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Supplementary Material Available: A listing of the anisotropic thermal parameters and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Kinetics of the Protodestannylation of Vinyltrialkyltins and Substituted Vinyltrialkyltins

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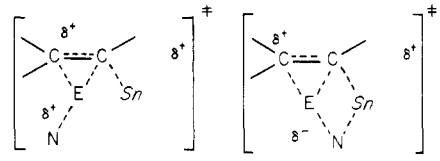
Results of a kinetic study of the protodestannylation of a number of vinyltrialkyltins and substituted vinyltrialkyltins by hydrogen chloride in methanol–water are reported. The relative rate constants are consistent with a steric sequence and open transition state. Substitution of a methyl group or phenyl group on the β-carbon leads to rate enhancement but in lesser magnitude than in the iodostannylation reaction. The effect of the concentration of water in methanol has been studied. Triphenylvinyltin underwent reaction with 2,4-dinitrobenzenesulfenyl chloride with the result that a tin–phenyl bond was cleaved.

Introduction

Electrophilic substitution involving cleavage of a carbon–metal bond has been studied in a number of systems. The favorite metal leaving groups have been those of group 4 and mercury while the carbon substrates have included alkyl, aryl, allyl, allenyl, and vinyl. Electrophilic agents have been bromine, iodine, mercuric halides, and the proton.[1] The order of substrate reactivity when the metal is tin has been shown to be allyl > allenyl > phenyl > vinyl > alkyl.[2,3]

Mechanistically the reaction can be described as S_E2 (S_E2' when the substrate is allyl[2] or a combination when the substrate is allenyl[3]), and the major point of discussion is the structure of the transition state. Since each electrophile carries with it one or more atoms with unshared pairs of electrons, the possibility exists for these atoms to provide nucleophilic assistance to the departing metal. Concomitant is the question of where the transition state lies on the reaction coordinate. An early transition state would presumably not involve significant nucleophilic assistance since not much charge is localized on the metal while a later transition state could involve nucleophilic assistance provided either by the attacking agent or by the solvent. Baekelmans et al.[4] and Abraham et al.[5] have described the two limiting cases as an open transition state (I) and a closed transition state (II).[6] It should be noted that the open transition state (I) does not preclude nucleophilic assistance from an appropriate solvent.[2]



I II

In vinylmetallic, allylmetallic, and allenylmetallic systems, the situation is more complicated in that the electrophile probably attacks the π electrons of the double bond. This suggests that the β-carbon of the vinylmetallic system will develop some positive charge in the transition state as the bond to the α-carbon is being formed.[6] Thus the electrophile may be coordinated to both carbons of the vinyl group. In studies of this system, Nesmeyanov et al.[7] and Beletskaya and Reutov[8] favor closed three-center and four-center transition states to account for retention of configuration in halo- and protodemercuration of vinylmercurials in dioxane, methanol, and DMF. Baekelmans et al.[4] suggests an open transition state for iododemetalation of a series of vinyltin compounds in methanol. Their conclusion was based primarily on a large positive salt effect. Also Gupta and Majee[9] report quantum mechanical calculations by the Del Re method which

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(6) This transition state may lead to an intermediate with a tetrahedral carbon at the site of substitution and a full positive charge on the β-carbon. See ref 10.
(7) Nesmeyanov, A. N.; Borisov, A. E. *Tetrahedron* **1957**, *1*, 158.
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Table I. Second-Order Rate Constants and Activation Parameters for the Protodestannylation of Vinyltins and Substituted Vinyltins

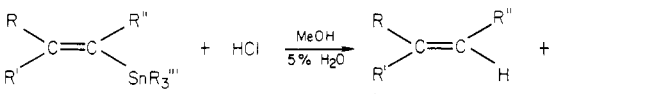
compds	k_2,[a] M^{-1} s^{-1} 25.0 ± 0.1 °C	35.0 ± 0.1 °C	45.0 ± 0.1 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal mol^{-1} deg
1, CH_2=CHSnMe_3	0.005 26	0.0118	0.0234	12.9	−26.0
2, CH_2=CHSnEt_3	0.003 53	0.008 04	0.0163	13.2	−25.6
3, CH_2=CHSn-*n*-Pr_3	0.001 48	0.003 39	0.008 23	14.9	−21.6
4, CH_2=CHSn-*n*-Bu_3	0.001 48	0.003 57	0.008 38	15.1	−21.0
5, (*E*)-CH_3CH=CHSnMe_3	0.152	0.302		11.8	−22.9
6, (*Z*)-CH_3CH=CHSnMe_3	0.108	0.222	0.368	10.5	−27.8
7, CH_2=C(CH_3)SnMe_3	0.003 13				
8, (*E*)-C_6H_5CH=CHSn-*n*-Bu_3	0.0861	0.211	0.327	11.5	−25.0
9,[b] (CH_2=CH)$_2$Sn-*n*-Bu_2	0.000 640	0.001 53	0.004 56	17.2	−15.8
10,[b] (CH_2=CH)$_4$Sn		0.000 440	0.001 10	15.9	−22.6

[a] Values for k_2 are the mean of at least three determinations which agree to within ±3%. [Sn] = 1.00 × 10^{-3} M; [HCl] = 50.0 × 10^{-3} M; [H_2O] = 5% in MeOH. [b] Experimental rate constants for **9** and **10** reduced by 2 and 4, respectively, to account for the statistical factor.

suggest an open transition state based on the substituent effects found by Baekelmans.[4]

In a recent report, Eaborn and co-workers[10] propose a two-step mechanism for the protodestannylation of a series of (β-styryl)trimethyltins. The initial rate determining step involves addition of a proton at the carbon bearing the tin group to give a carbenium ion which then goes on in a second step to lose the tin group. The intermediacy of the carbenium ion is based on the correlation with σ^+ constants although the ρ value was quite small (−1.1).

We report the protodestannylation of a series of vinyltin compounds in methanol–5% water. The reaction, as shown below, was studied kinetically, and activation parameters were obtained from the rate data at 25, 35, and 45 °C. The stereochemistry of the reaction was shown to be retention of configuration for one substrate, and the effect of the concentration of water on the rate was determined (eq 1).



$R_3'''SnCl$ (1)

Results

The compounds included in this study were synthesized by reaction of the appropriate olefinic Grignard reagent or lithium reagent with a trialkyltin chloride or by addition of trialkyltin hydride to a substituted acetylene. The stereochemistry of the (*Z*)- and (*E*)-propenyltrimethyltins and the (*E*)-(β-styryl)tributyltin was determined by IR and NMR spectroscopy, and the spectra corresponded to those previously reported by Seyferth et al.[11]

The kinetic studies were carried out by taking advantage of the ultraviolet spectra of the unsaturated tin compounds. All of the compounds possessed a broad and intense absorption at about 190–200 nm which is associated with the C=C—Sn system. Beer–Lambert law plots showed the concentration dependency of this absorption. When the diminution of this absorption on the shoulder at 225 nm was observed, as a function of time, satisfactory second-order and pseudo-first-order (excess electrophile) rate plots were obtained through at least 3 half-lives for the reaction. The rate constants agreed to ±3%. The concentration of tin compound was approximately 10^{-3} M, and for most compounds the concentration of HCl was varied from stoichiometric to 50-fold excess. The composition of the solvent system, methanol–water, had a significant effect on the value of the second-order rate constant and will be discussed below. Rate constants were obtained at three temperatures (25, 35, and 45 °C) for most compounds and enthalpies and entropies of activation calculated by computer least-squares techniques. The errors in the values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were no greater than 10 percent as indicated by the standard deviation of the slopes of the lines. The products of the reactions were determined by sweeping reaction mixtures with nitrogen and collecting the products in a liquid-nitrogen trap. Ethylene and propylene were characterized by IR spectroscopy. In the case of styryltributyltin, sodium fluoride was added to the system after reaction and the tributyltin fluoride filtered and characterized by melting point.

Table I lists the second-order rate constants at each of three temperatures and the corresponding activation parameters. Comparison of the k_2 value for **1** with second-order rate constants for the reaction of **1** with iodine in methanol (306 M^{-1} s^{-1})[4] and mercuric chloride in methanol (660 M^{-1} s^{-1})[12] shows that the HCl–methanol system is much less reactive. A similar decrease in reactivity for allyltins with HCl in methanol[2] compared to I_2 or mercuric chloride in methanol[12] has been reported. A qualitative explanation for the decreased reactivity of the solvated proton as an electrophile in these systems is that the proton is a "hard" acid while iodine and mercuric chloride are "soft" acids. The electrophile attacks the "soft" electrons of the olefinic tin compounds and allyltin compounds.

The rate constants for **1–4** show the effect of alkyl substitution on tin. The order of reactivity is Me > Et > *n*-Pr ≈ *n*-Bu, which is characteristic of the steric sequence of Abraham and Hill.[13] However, it should be noted that this steric sequence is somewhat compressed compared to the reported tetralkyltin sequences, Me (100), Et (67.1), *n*-Pr (28.1), *n*-Bu (28.1) compared to Me (100), Et (12), *n*-Pr (1.5), Bu (0.6), *i*-Pr (0.06)[14,15] and Me (100), Et (0.81), *n*-Pr (0.13), *n*-Bu (0.14), *i*-Pr (10^{-5}),[16] and also somewhat different from that reported by Baekelmans et al,[4] Me (100), Et (109), *n*-Pr (53.6), *i*-Pr (16.0).

Focusing on the rate constants for **1**, **4**, and **5–8** the effect of substitution on the vinyl skeleton can be seen. At 25

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Table II. Effect of Water Concentration on the Rate of Protodestannylation of Tributylvinyltin

$[H_2O]$ in MeOH, mol/L	k_2, M^{-1} s^{-1} (at 25.0 °C)	$[H_2O]$ in MeOH, mol/L	k_2, M^{-1} s^{-1} (at 25.0 °C)
0.55	0.004 25	2.78[a]	0.001 48
1.10	0.002 68	3.33	0.001 41
1.67	0.002 07	3.89	0.001 39
2.22	0.001 77		

[a] This concentration corresponds to 5% water and is the solvent used in kinetic studies.

°C substitution of a methyl group on the β-carbon increases the reactivity by a factor of about 30 when the methyl group is trans to the tin and by about 20 when the methyl group is cis to the tin.[17] Substitution of a phenyl group is even more effective in increasing the reactivity (×60) when it is β and trans to the tin and the leaving group is tributyltin (entries 4 and 7). Finally, the substitution of a methyl group on the α-carbon decreases the reactivity by a factor of about 2. Baekelmans et al.[4,18] report similar effects for the iododestannylation of substituted vinyltins. However, as with the relative reactivities of the steric sequence discussed above, the difference in reactivity is not as large when the solvated proton is the electrophile.

Finally, the rate constants for compounds 4, 9, and 10 at 35 °C show the decrease in reactivity caused by substitution of vinyl groups for butyl groups on tin. One substitution decreases the reactivity by a factor of 2 while complete substitution leads to an eightfold decrease. The latter change is very similar to that reported by Baekelmans.[4]

The stereochemistry of the reaction was investigated for one substrate by carrying out the reaction of (*E*)-(β-styryl)trimethyltin (11) with DCl in CD_3OD in an NMR tube. The spectrum of the product showed only 18-Hz coupling expected for trans protons in (*E*)-2-phenylethene-*1-d*,[19] indicating that the electrophilic substitution in this case took place with retention of configuration. The product was checked for isomerization stability under the reaction conditions. Also if isomerization did take place, it would not be expected to yield pure *E* isomer but rather a mixture containing substantial amounts of the *Z* isomer. This work further substantiates the previous reports that bimolecular electrophilic substitution for tin at a vinylic carbon takes place with retention of configuration.[4,20]

Verdone et al.[21] have reported that variations in the concentration of water in methanol lead to large changes in the second-order rate constants for the protodestannylation of allyltins. They interpret the phenomenon on the basis of the greater ability of the methyloxonium ion as a proton-transfer agent than the hydronium ion. An increase in the concentration of water shifts the equilibrium in eq 2 toward the less reactive electrophile.

$$MeOH_2^+ + H_2O \rightleftharpoons MeOH + H_3O^+ \qquad (2)$$

(17) The greater reactivity in electrophilic substitution of trans isomers compared to cis isomers has been noted previously. See ref 4 for reference to previously reported examples.

(18) This work confirms the assumption by Baekelmans et al.[4] that an α-methyl group decreases the reactivity about the same as an α-ethyl group. See ref 4, footnote *a*, to Table II.

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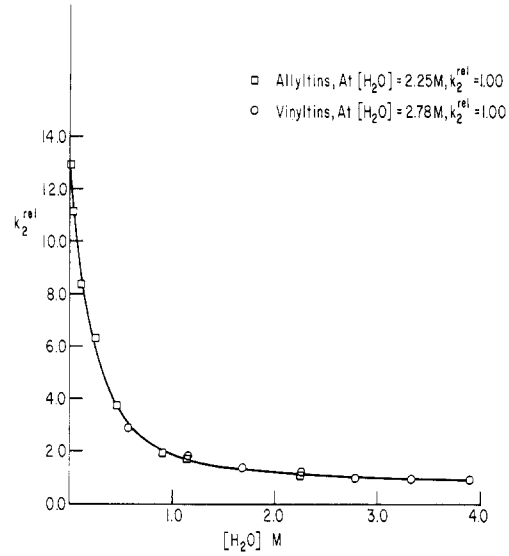
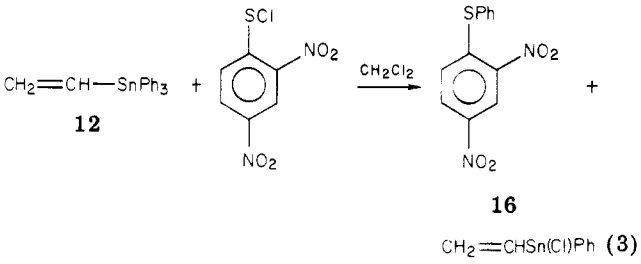


Figure 1. Effect of molar concentration of water on the relative rates of protodestannylation.

We have studied the effect of changes in the concentration of water on the rate of protodestannylation of tributylvinyltin (4) and find a similar effect on the magnitude of the second-order rate constant. The data are given in Table II, and Figure 1 shows a plot of relative rate constants for allyltrimethyltin and 4 as a function of water concentration.

2,4-Dinitrobenzenesulfenyl chloride has not been used extensively as an electrophile for the cleavage of carbon–metal bonds. Its utility, however, lies in the fact that the organic group cleaved from the metal is easily characterized as the corresponding thioether. It has been reported that changes in the nature of the electrophile or changes in the solvent[11] can alter the order of reactivity of groups attached to the metal. The reaction, shown in eq 3, between triphenylvinyltin (12), indicates that a phenyl group is more



(3)

reactive than a vinyl group with this electrophile. The diaryl sulfide was the only dinitrophenylthio product found and was characterized by melting point and IR spectroscopy.

Three additional vinyltin compounds were studied: divinyltin dichloride (13), vinyltin trichloride (14), and perfluorovinyltributyltin (15). Each of the compounds exhibited the intense absorption at about 200 nm, and thus we employed the usual diminution in absorbance technique to follow the cleavage reaction with HCl in MeOH–5% H_2O at 25 °C. No change in absorbance was observed over periods of 66 h for 13, 18 h for 14, and 90 h for 15. This suggests that the olefinic carbon–tin bond remains unbroken under these conditions. In the case of 15, this result is surprising in view of the reactivity of perfluorovinyltins with gaseous hydrogen bromide and other electrophiles.[22]

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To further explore the low reactivity, bromine in methanol and also in acetonitrile was allowed to react with **14**. Although no products were isolated, the NMR spectrum of the reaction mixture indicated only addition of bromine to the double bond.

$$CH_2{=}CHSnCl_3 + Br_2 \xrightarrow[\text{or } CH_3CN]{MeOH} CH_2Br{-}CHBrSnCl_3 \quad (4)$$

Discussion

The results presented above suggest that protodestannylation at an olefinic carbon passes through an open type transition state of the type proposed by Baekelmans et al.[4] A major difference between the transition state of this system and that of iododestannylation seems to be the amount of positive charge located on the β-carbon. Rate enhancement due to stabilization of β-methyl groups is not as evident in these reactions (*trans*-CH_3, ×30, *cis*-CH_3, ×20 vs. *trans*-CH_3, ×340, *cis*-CH_3, ×110). Even more conclusive is the fact that a *trans*-β-phenyl group is only twice as activating as the methyl group. If there was a substantial positive charge on the β-carbon, the phenyl group should exert a far greater effect.

It follows that if the magnitude of positive charge on the β-carbon is diminished, then more positive charge must be stabilized on tin. This stabilization can arise from electron donation from the solvent or an extended solvated electrophile. The effect of water on the rate constants noted above suggests that at 5% water, the proton is solvated primarily by water rather than methanol.

The activation parameters provide evidence for solvent participation in the transition state. As noted for protodestannylation of a series of trialkylallyltins in which the size of the alkyl groups increased, the effect on the rate was a small decrease as size increased.[2] The similarity in rates was due to compensating increases in enthalpy and entropy of activation. A similar compensating effect in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is seen here although the differences, especially in $\Delta S^{\ddagger}$, are even smaller. An increase in electron-donating ability by the alkyl groups on tin decreases both the need for and space for stabilization of the transition state by the solvent acting as a Lewis base. The activation parameters for compounds **1–4** fall into two groups instead of showing a continuous change. The electron-donating ability of propyl in compound **3** should not be much different from ethyl in compound **2**, but the increased size becomes significant.

The same phenomenon can be seen in comparing the activation parameters for compounds **4**, **9**, and **10**. Substitution of vinyl groups for butyl groups decreases the extent of electron donation such that the major contribution to the decreased reactivity is in the enthalpy term.

Experimental Section

Syntheses. Compounds **1–4**, **11**, **12**, **14**, and **15** were synthesized from the vinyl Grignard reagent and the appropriate trialkyltin halide.[22-24] They were purified by distillation and checked for purity by gas chromatography. Structures were verified by boiling point and IR and NMR spectroscopy. Compounds **5**, **6**, and **7** were prepared from the appropriate propenyllithium compound and trimethyltin chloride.[11a] *Z* and *E* isomers (**5** and **6**) were separated by gas chromatography on a 9-ft, 17% XF-1150 on Chromosorb P column. Compounds **8** and **11** were prepared by the addition of the appropriate trialkyltin hydride to phenylacetylene.[25] Compound **14** was prepared by symmetrization of dichlorodivinyltin and tin tetrachloride.[26] Compounds **9**, **10**, and **13** were gifts from M & T Corp. They were redistilled, checked for purity by gas chromatography, and characterized by IR and NMR before use. Table III lists boiling point and ^{1}H NMR data for the substrates.

Table III. Physical and ^{1}H NMR Data[a] for Vinyltin Substrates

compd	bp °C	^{1}H NMR (neat, ppm, Me_4Si)	*J*, Hz
1	97–99	0.11 (9 H)	$^{117/119}$Sn-CH 53/55
		5.29–6.70 (3 H)	
2	66–68 (14 torr)	0.51–1.44 (15 H)	
		5.39–6.73 (3 H)	
3	101 (19 torr)	0.67–1.87 (21 H)	
		5.34–6.73 (3 H)	
4	82 (0.4 torr)	0.57–1.71 (27 H)	
		5.28–6.66 (3 H)	
5	124–126[b]	0.04 (9 H)	$^{117/119}$Sn-CH 54/56
		1.80 (3 H)	
		5.92 (2 H)	
6	124–126[b]	0.15 (9 H)	$^{117/119}$Sn-CH 52/54
		1.76 (3 H)	CH_3-CH 6.5
		5.75 (1 H)	CH_3-C=CH 1.0
		6.50 (1 H)	CH=CH 12
7	115–117	0.05 (9 H)	$^{117/119}$Sn-CH 53/55
		1.12 (3 H)	
		4.94 (1 H)	
		5.47 (1 H)	CH_2=C <1
8	160–164 (0.5 torr)[c]	0.3–1.7 (27 H)	
		6.7 (2 H)	CH=CH <1
		7.1–7.5 (5 H)	
9	114–116 (15 torr)	0.71–1.85 (18 H)	
		5.46–6.73 (6 H)	
10	61–62 (20 torr)	5.54–6.77	
11	125–131 (12 torr)[c]	0.14 (9 H)	$^{117/119}$Sn-CH 53/55
		6.75 (2 H)	CH=CH <1
		7.0–7.5 (5 H)	
12	36.5–38[d]	5.64–6.80 (3 H)[e]	
		7.03–7.68 (15 H)	
13	81–83 (15 torr)	5.94–7.00	
14	61–63.5 (17 torr)	6.13–7.02	
15	91–92 (0.8 torr)		

[a] ^{1}H NMR recorded on Perkin-Elmer R-24 or Varian A60 spectrometers. [b] See Experimental Section for separation of **5** and **6**. [c] Separated from the *Z* isomer by preparative GLC on 10-ft, 10%, SE-30 on Chromosorb W column. [d] Melting point (uncorrected). [e] ^{1}H NMR spectrum run in CCl_4.

Kinetic Procedure. All glassware was thoroughly cleaned by soaking overnight in concentrated nitric acid, rinsed ten times with distilled water and three times with methanol, and dried in an oven at 60 °C. Solutions of tin compounds in methanol,

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standardized hydrochloric acid in methanol, and methanol-deionized water (to bring the final water concentration to 5%) were thermostated prior to mixing. After the reaction solution was mixed, it was transferred to a cuvette and the absorbance read as a function of time in a Beckman DU-Gilford with a thermostated cell compartment. Most substrates were run under second-order conditions (nearly equal concentrations of tin compound and acid in the range of 10^{-3} M) at least at one temperature and also under pseudo-first-order conditions with a 50-fold excess of acid. Second-order rate constants and activation parameters were obtained from a standard least-squares plot.

Reaction of Triphenylvinyltin (12) with 2,4-Dinitrobenzenesulfenyl Chloride. A solution of 0.620 g (2.65×10^{-3} mol) of 2,4-dinitrobenzenesulfenyl chloride in 5 mL of methylene chloride was added dropwise with stirring to 1.00 g (2.65×10^{-3} mol) of triphenylvinyltin (12) in 5 mL of methylene chloride. The reaction mixture was allowed to stir overnight. The solution was washed twice with water, dried over magnesium sulfate, and evaporated to dryness. The residue was dissolved in hot ethanol. On cooling, 0.49 g (67%) of yellow crystals was formed. A second recrystallization gave crystals of 2,4-dinitrophenyl phenyl sulfide **16**, mp 118–119 °C [lit.[27] 119.5–120.5 °C]. The NMR spectrum showed only aromatic protons.

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The Diethynylcyclobutadiene Rearrangement: A Degenerate Ligand Reorganization in the Coordination Sphere of (η^5-Cyclopentadienyl)cobalt[1]

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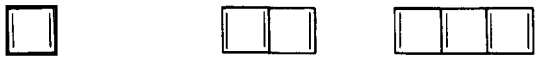
Reaction of $CpCo(CO)_2$ with bis(trimethylsilyl)butadiyne leads to small amounts of silylated 1,2- and 1,3-diethynylcyclobutadiene complexes **13** and **18** among other products. Alternatively, cocyclization of bis(trimethylsilyl)hexatriyne with bis(trimethylsilyl)acetylene furnishes **13** in 64.2% yield. These compounds may be protodesilylated with alcoholic KOH or fluoride. Flash vacuum thermolysis of the 1,2-diethynylcyclobutadiene complexes **9**, **19**, and **49** induces a clean rearrangement in which the four sp carbons of the ethynyl groups cyclize to form a new cyclobutadiene ring and the original cyclobutadiene ring retrocyclizes to generate two new alkyne groups. In this way **9** undergoes a degenerate rearrangement, whereas **19** converts to **30**, and **49** equilibrates with **50**. Mechanistic speculation is offered which suggests a CpCo-complexed cycloocta-3,7-diene-1,5-diyne (**11**) or cycloocta-1,2,3,5,6,7-hexaene (**12**) as a likely intermediate. A topologically equivalent alternative, (η^4-tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene)(η^5-cyclopentadienyl)cobalt (**10**), appears less favored on theoretical grounds.

Polycyclic benzenoid hydrocarbons have played an important part in the development of the theory of π-electronic cycles. They have received renewed recent attention in connection with diverse areas such as those concerned with the mechanism of carcinogenicity induced by environmentally abundant polycyclic benzenoids[4] and the conversion of coal to liquid and gaseous fuels.[5] These compounds are conceptually derived by linear and angular fusion of benzene rings, the latter constituting the prototype aromatic molecule.[6] One might conceive of nonbenzenoid analogs of the benzenoid aromatics formed by fusion of the prototype "antiaromatic"[7] molecule: cyclobutadiene.[8] The first three members of such a series (which can only be linear) are cyclobutadiene (1), butalene



1 2 3

(bicyclo[2.2.0]hexa-1,3,5-triene) (**2**), and tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene (**3**), for which in analogy with the trivial naming of biphenylene, the name bicyclobutadienylene may be proposed. Interestingly, and in contrast to the benzenoid series, only the first member, cyclobutadiene, has been studied relatively thoroughly.[8] Compound **2** has been invoked as a reactive intermediate,[9]

(1) Taken in part from the Ph.D. Thesis of J. R. Fritch, University of California, Berkeley, 1980.
(2) Regents' Predoctoral Fellow (1977–1978) and Gulf Oil Fellow (1978–1979).
(3) Alfred P. Sloan Foundation Fellow (1976–1980), Camille and Henry Dreyfus Teacher-Scholar (1978–1983).
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