY   ALDEN G. SHERWOOD
UNIVERSITY OF ALBERTA   HARRY E. GUNNING
EDMONTON, ALBERTA, CANADA

Rapid Ligand Exchange in Zirconium(IV) Chelates

Sir:

Several unsuccessful attempts to detect geometric or optical isomers of tetrakis-β-diketone complexes of Zr(IV) and Hf(IV) suggest that in solution rapid ligand exchange is occurring. This hypothesis has been verified by the n.m.r. spectra of mixtures of tetrakis-(2,4-pentanediono)-zirconium(IV), Zr(acac)$_4$, and tetrakis-(1,1,1-trifluoro-2,4-pentanediono)-zirconium(IV), Zr(tfac)$_4$.

Zr(acac)$_4$ and Zr(tfac)$_4$ were prepared by a previously reported method[1] and were characterized by their melting points and infrared spectra. The n.m.r. spectra were obtained on a Varian Associates Model A-60 spectrometer at 60 Mc. Samples were prepared by weighing the appropriate amounts of Zr(acac)$_4$ and Zr(tfac)$_4$ to the nearest 0.0001 g. and then adding benzene to make a 10% solution. Areas of the resonance peaks were measured in mm.[2] and the total area of the methyl proton resonance was normalized to 4000 mm.[2] The chemical shifts were measured to ±0.5 c.p.s. relative to benzene.
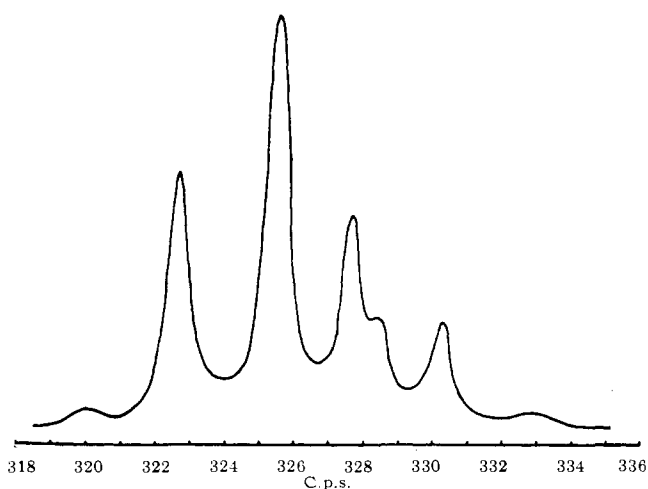

Fig. 1.—The proton n.m.r. spectrum (chemical shift in c.p.s. relative to benzene) of a mixture of Zr(acac)$_4$ and Zr(tfac)$_4$; $X = 0.70$.

A benzene solution of Zr(acac)$_4$ has a methyl resonance at 320.0, the Zr(tfac)$_4$ at 332.5 c.p.s. Geometric isomers of octahedral complexes containing three un-

(1) E. M. Larsen, G. Terry, and J. Leddy, *J. Am. Chem. Soc.*, **75**, 5107 (1953).
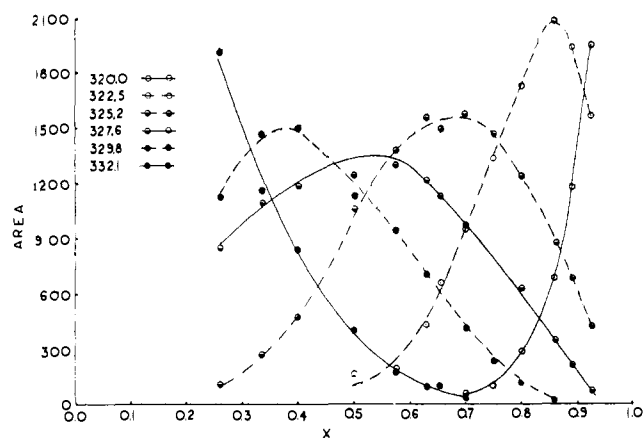

Fig. 2.—The concentration dependence of the methyl resonances.

symmetrical bidentate ligands have been detected by the splitting of the methyl resonance in the n.m.r. spectra.[2,3] With Zr(tfac)$_4$, rapid ligand exchange makes all the methyl protons equivalent and no splitting is observed. Mixtures of Zr(acac)$_4$ and Zr(tfac)$_4$ have methyl resonances at 320.0, 322.5, 325.2, 327.6, 329.8, and 332.1 c.p.s. A typical spectrum is shown in Fig. 1. In several of the spectra the resonances at 325.2 and 327.6 c.p.s. are asymmetric, indicating that two or more peaks are not being resolved. The concentration dependence of the areas of the individual resonances is shown in Fig. 2. Here X represents the mole fraction of the acetylacetonate methyl groups and is equal to $2[acac]/(2[acac] + [tfac])$, where [acac] and [tfac] represent the total number of moles of acetylacetone and trifluoroacetylacetone, respectively.

Because of rapid exchange of the ligands, a solution of Zr(acac)$_4$ and Zr(tfac)$_4$ contains the following five compounds: Zr(acac)$_4$, Zr(acac)$_3$(tfac), Zr(acac)$_2$(tfac)$_2$, Zr(acac)(tfac)$_3$, and Zr(tfac)$_4$. For each of the "mixed" compounds, the n.m.r. spectrum is expected to show two methyl resonances, one for the acetylacetone methyl protons and one for the trifluoroacetylacetone methyl protons. Zr(acac)$_4$ and Zr(tfac)$_4$ each have one methyl resonance. Thus, eight resonances are expected for the mixture. This is in agreement with experimental results if one assumes that the resonances at 325.2 and 327.6 c.p.s. are unresolved doublets.

For assignment of the resonances, consider the concentration $X = 0.925$. The total concentration of acetylacetone is six times as great as the total concentration of trifluoroacetylacetone; consequently, Zr(acac)$_4$ and Zr(acac)$_3$(tfac) are expected to be the most important species in solution. At this concentration the peak at 320.0 c.p.s. is the only resonance which is not decreasing in intensity; therefore, this resonance is assigned to the methyl protons of Zr(acac)$_4$. The peak of second greatest intensity, at 322.5 c.p.s., is assigned to the acetylacetone methyl protons of Zr(acac)$_3$(tfac). The intensity of the resonance caused by the trifluoroacetylacetone methyl protons of this compound is one sixth of the intensity of the peak at 322.5 c.p.s. At this concentration, the area of this trifluoroacetylacetone methyl peak is expected to be 260 mm.[2] The only way of satisfying this is to assume that part of the intensity of the peak at 325.2 c.p.s. is caused by these methyl protons. The remaining area of the peak at 325.2 c.p.s., 160 mm.[2], is approximately twice the area of the resonance at 327.6 c.p.s.; therefore, the resonance at 325.2 c.p.s. is assigned to the acetylacetone methyl protons of Zr(acac)$_2$(tfac)$_2$ and the

(2) R. C. Fay and T. S. Piper, *ibid.*, **84**, 2303 (1962).
(3) R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963).