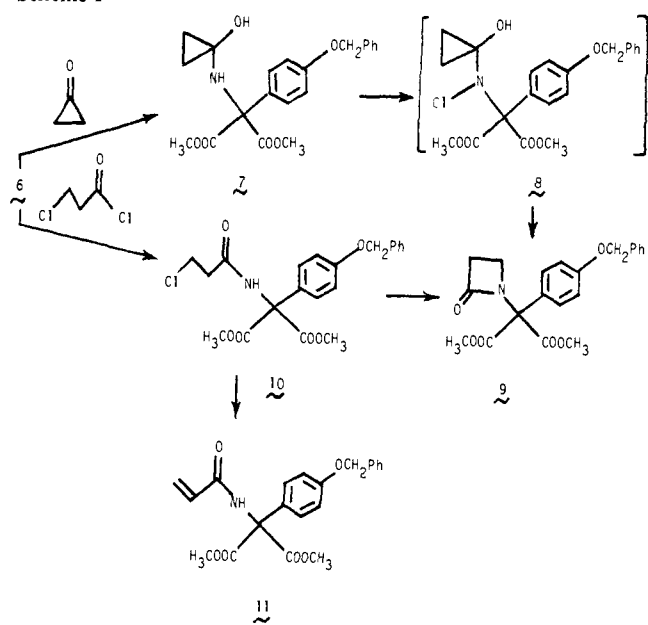
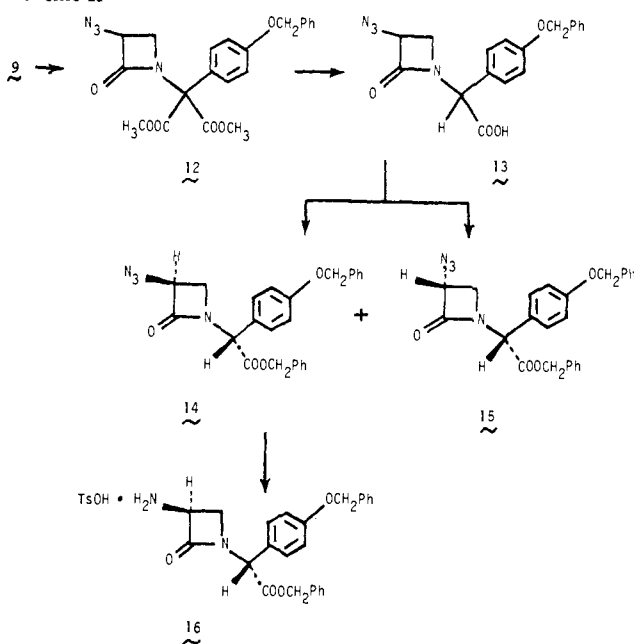


Scheme I



Scheme II



II). Thus, formation of the anion at the 3 position of the β -lactam with LDA in THF (-78°C , 2 h) was followed by treatment with *p*-toluenesulfonyl azide and then trimethylsilyl chloride affording the 3-azido lactam **12** (80%). Hydrolysis of **12** with 1 N NaOH in methanol (0°C , 4 h), followed by acidification to pH 2 with 1 N HCl, resulted in decarboxylation with the formation of **13** as a 1:1 mixture of diastereomers (70%). Treatment of the mixture with benzyl bromide and triethylamine in acetonitrile (reflux, 6 h) gave the benzyl esters **14**¹³ and **15**¹⁴ (80%). The diastereomers were separated at this stage using a Waters Prep LC/System 500 liquid chromatograph,¹⁵ and each isomer was reduced with hydrogen sulfide (Et_3N , CH_2Cl_2 , 25°C , 15 min).¹⁶ In this way, the amine tosylate **16** and its epimer were separately isolated (70%). Comparison of **16** and its epimer with an authentic sample¹⁷ showed **16** to be identical (IR, NMR, and TLC behavior) with the chiral product synthesized by the Lilly group.^{3a} Additional quantities of the desired benzyl ester **14** could be obtained by equilibration of **15** with potassium *tert*-butoxide (*tert*-butyl alcohol, THF, 0°C , 2 h) whereby a 1:1 mixture of **14** and **15**

was formed in quantitative yield. The final conversion of the dibenzylamine tosylate **16** to 3-ANA by reduction has already been reported,^{3a} as has the introduction of the side chain at position 3. Our preparation of the dibenzyl 3-ANA tosylate salt **16** thus constitutes a formal total synthesis of (\pm)-nocaridicin A.¹⁸

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- (8) IR (CHCl_3) 3400 , 1740 , 1680 , 1500 cm^{-1} ; NMR (CDCl_3) δ 2.73 (t, $J = 6\text{ Hz}$, 2 H), 3.76 (m, 8 H), 5.04 (s, 2 H), 6.94 (d, $J = 9\text{ Hz}$, 2 H), 7.2-7.5 (m) and 7.53 (d, $J = 9\text{ Hz}$) (8 H); mass spectrum m/e 419 (M^+).
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- (14) IR (CHCl_3) 2120 , 1760 , 1740 cm^{-1} ; NMR (CDCl_3) δ 3.36 (apparent t, $J = 6\text{ Hz}$, 1 H), 3.57 (dd, $J = 3$, $J = 6\text{ Hz}$, 1 H), 4.47 (dd, $J = 3$, $J = 5\text{ Hz}$, 1 H), 5.05 (s, 2 H), 5.21 (s, 2 H), 5.58 (s, 1 H), 6.94 (d, $J = 9\text{ Hz}$, 2 H), 7.12 (d, $J = 9\text{ Hz}$, 2 H), 7.26-7.42 (m, 10 H); mass spectrum m/e 414 ($\text{M}^+ - 28$).
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- (17) Provided by Dr. G. A. Koppel, The Lilly Research Laboratories, Eli Lilly and Co.
- (18) Yields given in this synthesis are for pure isolated products having satisfactory spectroscopic properties and elemental analyses.

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Classical Configurations Associated with Nonclassical Molecules: Three Carboranes as Examples

Sir:

The boranes and carboranes, two well-known classes of "nonclassical" molecules, have been the subject of extensive

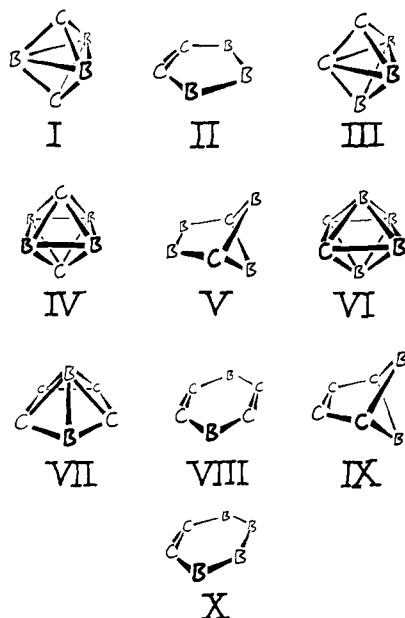


Figure 1. Possible isomers of $C_2B_3H_5$, $C_2B_4H_6$, and $C_4B_2H_6$. Structures I, III, IV, VI, and VII are structural representations only, while structures II, V, VIII, IX, and X represent idealized valence structures (see text). The hydrogen atoms have been omitted for clarity.

experimental and theoretical investigation.¹ The characteristic feature common to the bonding of these types of molecules is the consistent utilization of all four boron valence orbitals, while boron, of course, can contribute only three valence electrons. This "electron deficiency", or equivalently "orbital overabundance", is the major reason that boron chemistry is dominated by polyhedra and polyhedral fragments. In this communication, we present a theoretical study of the relative stabilities of several classical structures, possessing formal orbital vacancies, associated with three well-known nonclassical molecules: $C_2B_3H_5$, $C_2B_4H_6$, and $C_4B_2H_6$. We show that in each case classical structures may be postulated that are comparable in energy with their nonclassical counterparts and are plausible as intermediates in rearrangements or as preferred structures for B-substituted derivatives with electron-rich groups.

The theoretical methods used to determine the energies of the final optimized structures were molecular orbital calculations in the approximation of partial retention of diatomic differential overlap (PRDDO),² in one case with configuration interaction (CI) corrections, and ab initio 4-31G calculations.³ All of the molecular structures reported in Figure 1 were fully optimized at the PRDDO level except for the C—H and B—H bond lengths, which were held constant at standard values of 2.06 and 2.249 au, respectively.

For $C_2B_3H_5$, we find that isomers II and III are 37 and 50 kcal/mol higher in energy relative to structure I at the 4-31G level (see Table I). All three of these structures lie in local energy wells. Thus, the classical ring structure II is predicted to be slightly more stable than the polyhedral structure III, although correlation corrections not included in this calculation are expected to favor III. Certainly II is a plausible intermediate in the synthesis of I or III from acetylene and various small boranes.⁴⁻⁷ Although the NMR data for a dimethyl derivative of $C_2B_3H_5$ ⁷ and the fact that two distinct C,3,4,5-tetramethyl compounds have been reported⁸ make it seem probable that these carboranes possess 1,2-trigonal-bipyramidal structures, planar configurations similar to II must be considered as possible structures for derivatives of $C_2B_3H_5$, especially those bearing electron-donating substituents (see below).

Remarkably, 4-31G calculations on the $C_2B_4H_6$ compounds

Table I. Relative Energies in Kilocalories/Mole

structure	no.	PRDDO	4-31G
$C_2B_3H_5$	I	0	0
	II	+48	+37
	III	+54	+50
B-fluoro $C_2H_2B_3F_3$	I	0	
	II	+2	
	III	+71	
$C_2B_4H_6$	IV	+20 ^a	+6
	V	0	0
	VI	+31	
B-fluoro $C_2H_2B_4F_4$	IV	+134	
	V	0	
	VI	+130	
$C_4B_2H_6$	VII	0	
	VIII	+9	
	IX	+30	
B-fluoro $C_4H_4B_2F_2$	VII	+43	
	VIII	0	
	IX	+2	

^a CI corrections yield IV 2 kcal/mol lower in energy relative to V.

predict V to be 6 kcal/mol more stable than the experimentally observed structure IV.⁹ PRDDO predicts a corresponding 20-kcal/mol gap. The classical structure V is essentially identical with the lowest energy configuration for $C_2B_4H_6$ found in a recent MNDO study.¹⁰ We find that the correct energy ordering is obtained only after correlation corrections are added. An independent electron pair CI correction to the PRDDO energy, including all double excitations into the virtual space of the localized framework orbitals, yielded a CI correction to the total energy of structure IV relative to V of 22 kcal/mol and placed IV \sim 2 kcal/mol lower in energy than V. The unexpected stability of V relative to IV led us to reinvestigate the thermal interconversion of 1,2- $C_2B_4H_6$ (VI) to 1,6- $C_2B_4H_6$ (IV). Orthogonally optimized quadratic synchronous transits¹¹ from the known isomers IV and VI to V yielded nearly identical 30-kcal/mol maximum energy barriers for rearrangement to structure V at the PRDDO level without CI corrections. Our analysis clearly shows that the true stable intermediate in the rearrangement is V and not a distorted trigonal prism as was originally thought.¹²

PRDDO calculations on isomers of $C_4B_2H_6$ predict VII to be 9 kcal/mol more stable than VIII and 30 kcal/mol more stable than IX. The surprising relative stability of VIII may be rationalized by the fact that the formally vacant boron p orbitals perpendicular to the molecular plane are partially populated (by \sim 0.17 electrons) through π -electron delocalization. This delocalization effect operates to a lesser extent in the planar $C_2B_3H_5$ isomer (II), where the boron p orbitals adjacent to the C=C bond are partially occupied (0.13 electrons), but the corresponding orbital of the nonadjacent boron is nearly vacant (0.03 electrons). The complete vacancy of the nonadjacent boron p orbitals of hypothetical structures such as X helps to explain why planar isomers of $C_2B_4H_6$ were found to be energetically unfavorable relative to the other geometries considered.

The existence of formally vacant orbitals in the classical structures suggests that placing electron-rich substituents on boron should stabilize these structures. To test this hypothesis, we have performed PRDDO calculations on the B-fluoro derivatives of compounds I-IX using the optimized unsubstituted carborane geometries, but replacing B—H bonds by B—F bonds with an assumed standard length of 2.495 au. The dramatic effect of fluorine substitution may be seen by examining the relative energies in Table I. The classical $C_2H_2B_3F_3$ structure (II) is now only 2 kcal/mol higher in energy than the fluorinated derivative of I, while the planar structure VIII

becomes the most stable $C_4H_4B_2F_2$ isomer by 2 kcal/mol and is the molecule observed experimentally.¹³ The classical structure V is also found to be greatly stabilized relative to the nonclassical structures IV and VI upon B-fluorination.

The probable existence of energetically competitive classical structures for these small carboranes suggests, and the study of the 1,2- $C_2B_4H_6$ to 1,6- $C_2B_4H_6$ rearrangement confirms, that reactions of nonclassical molecules may involve classical intermediates. While the importance of vacant orbital structures in the correct topological description of electron-deficient molecules has been previously recognized,^{14,15} our results suggest that such structures, whether purely classical (as in the small molecules studied here) or quasi-classical (involving only one or two vacant orbitals in a large nonclassical molecule), may be even more important as intermediates in reactions and rearrangements.^{16,18}

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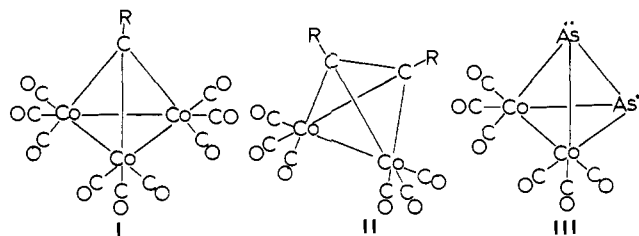
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Arsaacetylenes, $RC\equiv As$, as Ligands in Dicobalt Hexacarbonyl Complexes: Novel Main Group Element-Transition Metal Hybrid Cluster Compounds

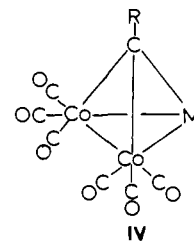
Sir:

The alkylidynetricobalt nonacarbonyl complexes, I,¹ and the related acetylenedicobalt hexacarbonyls,² which also have a cluster structure,³ II, have a well-developed chemistry. The former and, to a lesser extent, the latter show remarkable

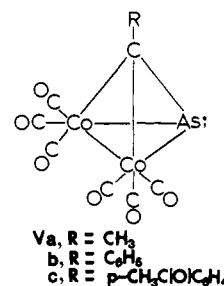
thermal and oxidative stability, compared with simple cobalt alkyls, e.g., $RCo(CO)_4$.⁴ Also known are tetrahedral cluster complexes which contain triply bridging silicon,⁵ germanium,⁶ phosphorus,⁷ arsenic,⁸ sulfur,⁹ selenium,¹⁰ boron,¹¹ and aluminum¹² in place of the RC group of I. Arsenic and phosphorus analogues of the acetylenedicobalt hexacarbonyl complexes also have been described,^{7,13} and the diarsenic compound was shown to have structure III.¹³ However, organometallic clus-



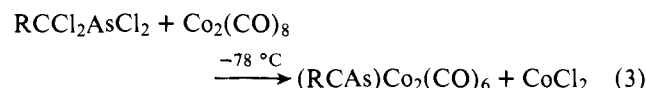
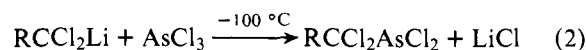
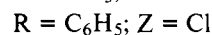
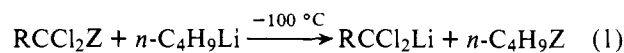
ters containing both a transition metal and a main group element in addition to the carbon function, e.g., IV, have not been



reported to date. The preparation of such complexes, a comparison of their reactivity with that of analogues of I, II, and III, and a study of their thermal and chemical decomposition with the aim of releasing and trapping an $RC\equiv M$ intermediate would be of considerable interest, and we have initiated such investigations. We report here our studies of such complexes which contain carbon, arsenic, and cobalt in the tetrahedral cluster, V.



Complexes of type $RCCO_3(CO)_9$ are prepared by the reaction of a substituted trihalomethane, RCX_3 , with dicobalt octacarbonyl,¹ while the reaction of arsenic trichloride with dicobalt octacarbonyl gives III.¹³ Our route to Va and Vb utilizes intermediates in which the C-As bond already is present, as shown in eq 1-3. The preparation of $(CH_3CA_s)Co_2(CO)_6$ is described to illustrate the procedure used.



1,1-Dichloroethyl lithium was prepared at $-100^\circ C$ in 4:1:1 THF/Et₂O/pentane using our published procedure.¹⁴ This