

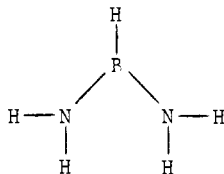
Table I. Rotational Constants for Four Isotopic Species of Diaminoborane

	$^{10}\text{B}(\text{NH}_2)_2$	$^{11}\text{B}(\text{NH}_2)_2$	$^{10}\text{B}(\text{ND}_2)_2$	$^{11}\text{B}(\text{ND}_2)_2$
<i>A</i> , MHz	53752.6 ± 0.42 ^a	52382.9 ± 0.47	33035.1 ± 1.2	32507.6 ± 2.7
<i>B</i> , MHz	9092.31 ± 0.074	9093.23 ± 0.085	7424.7 ± 0.37	7424.8 ± 0.87
<i>C</i> , MHz	7777.42 ± 0.052	7748.59 ± 0.060	6064.4 ± 0.37	6045.9 ± 1.2
κ	-0.942800	-0.939749	-0.89913	-0.89578
Δ , amu Å ²	-0.0047 ± 0.001	-0.0032 ± 0.001		

^a Error limits are one standard deviation.

The product and excess ammonia were collected in a -196 °C trap. The product was then separated from ammonia by fractional condensation in a -104 °C trap. Yields were 10-17%. Anal. Calcd for BN_2H_5 : B, 24.65; N, 63.86; H, 11.49. Found: B, 24.15; N, 60.66; H, 11.60. In the liquid state, diaminoborane decomposes to form a glassy solid with the evolution of ammonia. Hence properties such as the melting point and the vapor pressure of the liquid have not been determined. However, as a vapor the compound can be kept for several days at room temperature with negligible formation of ammonia, and solutions in liquid ammonia appear to be indefinitely stable even at room temperature. No significant mass spectral peaks with $m/e > 44$ (corresponding to $^{11}\text{B}(\text{NH}_2)_2$) were observed for $\text{BH}(\text{NH}_2)_2$ or mixtures of $\text{BH}(\text{NH}_2)_2$ and NH_3 .

The ^{11}B NMR spectrum of $\text{BH}(\text{NH}_2)_2$ in either liquid ammonia or tetrahydrofuran is a 126-Hz doublet, consistent with the structure shown. When either borazine or the glassy



solid from the decomposition of $\text{BH}(\text{NH}_2)_2$ is dissolved in liquid ammonia, the ultimate products are $\text{BH}(\text{NH}_2)_2$ and a small amount of NH_3BH_3 and $\text{B}(\text{NH}_2)_3$. ^{11}B NMR spectra show that several intermediates are involved in these reactions. The chemical shifts in liquid ammonia of $\text{BH}(\text{NH}_2)_2$ and $\text{B}(\text{NH}_2)_3$ are 28.0 and 26.7 ppm downfield of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, respectively.

The infrared spectrum of gaseous diaminoborane has not been completely assigned, but several features are clearly evident. There are four strong N-H stretching bands (two at 3556 cm^{-1} and two at 3464 cm^{-1}) and a strong BH stretch at 2517 cm^{-1} . A preliminary normal coordinate analysis shows the B-N stretching to be highly mixed with the motions of other internal coordinates. Consequently, it is not obvious which of the strong bands at 1605 or 1393 cm^{-1} corresponds to the often cited⁹ asymmetric B-N stretch.

A total of 33 rotational transitions in the 8-42-GHz region have been assigned for four different isotopic species of diaminoborane. The spectra are consistent with a slightly asymmetric top having a permanent dipole parallel to the *B* principal axis. Determination of the line centers is complicated by the splitting due to the nuclear electric quadrupole coupling of the boron and the two nitrogens.

Table I lists the rotational constants based on a least-squares fit of the transition frequencies. Because of a limited supply of the two perdeuterio species, their rotational constants have not yet been as well determined as those of the normal species. The small negative inertial defect Δ strongly suggests a planar C_{2v} structure for diaminoborane. Using the 12 rotational constants, and assuming a planar structure, a least-squares procedure was used to determine the following bond lengths and angles:¹⁰ $r_{\text{BH}} = 1.190 \pm 0.02$, $r_{\text{BN}} = 1.419 \pm 0.002$, $r_{\text{NH cis}} = 1.028 \pm 0.01$, $r_{\text{NH trans}} = 0.983 \pm 0.01$ Å; $\angle\text{NBN} = 121.95$

± 0.1, $\angle\text{BNH (cis)} = 117.5 \pm 2.0$, and $\angle\text{BNH (trans)} = 125.0 \pm 2.0^\circ$. There are large error limits for the two BNH angles because they are highly correlated. The rotational constants of unsymmetrically deuterated species are being determined since they substantially reduce this correlation and the other error limits. The 1.42-Å BN bond length is between the single-bond length of 1.54 Å and double-bond length of 1.36 Å. This indicates substantial π bond character in the NBN framework. The other bond lengths are typical.

From Stark splitting data, the dipole moment is found to be 1.25 ± 0.01 D (OCS taken as 0.71521) and is coaxial with the B-H bond. The sign of the dipole moment has not been determined.

Acknowledgments. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (T.S.B. and W.L.J.), and the National Science Foundation (W.D.G. and L.R.T.)

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- (10) The NH hydrogens are either cis or trans relative to the BH hydrogen.

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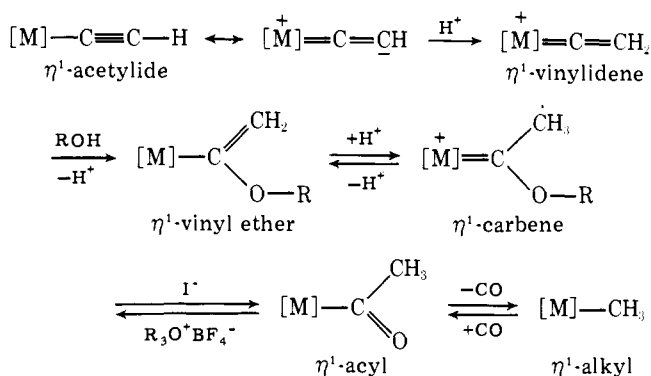
Stable Dimethyl, Methyl, and Unsubstituted Vinylidene Complexes

Sir:

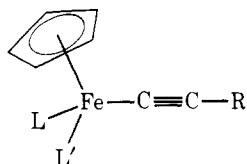
Vinylidene ($>\text{C}=\text{CH}_2$), the valence tautomer of acetylene, occupies an important position among monohapto carbon ligands in transition metal chemistry.¹⁻⁵ Some chemical transformations which relate these monohapto ligands are shown in Scheme I. This scheme also emphasizes similarities in the electrophilicity of the α position and the nucleophilicity of the β position in the isoelectronic series: terminal metal carbonyl, acetylide, and vinylidene.⁶ The electrophilicity of a vinylidene complex depends markedly^{2,5} on the auxiliary ligands, the metal, and the total charge on the complex.

We recently reported⁵ on the reactivity of the iron acetylides Ia and Ib toward electrophiles. Whereas protonation of Ib

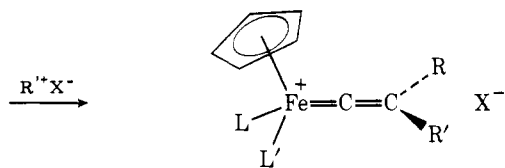
Scheme I



produces a marginally stable salt, IIb, the reactions of Ia under protic conditions implicate the intermediacy of a very reactive metalvinyl cation (vinylidene), IIa. However, using the bidentate ligand bis(1,2-diphenylphosphino)ethane (dppe) enhances the π -donor capability of the CpFeL₂ moiety. We have isolated a series of stable cationic vinylidene complexes, IIc, IIId, and IIe, from the electron-rich iron acetylides Fp'-C≡CCH₃ (Ic) and Fp'-C≡CH (Id).



- Ia, L = L' = CO; R = Ph
 b, L = CO; L' = PPh₃; R = Ph
 c, L + L' = dppe; R = CH₃
 d, L + L' = dppe; R = H



- IIa, L = L' = CO; R = Ph; R' = H; X = BF₄⁻
 b, L = CO; L' = PPh₃; R = Ph; R' = H; X = BF₄⁻
 c, L + L' = dppe; R = R' = CH₃; X = SO₃F⁻
 d, L + L' = dppe; R = CH₃; R' = H; X = PF₆⁻
 e, L + L' = dppe; R = R' = H; X = PF₆⁻

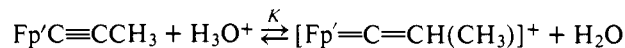
The red crystalline acetylide Fp'-C≡CCH₃ (Ic) was prepared by the reaction of propynyllithium with Fp'Cl^{7a} or Fp'BF₄^{7b} in THF (31 and 53%, respectively): mass spectrum parent ion *m/e* 558; IR $\nu(C\equiv C)$ 2100 cm⁻¹; ¹H NMR (CDCl₃) δ 8.0–7.2 (20 H, Ph), 4.17 (t, ³J_{P-H} = 1.3 Hz, 5 H, Cp), 2.9–1.9 (m, 4 H, PCH₂), 1.60 (t, ⁵J_{P-H} = 2.15 Hz, 3 H, CH₃); ¹³C NMR⁸ (CDCl₃) 142.7–127.1 (m, Ph), 112.6 (s, C_α), 97.5 (s, C_β), 78.8 (s, Cp), 28.4 (t, ¹J_{P-C} = 22.5 Hz, PCH₂), 7.7 ppm (s, CH₃). Anal. (C₃₄H₃₂FeP₂) C, H, P. It reacted rapidly with methylfluorosulfonate in benzene to give [Fp'=C=C(CH₃)₂]SO₃F as a pale orange solid: IR $\nu(C=C)$ 1675 cm⁻¹, $\nu(SO_3F^-)$ 1280, 1090, 1065 cm⁻¹; ¹H NMR (1:1 CDCl₃-CD₂Cl₂ (v/v)) δ 7.7–6.9 (m, 20 H, Ph), 5.06 (t, ³J_{P-H} = 0.8 Hz, 5 H, Cp), 2.86 (d, ²J_{P-H} = 13.0 Hz, 4 H, PCH₂), 0.96 (t, ⁵J_{P-H} = 0.8 Hz, 6 H, CH₃¹⁰); ¹³C NMR (CDCl₃-CD₂Cl₂) 363.3 (t, ²J_{P-C} = 33.3 Hz, C_α), 136.5–129.6 (m, Ph), 127.8 (s, C_β), 88.0 (s, Cp), 28.4 (t, ¹J_{P-C} = 23.0 Hz, PCH₂), 12.0 ppm (s, CH₃¹⁰). Anal. (C₃₅H₃₅FFeO₃P₂S) C, H, P, S. The addition of HPF₆·O(C₂H₅)₂ to a benzene solution of Ic rapidly precipitated [Fp'=C=CH(CH₃)]PF₆ (IIId) as a pale orange solid. Recrystallization (CHCl₃-2-propanol) gave orange crystals: IR (CHCl₃) $\nu(C=C)$ 1658 cm⁻¹, $\nu(PF_6)$ 840 cm⁻¹; ¹H NMR (acetone-*d*₆) δ 7.9–7.2 (m, 20 H, Ph), 5.30

(t, ³J_{P-H} = 0.45 Hz, 5 H, Cp), 4.37 (q of t, ⁴J_{P-H} = 3.0 Hz, ³J_{H-H} = 7.6 Hz, 1 H, H_β), 3.15 (d, ²J_{P-H} = 13.0 Hz, 4 H, P-CH₂), 1.02 (d of t, ⁵J_{P-H} = 0.7 Hz, ³J_{H-H} = 7.6 Hz, 3 H, CH₃); ¹³C NMR (acetone-*d*₆) 358.3 (t, ²J_{P-H} = 33.3 Hz, C_α), 137.3–129.7 (m, Ph), 118.0 (s, C_β), 89.5 (s, Cp), 29.0 (t, ¹J_{P-C} = 1.4 Hz, PCH₂), 4.68 ppm (s, CH₃). Anal. (C₃₄H₃₃F₆FeP₃) C, H, P.

Similarly the reaction of Fp'BF₄ with ethynyllithium-ethylenediamine complex in THF gave Fp'-C≡C-H (Id) as a red solid which was protonated to give the parent vinylidene complex, [Fp'=C=CH₂]PF₆ (IIe). Id: IR $\nu(C-H)$ 3270 cm⁻¹, $\nu(C\equiv C)$, 1925 cm⁻¹; ¹H NMR (C₆D₆) δ 8.0–7.4 (m, 20 H, Ph), 4.28 (t, ³J_{P-H} = 1.0 Hz, Cp), 2.04 (t, ²J_{P-H} = 38.0 Hz, 4 H, PCH₂), 1.76 (t, ⁴J_{P-H} = 5.5 Hz, C≡CH); ¹³C NMR (C₆D₆) 143.1–127.4 (m, Ph), 105.7 (s, C_α), 79.7 (s, Cp), 68.3 ppm (s, C_β). IIe: IR $\nu(C=C)$, 1625 cm⁻¹, $\nu(PF_6)$ 840 cm⁻¹; ¹H NMR (CDCl₃) δ 8.0–7.0 (m, 20 H, Ph), 5.30 (s, 5 H, Cp), 3.91 (t, ⁴J_{P-H} = 4.0 Hz, 2 H, H_β¹⁰), 3.12 (d, ²J_{P-H} = 13.0 Hz, 4 H, PCH₂).

The analytical and spectral data satisfactorily characterize these vinylidene complexes. The most significant feature in the ¹³C NMR spectra of these compounds is the marked deshielding of C_α (~250 ppm downfield from C_α of the parent acetylides). The resonances appear as triplets due to coupling with the effectively equivalent phosphorus atoms in the dppe ligand.¹³ Cyclopentadienyl-1,2-bis(diphenylphosphino)ethanevinylideneiron(II) hexafluorophosphate (IIe) is the first example of an unsubstituted vinylidene complex to be reported.¹⁵

The propensity of the electron-rich acetylides Ic and Id to undergo electrophilic attack at C_β is remarkable. The complexes Ic and IIId form a conjugate acid-base pair:



We have determined the equilibrium constant for this reaction in 2:1 THF-H₂O at 20 °C spectrophotometrically, by titration of either Ic with aqueous HCl or IIId with aqueous KOH.¹⁶ The titration curves obtained give a value of p*K* = 7.74 ± 0.05. (The deprotonation reaction of IIId with aqueous base leads to the isolation of Ic.¹⁸) Unlike the highly reactive vinyl cations obtained previously,⁵ the complexes IIc-e are thermally stable, air stable as solids, and are unreactive toward alcohols and water.

Our studies of other aspects of the nucleophilicity of electron-rich acetylides and the electrophilicity of cationic vinylidene complexes will be reported subsequently.

Note Added in Proof. After submission of this manuscript, we learned of the synthesis of ruthenium analogues of II, prepared by a similar route: M. I. Bruce (Adelaide). The structure of one of these (L = L' = PPh₃; R = R' = CH₃; X = PF₆) has been confirmed by crystal structure analysis by R. E. Davis (University of Texas). Personal communication from R. E. Davis.

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- Other isoelectronic complexes show similar patterns of reactivity; cf. cy-

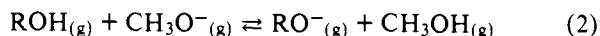
- anide, isocyanide, thio- and selenocarbonyl complexes.
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 - (8) ^{13}C NMR spectra were recorded on a JEOL FX-60Q spectrometer with internal deuterium lock and complete proton decoupling, at ambient probe temperature. Shifts are reported in parts per million downfield from Me_4Si . Generally, over 10 000 pulses were required to resolve the low-field triplets due to vinylidene α carbons, with nearly saturated (0.1-0.5 M) samples.
 - (9) $[\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{C}=\text{CHPh})]\text{BF}_4$ has $\nu(\text{C}=\text{C})$ at 1675 cm^{-1} . Assignment of $\nu(\text{C}=\text{C})$ for other terminal vinylidene complexes is uncertain owing to coupling with $\nu(\text{Ph})^{2,4}$ and $\nu(\text{CN})^5$ modes, but generally falls in the range $1400\text{--}1600\text{ cm}^{-1}$.
 - (10) The equivalence of the two methyl groups in $[\text{Fp}^{\text{I}}=\text{C}=\text{C}(\text{CH}_3)_2]\text{SO}_3\text{F}$ (Ic) in the ^1H and ^{13}C NMR spectra and the equivalence of the two H_3C 's in $[\text{Fp}^{\text{I}}=\text{C}=\text{CH}_2]\text{PF}_6$ infer that the plane of the vinylidene ligand bisects the effective ^{13}C molecular symmetry plane as found for $\text{CpMn}(\text{CO})_2(\text{C}=\text{CHPh})^{6a}$ and $\text{CpMo}[\text{P}(\text{OMe})_2]_2\text{Cl}[\text{C}=\text{C}(\text{CN})_2]$,^{3b} or that the vinylidene ligand rotates rapidly on the NMR time scale. The invariance of the ^1H NMR spectrum from -60 to $60\text{ }^\circ\text{C}$ favors the former possibility.
 - (11) This low $\nu(\text{C}=\text{C})$ is common in unsubstituted transition metal acetylides, which generally have $\nu(\text{C}=\text{C})$ below 2000 cm^{-1} .¹²
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 - (13) The conformation of the dppe-Fe chelate ring renders complexes of the type $\text{CpFe}(\text{dppe})\text{X}$ dissymmetric.¹⁴ A rapid fluxional motion of the chelate ring can account for the observation of clean triplets due to J_{FC} and J_{FH} in the NMR spectra of complexes Ic and Id and lic-e.
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 - (15) With the exception of Ila⁵ and the dicyano vinylidene complexes prepared by King and Saran,³ all terminal vinylidene complexes have resulted from the $\pi \rightarrow \sigma$ rearrangement of hypothetical^{2,4b,d} or isolated^{4a-e} terminal or Ph_3Sn substituted^{4b} η^2 -phenylacetylene complexes. Thus, they contain the phenylvinylidene ($\text{C}=\text{CHPh}$) ligand.
 - (16) The titrations of Ic and Id were carried out by the addition of aqueous HCl or KOH by microliter syringe to $2 \times 10^{-3}\text{ M}$ solutions of the complexes in THF-H₂O (2:1 (v/v)) maintained under nitrogen. pH was measured with a Broadley-James Corp. glass electrode in conjunction with a Corning Model 7 pH meter. Visible spectra of the resulting solutions were obtained on a Cary 17 spectrophotometer. Plots of absorbance at 490 nm vs. pH gave well-defined titration curves.¹⁷ The midpoints of these curves were determined graphically. The pK values obtained were 7.72 ± 0.05 and 7.76 ± 0.05 for Ic and Id, respectively.
 - (17) Ewing, G. W. "Instrumental Methods of Chemical Analysis". Third ed.; McGraw-Hill: New York; 1969, Chapter 3.
 - (18) Ic was isolated from the titrations of Ic and Id by raising the pH above 12, salting out the aqueous layer, evaporating the resulting THF solution to dryness, and comparing the resulting red solid with authentic Ic (IR, ^1H NMR, mass spectrum).

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Regarding the Separation of Polarizability and Inductive Effects in Gas- and Solution-Phase Proton-Transfer Equilibria¹

Sir:

The inductive effects of dipolar substituents on both experimental and theoretically calculated gas-phase acidities have been found to be generally consistent with the σ_1 scale from solution acidities.² However, major apparent exceptions occur with alkyl substituents at saturated (sp^3) carbon in both gas phase³ and in solution.⁴ Although gas-phase acidities are free from steric hindrance to ionic solvation that (with other factors) may interfere frequently with the observation of the very small inductive effects of alkyl substituents in solution, the polarizability effects of hydrocarbon substituents completely dominate any inductive effects in gas-phase proton-transfer equilibria,³ e.g.



where R is any group derived by substitution for the H's of the CH_3 group.

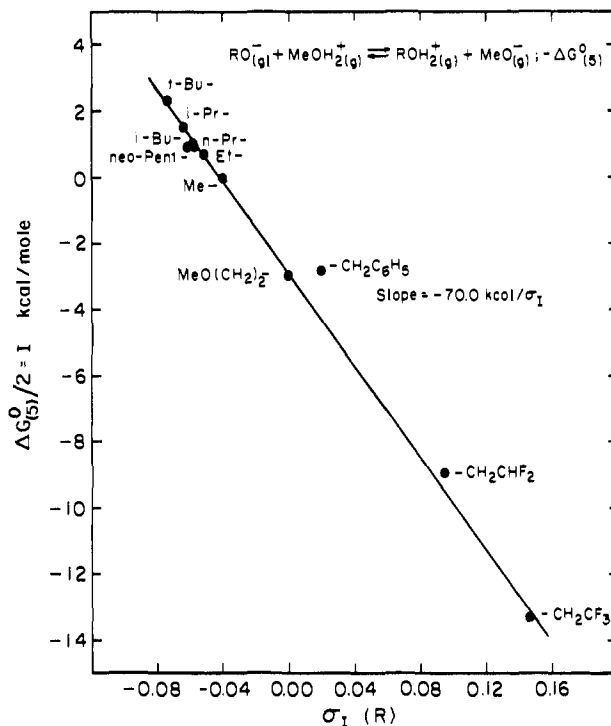


Figure 1. Correlation of gas-phase inductive effects with σ_1 parameters.

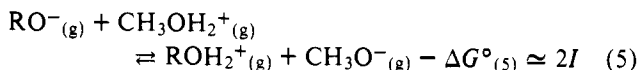
We report a separation of polarizability and inductive effects contributing to the values of $-\Delta G^0$ for reactions 1 and 2. The polarizability effect³ (P) for R relative to CH_3 arises from greater charge-induced dipole stabilization of both the cation or anion, i.e., ROH_2^+ relative to CH_3OH_2^+ and RO^- relative to CH_3O^- . An inductive electron-releasing effect of $\text{R}(I)^5$ will stabilize ROH_2^+ relative to CH_3OH_2^+ but will destabilize RO^- relative to CH_3O^- . We make the simplifying assumption (in view of the nature of reactions 1 and 2) that the magnitudes of these effects will be approximately equal,⁶ i.e., for reaction 1

$$-\Delta G^0_{(1)} \approx I + P \quad (3)$$

and for reaction 2

$$-\Delta G^0_{(2)} \approx -I + P \quad (4)$$

where I is the inductive effect of R compared to CH_3 (opposite in sign for reactions 1 and 2) and P is the stabilizing polarizability effect of R compared to CH_3 (+ for both reactions 1 and 2). Subtracting (2) from (1) gives an equilibria (hypothetical) between four ions, for which the polarizability effect has been minimized or eliminated, i.e., (1) - (2) = (5).



The results obtained from our combined studies by the pulsed ion cyclotron resonance equilibrium constant method⁷ are given in Table I. It is immediately apparent that the values of I obtained from the double proton-transfer equilibria, eq 5, are in the classical inductive order. The quantitative correlation of the I values with σ_1 values is shown in Figure 1. For alkyl substituents the σ_1 values used are based upon the method of Ingold^{5a} and Taft^{5b,c} involving alkaline- and acid-catalyzed ester ($\text{RCH}_2\text{CO}_2\text{Et}$) hydrolysis transition states.

For alkyl substituents, the electron-releasing inductive effects of R relative to CH_3 are substantial, i.e., up to 2.3 kcal/mol for $t\text{-Bu}$, but, nonetheless, these are three to seven times smaller than for the corresponding predominant polarizability (P) effects. As expected for inductive electron-withdrawing substituents, I values are negative but P values are positive.⁸