synthesis showed no significant residual electron density; the largest peak was 0.34 e/Å^3. See Table VI for a summary of crystallographic data.

Theoretical Calculations. Calculations were of the extended Hückel type,[27] with programs locally modified and supplied by Prof. Keith Purcell. Values of bond lengths and bond angles employed were taken from structural data.[1d,7,32] The V–C bond length was chosen to be the sum of their covalent radii (1.994 Å), and an N–V–C angle of 106° was assumed. Values of Slater exponents, coefficients, and atomic orbital energies for elements with $Z \leq 17$ were taken from the literature.[27] The Slater exponents (coefficients in parentheses) for vanadium (chosen to be in the +3 oxidation state) were determined[33] to be as follows: 3d, 4.75 (0.498), 1.90 (0.655); 4s, 1.6 (1.0); 4p, 1.6 (1.0). Atomic orbital energies for vanadium (calculated by the method of Gray et al.[34]) employed in the calculations were $H_{dd} = -12.55$ eV, $H_{ss} = -10.74$ eV, and $H_{pp} = -7.04$ eV.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8604359). D.D.D. thanks the Phillips Petroleum Corp. for a fellowship. The WM-400 NMR spectrometer employed in this work was purchased with the assistance of an NSF instrumentation award. We are grateful to Professors K. F. Purcell and P. M. A. Sherwood for their aid in implementing the EHMO calculations.

Supplementary Material Available: Tables of fractional coordinates of hydrogen atoms, anisotropic thermal parameters, complete bond distances and angles, and torsion angles (8 pages); listing of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Bridge Deprotonation of *nido*-2,3-RR′$C_2B_4H_6$ Carboranes and B_5H_9: A Kinetic Study

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Received May 19, 1987

Abstract: The heterogeneous reactions of the title compounds (R = alkyl, arylmethyl, or phenyl; R′ = R or H) with suspended NaH or KH in THF to give $M^+[RR'C_2B_4H_5^-] + H_2$ were studied as a function of temperature, with determination of reaction rates from the rate of formation of H_2. In all cases the kinetic rate law is pseudo-first order with linear plots of $-\ln k_1$ vs. $1/T$, and the rate is independent of the amount of metal hydride present. Reactions with NaD in place of NaH give no detectable incorporation of deuterium into the carborane anion. The main trend observed is a moderate decrease in reaction rate as the sizes of R and R′ are increased, the effect being greatest in the bis(chromiumbenzyl)carborane complex $[(CO)_3CrPhCH_2]_2C_2B_4H_6$. The data are interpreted as reflecting primarily steric inhibition of the reaction by the R groups, except in the diphenyl derivative $Ph_2C_2B_4H_6$ which exhibits very fast reaction rates at the higher temperatures measured (above −40 °C) and anomalously high activation energy (E_a) and low entropy of activation ($\Delta S^\ddagger$). In this instance, electron withdrawal by the phenyl groups via resonance and pronounced steric effects by the phenyls are proposed to account for the observed behavior.

A characteristic feature of most open-cage (non-closo) boranes and carboranes, and many of their metal-containing derivatives, is the presence of one or more three-center-bonded B–H–B groups on the open face of the molecule. These bridging hydrogens typically exhibit acidic behavior toward strong Lewis bases and can be removed to generate a conjugate base anion,[2] e.g.

$$B_5H_9 + NaH \rightarrow Na^+B_5H_8^- + H_2 \qquad (1)$$

Rarely, however, can more than one proton per molecule be removed even under forcing conditions. As first shown long ago by Onak and co-workers,[3] the *nido*-carborane 2,3-$C_2B_4H_8$ and its C- and B-substituted derivatives are readily converted to the corresponding monoanion[3,4] (eq 2 and Figure 1). The reactions proceed cleanly and quantitatively, as we have verified from high-resolution (115.8 MHz) ^{11}B NMR spectra of the anions produced. The neutral carboranes are readily accessible via the

$$C_2B_4H_8 + M^+H^- \rightarrow M^+C_2B_4H_7^- + H_2 \qquad (2)$$

base-promoted reaction of B_5H_9 with alkynes[5] and constitute a large carborane family with a steadily increasing role in synthesis.[6] In recent years, studies of C,C′-disubstituted $R_2C_2B_4H_6$ derivatives have disclosed a variety of synthetically useful processes based on these compounds (e.g., metal-induced oxidative fusion to form $R_4C_4B_8H_8$ clusters,[6,7] alkyne incorporation into the cage,[8] and cage expansion[9,10]).

In the course of our research we have prepared, as reagents for synthetic purposes, a number of *nido*-RR′$C_2B_4H_6$ species in

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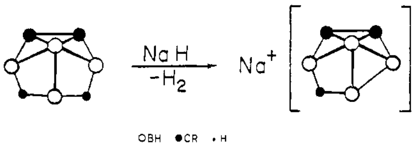

Figure 1. Deprotonation of *nido*-2,3-$R_2C_2B_4H_6$.

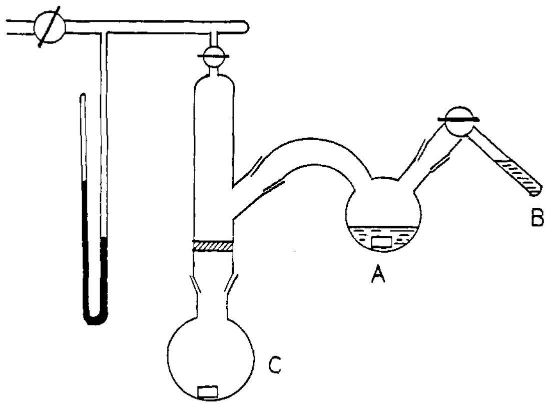

Figure 2. Apparatus for deprotonation rate measurements.

which R and/or R′ is alkyl, aryl, or arylalkyl;[6,11] it appears that almost any desired derivative can be made whose alkyne precursor, $RC\equiv CR'$, is accessible. We have noted that the reactivity of these carboranes toward NaH or KH in tetrahydrofuran (THF) varies significantly depending on the nature of the R and R′ substituents.[6,12] This property is useful in the designed synthesis of metal complexes of $R_2C_2B_4H_5^-$ ions and their subsequent fusion to give $R_4C_4B_8H_8$ clusters, since by the proper choice of R groups one can effectively stop the complexation/fusion sequence at a desired stage. In addition, these trends afford an opportunity to learn something about the relationship between structure and reactivity in this class of carboranes. Accordingly, we have determined rate constants and activation energies for the bridge deprotonation of a variety of $RR'C_2B_4H_6$ species, with B_5H_9 included to provide a non-carborane benchmark for comparison.

Experimental Section

Materials. Pentaborane(9) from a U.S. Government stockpile was used as received, and the $RR'C_2B_4H_6$ carboranes (except the diphenyl derivative) were prepared from $RC\equiv CR'$ and B_5H_9 by the method of Hosmane and Grimes[5b,c] as subsequently modified.[13] For the diphenyl compound, the reaction was conducted without Et_3N at 180 °C in a steel cylinder.[14] Details of the characterization and chemistry of the mono- and diindenylmethyl- and fluorenylmethylcarborane derivatives are given elsewhere.[12b] The dimethyl,[5a,b] diethyl,[5c] dibenzyl,[11] and bis(tricarbonylchromiumbenzyl)[6b] derivatives have been reported previously.

The carboranes employed for rate measurements were purified to 98+% (determined from ^{11}B and ^1H NMR and mass spectroscopy) either by vacuum distillation (for the Me_2 and Et_2 derivatives) or by column or plate chromatography on silica (for all others). Sodium and potassium hydride were obtained as mineral oil suspensions, and each sample used in a kinetic run was washed five times with 20-mL portions of dry *n*-hexane; following this treatment the hydrides were dry, free-flowing solids under vacuum. All solvents employed in this work were reagent grade and were thoroughly dried over molecular sieves or $LiAlH_4$ before use.

Rate Measurements. The reactions were conducted on a high-vacuum line in the apparatus shown in Figure 2, consisting of a 100-mL Pyrex reactor (A) containing a magnetic stirring bar and attached to a tipping tube (B) via a greased joint. With the metal hydride in A and a solution of the carborane in vessel B (frozen in liquid nitrogen), the entire apparatus was evacuated and dry THF was distilled into A at liquid nitrogen temperature. The carborane solution was thawed and a cold bath at the desired temperature was placed around reactor A. Following equilibration of the THF suspension in A, as determined by stabilization of the measured solvent vapor pressure (ca. 30 min), the carborane was transferred from B into the continously stirred hydride suspension in A and a stopwatch was started (time zero). The pressure of H_2, corrected for the vapor pressure of the solvent, was recorded as a function of time until all gas evolution had ceased. The volume in which H_2 was collected was adjusted to give total P_{H_2} readings greater than 20 Torr. For each carborane, the range of reaction temperatures was selected to provide rates of H_2 evolution that could be measured accurately. The reproducibility of the method was checked by duplicating several runs, which gave measured reaction rates in agreement by >92%. Tables of measured H_2 pressure versus time and plots of log *P* versus time are available as supplementary material.

At the completion of each experiment, flask A was tipped to transfer the $Na^+RR'C_2B_4H_5^-$ solution into flask C (Figure 2) through a sintered glass filter. Excess dry hydrogen chloride was added to reconvert the carborane anion in the solution to neutral $RR'C_2B_4H_6$, which was then recovered either via distillation and fractionation on the vacuum line (for volatile species) or via chromatography on silica.

Analysis of the Data. From eq 2 it is apparent that $[RR'C_2B_4H_5^-]$ is proportional to P_{H_2} at constant volume, hence the reaction rate $-d[RR'C_2B_4H_6]/dt = d[RR'C_2B_4H_5^-]/dt = d[P_{H_2}]/dt$ where P_{H_2} is the pressure of H_2 collected at time *t*. For each experiment, an Arrhenius plot of log P_{H_2} versus *t* was used to determine the first-order rate constant k_1 from the relation log $P = K_1t$ + constant. By using the linear portion of the P_{H_2} versus *t* plot (excluding the initial induction period), a best-fit line was calculated by least-squares linear regression analysis. Error analyses of the rate constant determinations, based on the deviation of points in the linear region from the calculated line, were carried out by standard statistical methods (described in the supplemental material).

For each carborane, a plot of −ln k_1 versus 1000/*T* (where *T* = reaction temperature in K) was found to be linear with a correlation coefficient (*r*) of >98%. For the entire series this yields confidence limits of >95–99%. On the basis of the relation

$$k_1 = \left(\frac{k_bT}{h}\right)e^{\Delta S^\ddagger/R}e^{(1-E_a/RT)}$$

values of E_a and $\Delta S^\ddagger$ were calculated from the slope and intercept, respectively, of each plot.

Results and Discussion

General Observations. Although the deprotonation of *nido*-2,3-$RR'C_2B_4H_6$ species can be conducted homogeneously, e.g., via reagents such as *n*-butyllithium in THF solution, it is more often carried out heterogeneously with suspensions of metal hydrides in THF. The latter procedure is usually employed in synthesis since its only byproduct is H_2 and most such reactions proceed at a convenient and controllable rate. Consequently, the present kinetic measurements were conducted with NaH or KH according to eq 2. In this work the substituent groups on carbon, R and R′, included small alkyl units, CH_2–aryl groups with aryls of varying size, and phenyl; in most cases R = R′, but a few monosubstituted species in which R′ = H were examined. For each compound, the general rate law is pseudo-first order and can be expressed as rate = $k_1[RR'C_2B_4H_6] = -k_1P_{H_2}$ in the heterogeneous system. As a check, the rates for several reactions were measured with a tenfold increase in the amount of metal hydride and found to exhibit no significant change. For certain species which interact only very slowly with NaH, KH (which is uniformly more reactive than NaH toward boranes) was used in order to produce faster rates.

These data are consistent with deprotonation occurring at the surface of the metal hydride, via attack of carborane B–H–B bridges on H^- ions in the lattice. The heterogeneous nature of the process is further evident in the fact that it can be conducted even in *n*-hexane. When the reaction in THF is conducted with sodium deuteride, the resulting $RR'C_2B_4H_5^-$ anion (R = R′ = Et; R = indenylmethyl, R′ = H) contains no measurable deuterium (as shown by mass spectral analysis of the neutral carborane produced by reprotonation of the anion). These results rule out an S_N2-type mechanism involving an $RR'C_2B_4H_6D^-$ intermediate, which would require some deuterium incorporation.

The observed rate constants (k_1) and calculated activation energies (E_a) and entropies of activation ($\Delta S^\ddagger$) are listed in Tables I and II, and plots of −ln k_1 versus 1/*T* are shown in Figures 3 and 4. Exclusive of the diphenylcarborane, the k_1 values exhibit

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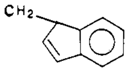
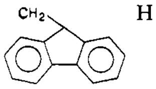
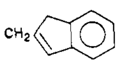
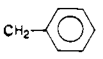
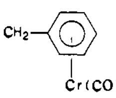
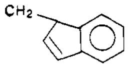
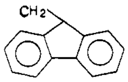
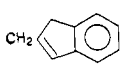
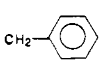
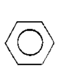
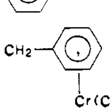
Table I. Observed k_1 (s^{-1}) × 10^{3a}

		reactions with NaH					reactions with KH					
		$T^b = 26$	$T^b = 0$	$T^b = -34$	$T^b = -54$	$T^b = -65$	$T^b = 26$	$T^b = 0$	$T^b = -23$	$T^b = -34$	$T^b = -55$	$T^b = -65$
B_5H_9				3.57 (6)	1.72 (4)	1.20 (9)						
$RR'C_2B_4H_6$												
R	R′											
CH_3	CH_3			3.21 (5)	1.45 (2)	0.71 (3)						
C_2H_5	C_2H_5		11.9 (3)^c	3.08 (1)	1.17 (1)	0.62 (7)				10.5 (2)	4.5 (2)	3.1 (2)
	H	15.4 (2)	9.8 (4)^d	2.39 (6)		0.37 (1)	30.2 (1)	13.5 (2)		5.25 (1)		1.32 (6)
	H	14.0 (2)	8.5 (3)	1.35 (1)		0.34 (1)						
	R′ = R	12.7 (6)	8.08 (9)	1.08 (3)		0.20 (1)	15 (2)		6.18 (8)	2.8 (2)		0.61 (1)
	R′ = R	12.9 (7)	8.7 (2)	1.30 (2)		0.28 (2)	30 (1)	11.2 (1)	7.74 (8)	4.27 (4)	1.66 (3)	
	R′ = R			6.0 (3)^e	0.79 (4)							
	R′ = R						12.6 (5)	4.45 (9)	0.78 (2)			

[a] Numbers in parentheses are standard deviations of the slope (S_β) for the least significant figure given. [b] Temperatures shown are ±1 °C. [c] k_1(NaD) at 0 °C = 5.1 (1) × 10^{-3} s^{-1}. [d] k_1(NaD) at 0 °C = 4.68 (8) × 10^{-3} s^{-1}. [e] k_1 at −23 °C = 17.8 (5) × 10^{-3} s^{-1}; k_1 at −38 °C = 5.4 (3) × 10^{-3} s^{-1}.

Table II. Activation Parameters, E_a (kcal mol^{-1}) and $-\Delta S^\ddagger$ (eu)^a

		E_a (NaH)	$-\Delta S^\ddagger$ (NaH)	E_a (KH)	$-\Delta S^\ddagger$ (KH)
B_5H_9		3.3 (4)	57 (2)		
$RR'C_2B_4H_6$					
R	R′				
CH_3	CH_3	4.6 (5)	52 (2)		
C_2H_5	C_2H_5	4.99 (7)	50.6 (3)	4.02 (5)	52.1 (2)
	H	5.3 (4)	50 (2)	4.2 (1)	53.2 (4)
	H	5.4 (4)	50 (2)		
	R′ = R	6.0 (5)	48 (2)	4.5 (7)	53 (2)
	R′ = R	5.6 (5)	50 (2)	4.5 (4)	52 (2)
	R′ = R	12 (1)	20 (2)		
	R′ = R			8.48 (1)	40.5 (2)

[a] Numbers in parentheses are estimated standard deviations for the least significant figure given.

a clear trend, being largest (over the temperature range studied) for R = CH_3 and C_2H_5, smaller for R = CH_2–aryl, and decreasing generally with increasing size of the aryl group (Figure 3). Over most of the temperature range, k_1 for B_5H_9 is larger than that for any carborane. This tendency can be explained primarily in terms of steric interference of the R substituents with the approach of the carborane open face to the metal hydride surface. Larger R groups would be expected to slow the reaction rate, but only moderately because their location on carborane carbon atoms is somewhat remote from the actual reaction site, i.e., the B–H–B bridge(s). This is essentially what is observed, and it supports a primarily steric rather than electronic effect of the R groups on reaction rate. Were there a major electronic effect, one would expect the replacement of CH_3 with moieties such as benzyl and indenylmethyl to produce much larger changes in k_1 than are actually found. Two compounds examined, the diphenyl and bis(tricarbonylchromiumbenzyl) derivatives, represent special cases and are discussed below.

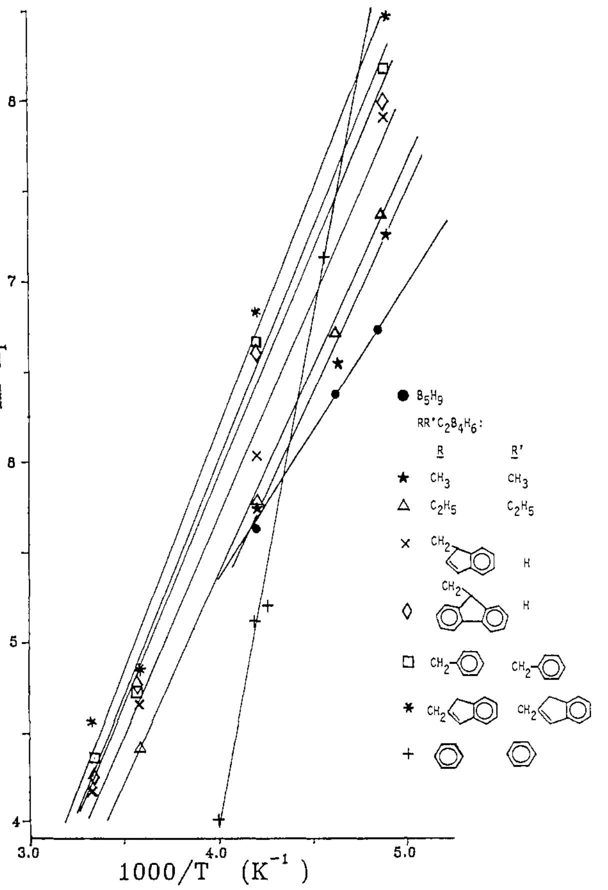


Figure 3. Arrhenius plots for reactions with NaH.

The hypothesis of a mainly steric role for the R groups is supported by the calculated E_a values, which (with the two exceptions just noted) are very similar for all the carboranes and increase only slightly with increasing size of R. The carborane

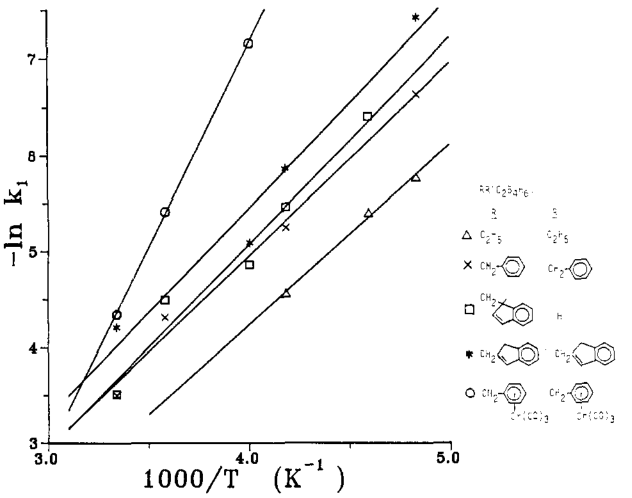


Figure 4. Arrhenius plots for reactions with KH.

entropies of activation ($\Delta S^{\ddagger}$) are also nearly the same and are strongly negative, consistent with a transition state involving a close encounter between the carborane B–H–B group and the metal hydride surface. Such an activated complex would experience a very considerable drop in entropy from that of the solvated carborane anion in solution, as observed. An apparent very slight decrease in $-\Delta S^{\ddagger}$ as R becomes larger (Table II) is not unexpected if one assumes that the carboranes with bulky R groups possess more ordered solvent spheres (lower entropy) than do those with smaller groups, and hence experience a smaller loss of entropy on complexation at the solid surface.

B_5H_9. The corresponding properties of pentaborane(9) afford some useful comparisons with the $RR'C_2B_4H_6$ carboranes. The B_5H_9 molecule exhibits a significantly lower E_a than any of the carboranes examined, which again may be a largely steric effect related to the absence of substituents on the borane and may also reflect the presence of four B–H–B sites as compared to two in the $RR'C_2B_4H_6$ carboranes. From the calculated Mulliken charges on the bridge protons in B_5H_9[15] and parent $C_2B_4H_8$[16] (0.01 and 0.018, respectively), one might expect roughly similar reactivities toward NaH, as observed; however, it has been pointed out that predictions on this basis are risky since ground-state charge distributions may differ significantly from those in the activated complex.[16] With more confidence, we observe that the relatively large negative entropy of activation for B_5H_9 (in comparison to the carboranes) extends the trend in $\Delta S^{\ddagger}$ noted above and is as expected since B_5H_9 in solution is surely a comparatively high entropy species whereas the $B_5H_9[NaH]_x$ activated complex is assumed to be similar to that of the $R_2C_2B_4H_6$ carboranes.

$[(CO)_3CrPhCH_2]_2C_2B_4H_6$. A particularly illuminating result that further supports the dominance of steric versus electronic effects in the deprotonation reaction is the low observed reaction rate and corresponding high E_a for the bis(tricarbonylchromium) complex of $(PhCH_2)_2C_2B_4H_6$. Normally, the complexation of $Cr(CO)_3$ to an aryl ring results in withdrawal of electron density from the ring with concomitant increase in the acidity of attached acid groups (e.g., COOH); consequently $Cr(CO)_3$-complexed arylcarboxylic acids are invariably stronger acids than their uncomplexed counterparts.[17] In this study the situation is exactly the reverse: complexation of the phenyl rings in $(PhCH_2)_2C_2B_4H_6$ produces a substantial *lowering* of reactivity toward metal hydrides (indeed, so much so that KH rather than NaH was required to effect a measurable rate). Given the well-established electron-withdrawing character of $Cr(CO)_3$, this would be difficult to explain via an electronic mechanism, but it is quite understandable as a consequence of the very large steric bulk of the $(CO)_3CrPhCH_2$ ligands attached to the cage. The presence of the $Cr(CO)_3$ units undoubtedly hinders the orientation of the C_2B_4 cage required for deprotonation on the hydride surface, essentially doubling the energy of activation of the uncomplexed dibenzylcarborane (8.48 versus 4.5 kcal mol^{-1}) and slowing the −23 °C reaction by an order of magnitude. Of course, electronic influence by the chromium groups may nevertheless affect the reaction rate to a small but indistinguishable extent. The coordination of one or two $Cr(CO)_3$ units to $(PhCH_2)_2C_2B_4H_6$ produces slight shielding of the ^{11}B NMR signals,[6b,12a] an effect opposite to that anticipated for electron withdrawal by chromium.[18]

$(C_6H_5)_2C_2B_4H_6$. The chemical reactivity of the diphenyl derivative, the only carborane in this study having an aryl ring directly attached to the cage, is in many respects different from those of other $RR'C_2B_4H_6$ derivatives and will be described in a full report elsewhere.[14] In the present investigation, the rate of deprotonation by NaH was found to have an extraordinarily large temperature dependence and an activation energy (12 kcal mol^{-1}) that is at least twice as large as that of any other species examined. At room temperature the reaction is extremely fast, and above ca. −40 °C the rate exceeds even that of B_5H_9 (see Figure 3). The anomalously low value of $-\Delta S^{\ddagger}$ (ca. 40% that of the other carboranes studied) can be understood on the basis that the phenyl groups have little freedom of movement, resulting in a relatively rigid structure that in turn produces a highly ordered, low-entropy solvation shell around the carborane. In other derivatives, the $-CH_2-$ "hinges" permit considerably greater motion of the attached substituents in solution and consequently a larger entropy decrease upon formation of the activated complex.

Less readily explained are the high measured E_a and very rapid reaction rate at higher temperatures for the diphenyl species. These properties imply a combination of steric inhibition of the reaction and enhancement of acidity via withdrawal of electron density from the B–H–B bridges. In our view the most likely mechanism for the latter effect is a resonance interaction (electron delocalization) between the phenyl groups and the C_2B_4 framework. Resonance interactions in organic acids typically produce higher acidity by weakening the carboxyl O–H bond; a somewhat analogous situation may well obtain in $(C_6H_5)_2C_2B_4H_6$, particularly in the region of the basal C_2B_3 rings where strong ring-current effects have been observed in NMR studies of $R_2C_2B_4H_6$ derivatives.[19] An inductive mechanism, on the other hand, would be expected to *lower* the acidity (hence the rate of deprotonation) via electron donation from the phenyls to the cage, in contrast to observation.

The rapid drop in the rate of deprotonation of $(C_6H_5)_2C_2B_4H_6$ as the temperature is lowered suggests severe stereochemical constraints on the formation of the activated complex at the metal hydride surface. It is likely that the bulky, relatively rigid phenyl rings (each larger in diameter than the carborane cage itself) restrict bridge hydrogen–metal hydride interactions to a narrow range of approach geometries. In the other derivatives, all of which contain CH_2 linking units, the effect is evidently less important since even the larger groups (e.g., indenyl) can swing out of the way and permit the basal ring of the molecule to approach the hydride surface. (The bis(chromiumbenzyl) complex presents a special case, as discussed above.) The steric role of substituents obviously becomes more significant as the temperature drops and molecular motion slows.

Summary. The general trends observed for *nido*-$RR'C_2B_4H_6$ carboranes suggest that under the conditions examined in this study, the R groups exert primarily stereochemical rather than electronic influence on the rate of deprotonation, except for the diphenyl derivative where electron withdrawal by the aryl rings promotes the acidity of the bridging protons. It is worth noting that our kinetic observations are closely paralleled by the Fe^{2+}

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complexation/fusion behavior of these same carboranes.[6,7,11,12] Thus, the more sterically hindered species, which exhibit slow deprotonation, similarly are the most sluggish toward formation of $(RR'C_2B_4H_4)_2FeH_2$ complexes and conversion of the latter to $R_2R'_2C_4B_8H_8$. Indeed, when R and R′ are both very large (e.g., indenylmethyl, fluorenylmethyl, or $(CO)_3CrPhCH_2$), fusion fails to occur at all.[12] This correlation further strengthens the rationale of a mainly steric role for the substituents in the deprotonation process.

Other aspects of the deprotonation reaction, including the consequences of B substitution on the basal ring and the kinetics of the homogeneous reactions with alkyllithium reagents, have not been addressed in this study but are worthy of investigation and may be examined in future work.

Acknowledgment. This work was supported in part by the National Science Foundation (Grant No. CHE 84-19401). We thank Henry Boyter, Jr., for the rate data on $Ph_2C_2B_4H_6$ and Professor Jack Steehler for assistance in data plotting.

Supplementary Material Available: Description of the method employed for error calculations and tables of observed P_{H_2} vs. time for deprotonation rate measurements (46 pages). Ordering information is given on any current masthead page.

Phases in the System XeF_2/XeF_5AsF_6 and Structural and Vibrational Evidence for the Following Ionization Pathway: $XeF_2 \rightarrow XeF^+ + F^-$

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Received June 1, 1987

Abstract: A fusion temperature versus composition curve has been obtained for the system XeF_2/XeF_5AsF_6. X-ray single-crystal and powder diffraction methods have been used in combination with Raman spectroscopy to characterize the various phases that are formed. The fusion temperature/composition curve indicates compound formation at XeF_2 to XeF_5AsF_6 ratios (fusion temperature in parentheses): 1:2 (89.5 °C), 2:1 (59.5 °C), and 3:1 (74.0 °C). Other simple integer combinations are also suggested at the ratios 1:1 (56.5 °C) and 3:2 (56.0 °C). The high viscosity of the 1:2 melt, at its melting point, suggests that the polymeric fluorine-bridged structure of the solid largely persists in the early liquid phase. In contrast the melts of the 1:1 and 2:1 are distinctly more mobile and probably consist of the monomeric formula unit species, which are characteristic of the crystalline phases. The deepest eutectic occurs at 49 °C, with 57 mol % XeF_2. This easily supercools to ambient temperatures. Another well-defined eutectic occurs at 56 °C with 71.0 mol % XeF_2. $XeF_2{\cdot}2(XeF_5AsF_6)$ is monoclinic, $P2_1/n$, with $a = 12.033$ (6) Å, $b = 7.024$ (4) Å, $c = 10.940$ (5) Å, $\beta = 95.43$ (5)°, $Z = 2$, and $D_x = 3.61$ g cm^{-3}. The linear symmetrical XeF_2 species [Xe–F = 2.0 (1) Å] are coordinated via their F ligands to two equivalent XeF_5^+ ions [F···Xe(VI) = 2.76 (2) Å and angle Xe(II)—F···Xe(VI) = 139.4 (6)°]. The XeF_5^+ ions are also bridge bonded to two AsF_6^- ions [Xe(VI)···F = 2.66 (1) and 2.74 (1) Å], the anion thus being coordinated to two cations, a three-dimensional polymer being thereby formed. $XeF_2{\cdot}XeF_5AsF_6$ is monoclinic, $P2_1/n$, with $a = 9.159$ (4) Å, $b = 10.158$ (5) Å, $c = 12.401$ (6) Å, $\beta = 106.66$ (5)°, $z = 4$, and $D_x = 3.51$ g cm^{-3}. The structural unit is the formula unit $XeF_2{\cdot}XeF_5AsF_6$. These units are not interconnected. The XeF_2 molecule is approximately linear [F–Xe–F = 178.1 (5)°], but the F ligand, which makes a bridge bond to the XeF_5^+, is elongated [Xe–F = 2.06 (1) Å] and the other XeF bond is appreciably shortened [Xe–F = 1.97 (1) Å]. The bridge bond to the XeF_5^+ from the XeF_2 is short [F(Xe)···Xe(VI) = 2.47 (1) Å] as is that from the AsF_6^- ion [F(As)···Xe(VI) = 2.59 (1) Å]. These two bridging F ligands are coplanar with the Xe(VI) atom and the axial fluorine of the XeF_5^+. The symmetry of the cation and its bridging ligands is roughly C_{2v}. $2XeF_2{\cdot}XeF_5AsF_6$ is monoclinic, $P2_1/a$, with $a = 12.295$ (9) Å, $b = 8.275$ (6) Å, $c = 13.455$ (7) Å, $\beta = 95.67$ (4)°, $z = 4$, and $D_x = 3.67$ g cm^{-3}. As in the 1:1 compound, the formula unit is the structural unit and these units are not interconnected. The XeF_2 molecules are again nearly linear [F–Xe–F = 177 (1) and 179 (1)°] and the Xe–F bond involving F bridging to the cation is in each case elongated [F···Xe(VI) = 2.05 (1) Å for each] and the nonbridging Xe–F is shortened slightly [1.99 (1) and 2.01 (1) Å]. These XeF_2 interactions with XeF_5^+ are evidently weaker than in the 1:1 compound, the F(Xe)···Xe(VI) bridging distances in this case being 2.53 (1) and 2.54 (1) Å. The bridging F ligands from the two attached XeF_2 molecules are coplanar with the axial Xe–F unit of the cation. This indicates that the closest F ligand of the AsF_6^- to the XeF_5^+, at 2.94 (1) Å, is interacting only weakly with the cation. Differences in the coordination number of the XeF_5^+ cation in these complexes account for the polymeric or nonpolymeric nature of the complexes. Such differences are determined by the extent of ionization of the XeF_2 species. The observed, essentially linear, distortions of XeF_2 are interpreted as points on the ionization pathway $XeF_2 \rightarrow XeF^+ + F^-$. From the force constants, and associated interatomic distances, the isolated XeF^+ ion is predicted to have a bond length of ~1.92 Å and a force constant of ≤4.48 mdyn/Å.

From theoretical considerations Jortner, Rice, and Wilson in 1963 concluded[2] that the bond ionicity in xenon difluoride was approximately $F^{-0.5}$–Xe^{1+}–$F^{-0.5}$ and on this basis they predicted that the enthalpy of sublimation, ΔH°_{sub}, should be 13.3 kcal mol^{-1}. This derived largely from the lattice energy contributed by the semi-ionic lattice. Subsequently Schreiner and his co-workers[3] determined the sublimation enthalpy by experiment and found $\Delta H^\circ_{sub} = 13.2 \pm 0.2$ kcal mol^{-1}. This gave striking support for the proposed high bond polarity in the molecule. Similar high

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