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Invited review

Forty years of *Umpolung* in organometallic chemistry: from carbanionic nucleophiles to metallic electrophiles

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Abstract

The evolution of mechanistic insight into the nature of organometallic reactions over the last forty years is recounted from the personal perspective of a chemist trained in the empirical tradition of organometallic chemistry. Starting from the viewpoint prevailing in the 1950s of organometallics as potential carbanionic nucleophiles, this investigator has become persuaded by his researches with Group 13 organometallics of the merits of treating these reagents as organometallic electrophiles. The profound effects that a tricoordinate boron center can exert on the structure and reactivity of boracyclopolyenes is a telling illustration of such boron electrophilicity operating in an intramolecular fashion. The elucidation of the mechanisms of both the carbalumination and the hydroalumination of olefins and acetylenes has adduced cogent evidence for the rate-determining step being the electrophilic attack of tricoordinate aluminum on the carbon–carbon π-electron cloud of the substrate. Finally, in an investigation of the molecular basis for Ziegler–Natta catalysis, the Breslow–Natta soluble catalyst for the polymerization of ethylene, Cp_2TiCl_2–R_nAlCl_{3-n}, was examined in detail and compelling evidence has been adduced that the active catalyst site is the solvent-separated ion-pair, $[Cp_2TiR]^+$ $[R_nAlCl_{4-n}]^-$. Here again, the polymerization reaction is initiated by an organometallic electrophile, indeed by an even more powerful cationic electrophile. The net effect of these studies has been an *Umpolung* in the manner with which this chemist and many of his colleagues view organometallic reaction mechanisms.

Keywords: Ziegler–Natta catalysis; Carbanions; Mechanism; Gallium; Aluminum; Boron

1. Introduction

In keeping with the license allowed for the articles in this Volume 500, I would like to offer a personal account of how our views of organometallic structure and reactivity have evolved over the last some 40 years. The account is personal because this period roughly coincides with my undertaking doctoral research in Henry Gilman's Laboratory at the then Iowa State College in January, 1953, and my subsequent academic career in organometallic chemical research. From this coincidence of developments in organometallic chemistry and my scientific career, I do not for a moment mean to imply that I have been principally responsible for all the mechanistic advances in understanding (I am not arguing post hoc, ergo propter hoc). However, I have been privileged to make some useful contributions to organometallic reaction mechanisms, especially those involving what we now term organometallic electrophiles. What I wish to recount here is the scientific milieu in which my research was carried out and how, in unforeseen ways, various experimental observations compelled me, and many other chemists, to formulate a deeper and more comprehensive view of organometallic reaction pathways.

2. Retrospective on organometallic structure and mechanism circa 1955

The rudimentary knowledge existing in the early 1950s concerning organometallic compounds becomes startlingly vivid when we recall that the discovery of ferrocene and its structure elucidation were reported in 1951–1952 [1–3], Ziegler's studies on the reactions of aluminum alkyls with olefins, either alone or in the presence of transition metal salts, in 1952–1955 [4,5], Natta's stereoregular polymerizations of 1-alkenes with aluminum alkyl–transition metal salts in 1954–1957

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[6–8], and Brown's hydroboration of olefins in 1956 [9], to name just a few of the astonishing developments. These findings uncovered new and completely unanticipated bonding and reactions modes for compounds then thought to possess simple, if somewhat polarized, covalent carbon–metal bonds.

The prevailing notions of reaction mechanisms were likewise unsophisticated and pragmatic. The older generation of chemists, such as Henry Gilman and Karl Ziegler, were largely uninterested in reaction mechanisms, considering them (probably rightly so then) as egregiously speculative. During my time in Karl Ziegler's institute, nothing could unleash the scorn of Karl Ziegler faster than a hapless *Doktorand* venturing to offer a reaction mechanism not involving radicals as part of the *Doktorand's* required Saturday morning *Kolloquium*. In Henry Gilman's group meetings a more tranquil atmosphere reigned, but it was equally clear that reaction mechanisms were then considered the fluff and not the substance of "serious" chemistry. When Ziegler and Gilman did give some attention to how C–M bonds might break, they preferred to think in terms of homolysis or radical formation. Once when a graduate student pressed for time during the presentation of a seminar to Gilman's group paused to comment that he had time to present only one of two suggested reaction mechanisms, one involving carbanions and the other free radicals, quickly came Gilman's response in his rich Bostonian accent: "Oh, by all means, Bob, let's have the radical view!"

The younger generation of organic chemists, on the other hand, cared deeply about reaction mechanisms. This generation was represented for me at Iowa State by a remarkable trio of junior professors, George Hammond, Ernest Wenkert and Charles DePuy, who were students of Paul Bartlett, Robert Woodward and William von Eggers Doering, respectively, and were thus enthusiastically imbued with the principles of physical organic chemistry. To them organometallic chemistry was, to all intents and purposes, the chemistry of carbanions with the metal cation being largely a spectator in reaction mechanisms. It was a heady experience to see how all the bewildering metal enolate reactions, uncovered by German chemists (Claisen, Knoevenagel, Mannich, Stobbe and others), could be aesthetically unified by the carbanion concept. A very popular textbook by Alexander, "Principles of Ionic Organic Reactions", embodying this interpretation of organometallic reactions, appeared in 1950 and sanctioned this carbanionic view [10]. A further, more sophisticatic and experimentally corroborated treatment by Cram, "Fundamentals of Carbanion Chemistry", appeared in 1965 and thus baptized anionic carbon as the accepted intermediate for organometallics of Groups 1 and 2 [11].

Prior to 1950 extensive studies from Gilman's laboratory had sought to establish the reactivities of a wide gamut of main-group organometallics in addition reactions to a variety of C=O and C=N linkages [12]. These ten empirical reactivity rules were then employed in 1957 by Rochow, Hurd and Lewis in their textbook, "The Chemistry of Organometallic Compounds", to relate the observed reactivity of the carbon–metal bond to its polarity, as derived from Pauling electronegativity values [13]. This correlation led to the conclusion that the greater the polarity (that is, the carbanionic character) of a covalent C–M bond, the greater the reactivity of the organometallic. Thus by the late 1950s even a prominent organometallic textbook had espoused the view that organometallic reaction mechanisms were best explained in terms of available carbanions in R^-M^+ or, at a minimum, potentially available carbanions in polar organometallics $R^{\delta-}$–$M^{\delta+}$, which might be set free upon complexation with the polar substrate, $R_2C=O$. In either event, such substitution or addition reactions were accordingly viewed as occurring by nucleophilic initiation by carbanions, S_N or A_N [14].

Thoroughly convinced by the carbanionic approach, I made extensive use of it in my doctoral dissertation research on the reactions of azomethine and azaaromatic substrates with organolithium and Grignard reagents [15]. With Gilman's encouragement, I correlated the observed reactivities and reaction patterns with Hückel semiempirical MO calculations and we published these results in Chemical Reviews in 1957 [16].

But already in the 1950s novel organometallic reactions came to light that were inconsistent with this mechanistic carbanion view: (1) Ziegler and coworkers found that aluminum alkyls, hardly a source of carbanions, added readily to nonpolar olefins and acetylenes, as did the covalent aluminum hydrides R_nAlH_{3-n}; (2) transition metal alkyls, of both low polarity and stability, were found by Ziegler and by Natta to add readily to olefins to form polyolefins, especially when cocatalyzed by aluminum alkyls; (3) Brown found that diborane, nonpolar and reportedly unreactive toward olefins, actually adds readily to olefins and acetylenes in the presence of ethers; and (4) the normally air- and moisture-sensitive cyclopentadienyl carbanion became transformed when bonded to many transition metal cations. The amazing thermal and environmental stability of bis(cyclopentadienyl)iron or ferrocene actually facilitated its discovery and isolation [1,2].

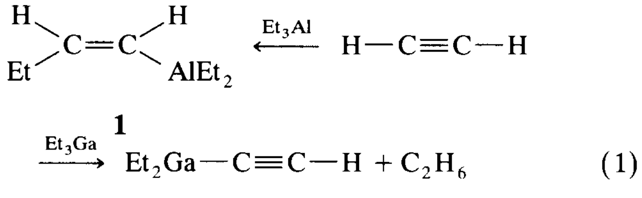
These discoveries piqued my curiosity to an extreme, especially since I was determined to become a physical organic chemist, who as George Hammond stressed, has the noble calling of striving to understand chemistry on a molecular level. When Gilman presented me with the opportunity of studying in Ziegler's institute under a Union Carbide fellowship, I leapt at the chance. A further inducement was that my grandfather, Joseph Eisch, had come to America from Bavaria, where Eisches have been glassblowers for over 300 years.

3. Initiation into Group 13 chemistry

When I joined the Max-Planck-Institut für Kohlenforschung in April 1956, it was the center of revolutionary developments that later were termed "Ziegler Chemistry". Not only was Karl Ziegler's core research team developing the discoveries in aluminum alkyls and ethylene polymerization technology that were to make the institute world-renowned and Ziegler rich and famous, but a productive and imaginative ring of group leaders were blazing promising research trails out from this central theme. Günther Wilke, with whom I was to be most closely associated, was studying the basic interactions of aluminum alkyls with transition metal salts, which were to spawn all of the insights into nickel chemistry and olefin oligomerization [17]. Roland Köster was deeply engaged in organoboron chemistry, which led to his independent discovery in 1956 of hydroboration, effected through the transfer of B–H bonds from boron alkyls to olefins [18]. Herbert Lehmkuhl and Ziegler were pursuing electrolytic studies on aluminum and related alkyls as a commercial method for purifying and plating metals [19]. Wilhelm Neumann was immersed in investigations of aluminum hydrides and tin alkyls, which were to shape his life-long scientific activity [20]. Heinz Hoberg was conducting mechanistic studies on the additions of aluminum alkyls and hydrides to olefins and on the generation and reactions of aluminum carbenoid sources [21].

Once I overcame the shock of having to work with the spontaneously flammable and explosively hydrolyzable aluminum alkyls, Ziegler set me the task of synthesizing gallium and indium analogs of R_3Al and R_2AlH and of determining how these compounds behaved when heated alone, when mixed with olefins, or when mixed with transition metal salts and olefins. The overall question in Ziegler's mind was how the chemistry of gallium and indium alkyls would compare with the recently observed behavior of aluminum alkyls. I was presented with a small lump of costly gallium metal and told to get started. To an American chemist grown accustomed to obtaining necessary starting materials from the departmental storeroom, this was a rude awakening. In those postwar years in Germany, I was to learn the necessity of often starting from scratch or conducting extensive purification, in order to get suitable starting materials. In retrospect, I affirm that such necessity is excellent experience.

Upon completion of my year at the institute, I had reached two firm conclusions: (1) gallium and indium alkyls undergo reactions similar to those of aluminum alkyls but at significantly lower rates; thus they offered no practical substitute in "Ziegler Chemistry"; and (2) the carbanionic mechanistic view which I had formed at Iowa State was completely worthless in understanding the reaction patterns and relative reactivities of Group 13 alkyls. But I did also form what proved to be a fruitful hypothesis: the explanation of Group 13 organometallic reactivity lies not in C–M bond polarity but in the metal center's Lewis acidity. What prompted this concept was one difference I did observe between aluminum and gallium alkyls and that was their reaction with acetylene (eq. (1)). Even though Et_3Ga has the less polar C–M bond, it behaved like RLi or RMgX and metallated acetylene to form **2**. The more polar C–Al bond in Et_3Al added smoothly to acetylene to yield *syn*-adduct **1**, a result inexplicable in any carbanionic or polar view. Looking for another basis for this difference in reaction, I suggested that the greater Lewis acidity of monomeric Et_3Al over Et_3Ga would permit the Al center to form a π-complex with acetylene more readily (**3**) as a prelude to addition. The like-sized but weakly acidic Ga center might preferentially require the formation of a σ-complex (more charge localization in the transition state) and thus induce substitution (**4**).



$$\xleftarrow{Et_3Al} H-C\equiv C-H \xrightarrow{Et_3Ga} Et_2Ga-C\equiv C-H + C_2H_6 \quad (1)$$

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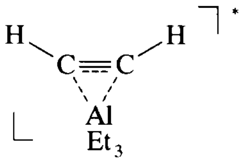

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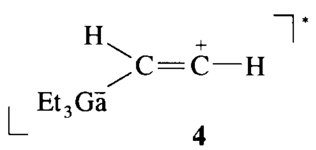

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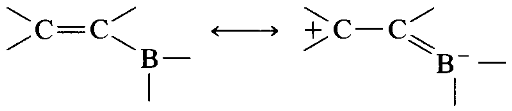
These ideas and conclusions were eventually published in 1962 after Ziegler's delayed approval [22,23].

The remaining six months in 1957 before assuming my first academic position I spent at Union Carbide's European Research Associates Laboratory in Brussels. Here I participated in the intensive effort to elucidate the mechanism of Ziegler–Natta polymerization catalysis. Most large chemical corporations worldwide had by then mounted similar research programs. For my part, I set out to prepare some recently reported aryltitanium(IV) alkoxides [24] and study their behavior with aluminum alkyls. Since Herman and Nelson offered evidence that such titanium aryls could be sources of free radicals, my thinking was set off on a mistaken search for a radical explanation for such olefin polymerization. Not until some 15 years later did I take up this tantalizing problem again.

4. Investigations of Group 13 Lewis acidity and electrophilicity

In launching my academic research I set out in a two-pronged attack to understand the role of Lewis acidity in determining the structure and reactivity of chiefly organoboron and organoaluminum compounds. With organoaluminum compounds my main goal lay in elucidating their intermolecular reactions with carbon–carbon unsaturated substrates, such as that exemplified in Eq. (1). With organoboranes, which generally do not interact with or add to carbon–carbon unsaturation (presumably for steric reasons), it was desirable to study such boron–carbon π-interactions in an intramolecular case by looking for indications of π-bonding in vinylic boranes (**5**). Although both of these intramolecular and intermolecular researches on Group 13-π-electron interactions have been carried in a more or less parallel fashion over the last 30 years, I will first describe our findings with organoboranes. The reader will appreciate that much of the logical relation apparent among these experimental results has been the product of hindsight rather than foresight. More often than not, my students and I had no serious clue of what our studies would reveal.



5a **5b**

5. Synthesis and properties of boracyclopolyenes

Planning to maximize intramolecular Lewis acidity by boron centers toward adjacent carbon–carbon π-bonds, we did set out to lock boron centers and C=C bonds in rings of varying sizes (**6**–**8**).

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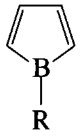

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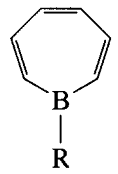

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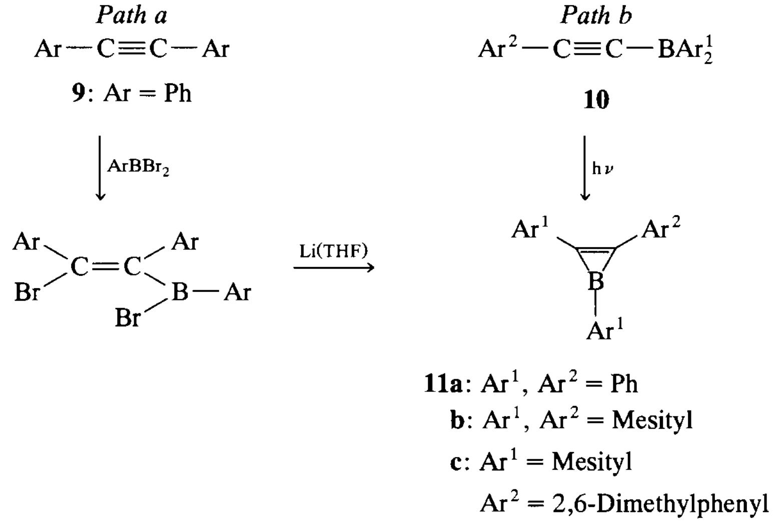
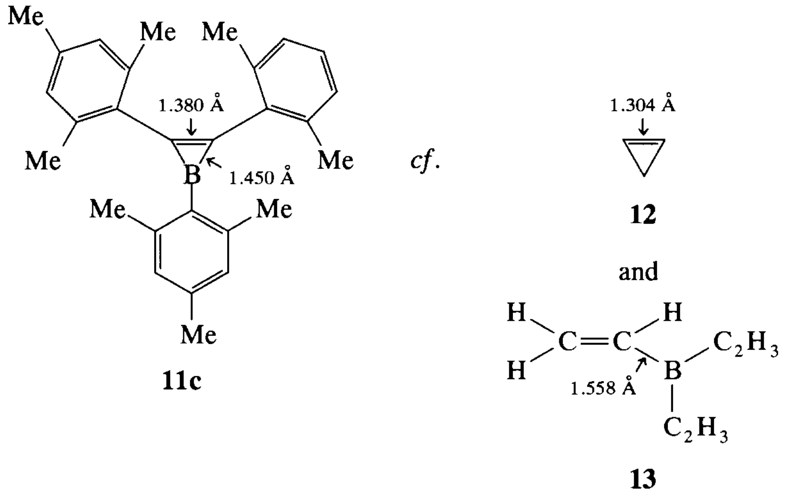


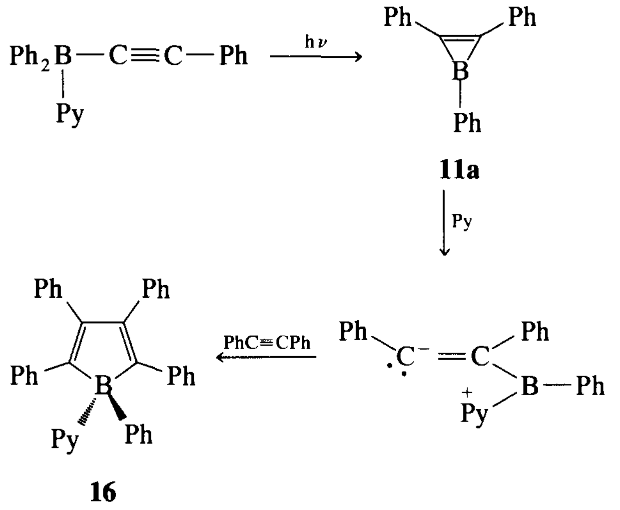
Scheme 1.



Scheme 2.

Furthermore, we did entertain the hopes, on the basis of Hückel MO theory, that borirene **6** and borepin **8** might have the aromatic stabilization of 2- and 6-π-electron rings, if the nuclear atoms would all lie in one plane. Such a configuration would maximize the π-overlap of adjacent B $2p_z$- and C $2p_z$-orbitals. Borole **7**, however, would be a 4-π-electron ring that by the same Hückel theory should be destabilized by such π-overlap and thus be antiaromatic.

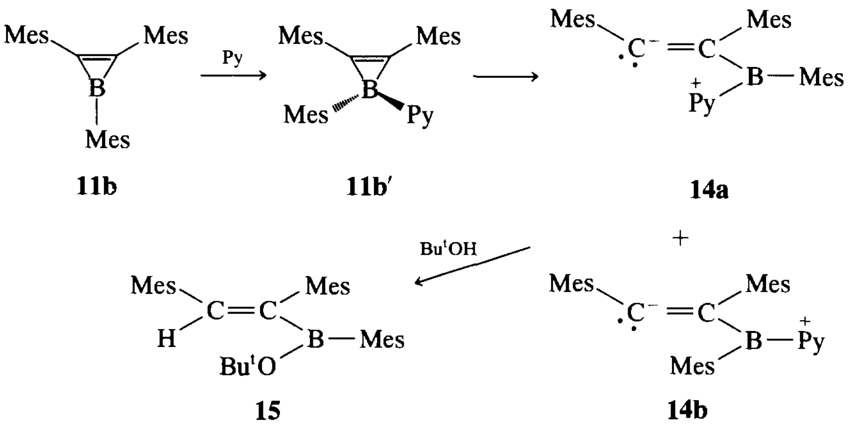
After many abortive attempts we did devise two routes to substituted borirenes (**11**): (1) haloboration of alkyne **9** followed by alkali metal ring closure (Scheme 1, path a) [25]; (2) di-π-methane-like photorearrangement of diaryl(arylalkynyl)borane (**10** [26,27] path b). A pure, crystalline borirene suitable for a definitive XRD analysis could be obtained via path b and by employing substituents in **10** that produced unsymmetrically substituted borirene **11c**. The C–C and C–B ring distances in **11c**, at 1.380 and 1.450 Å, were lengthened and shortened, respectively, compared with the C=C bond in cyclopropene (**12**) (1.304 Å) and the C–B bond in trivinylborane (**13**) (1.558 Å) and thus were consistent with π-electron aromatic stabilization among the three ring atoms (Scheme 2). But then surprises surfaced: when colorless **11b** was treated with pyridine, the solution turned deep yellow and the simple ^{13}C NMR spectrum of **11b** (nine visible signals) was transformed into a 30-line multiplet. Addition of ^{t}BuOH quenched the yellow color and formed **15** (^{t}BuOH and **11b** alone do not react). These observations are consistent with pyridine coordinating with the B atom in **11b** and the ring opening to the isomeric zwitterions **14a** and **14b** (17 possible ^{13}C signals each). The ^{t}BuOH no longer has any steric problem adding to **14** to yield **15** (Scheme 3). Further reflection on this amazing transformation allows one to conclude that π-bond stabilization is really the only bonding protecting the ring integrity of borirenes. Once the B center coordinates with pyridine (**11b′**), the B $2p_z$-orbital is removed from π-overlap and the ring is destabilized [28].



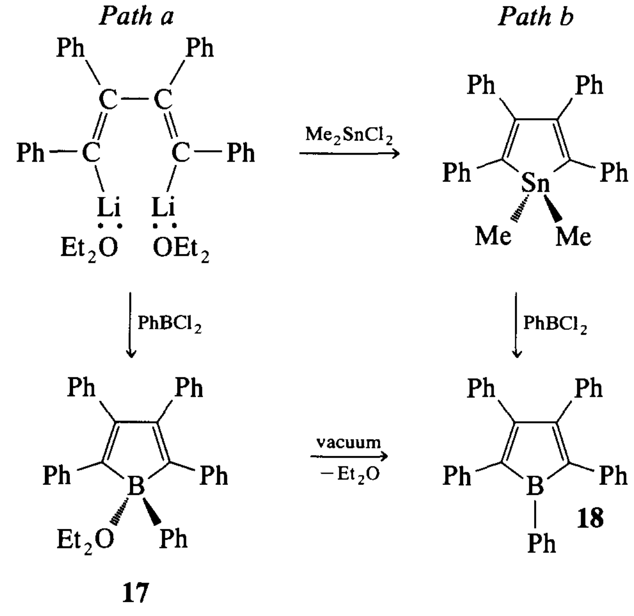
Scheme 4.

By generating borirenes with smaller substituents (**11a**: Ar^1, Ar^2 = Ph) in the presence of pyridine and an alkyne, such zwitterions could be directly trapped as borole–pyridine complexes [26] (**16** in Scheme 4).

Although the latter reaction did provide a route to boroles, a ring of equal interest for us (**7**), we required uncomplexed boroles for the study of the effect of cyclic π-electron delocalization on ring stability. Again, we were able to develop two practical routes to the desired borole (**18**) (Scheme 5, paths a and b); either permitted the isolation of the pure borole if only weak donors, such as ether, were present in the reaction mixture. The visible spectra of **17** (or the pyridine complex) and **18** were strikingly different: **17** was pale yellow (λ_{max}330nm) and **18** was deep blue (λ_{max}567nm) [29]. Hence, clearly an available B $2p_z$-orbital in **18** allows cyclic π-electron delocalization and a narrowing

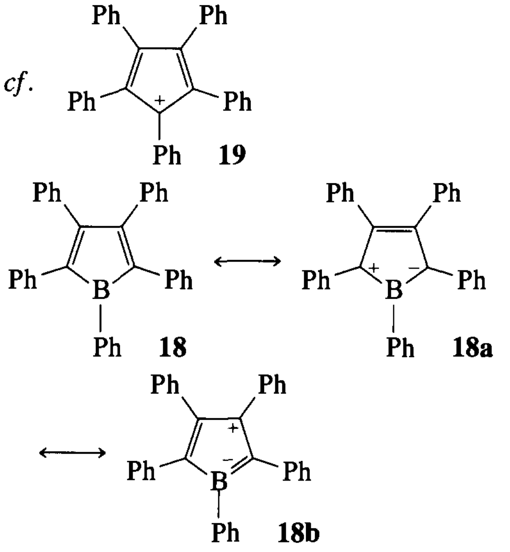


Scheme 3.

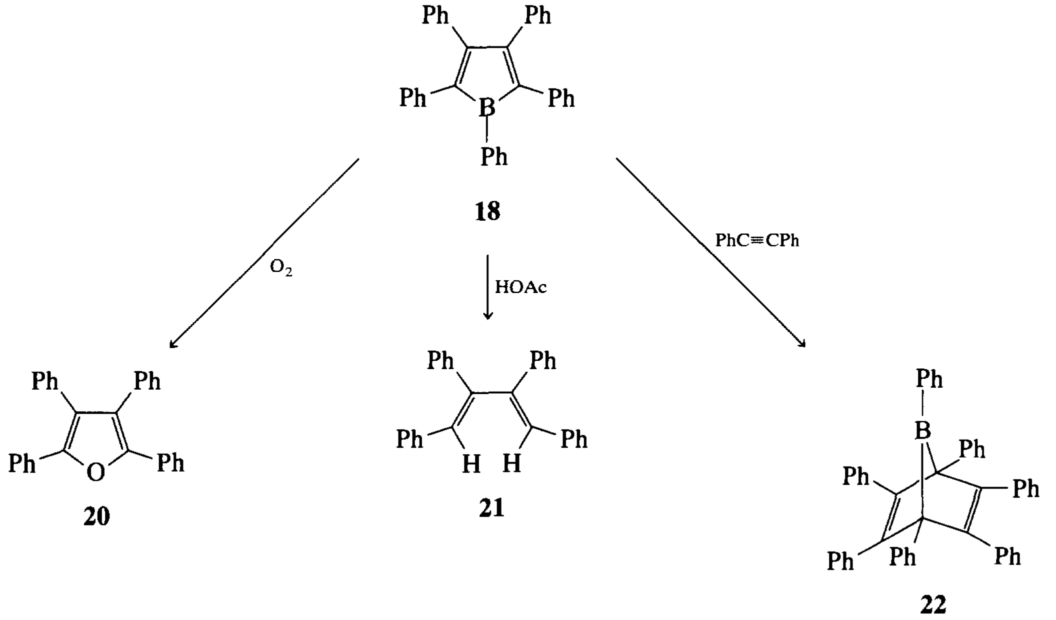


Scheme 5.

crystals of **18** suitable for an XRD analysis and the determination of ring C–C and C–B distances could not be obtained, the spectral and chemical properties of **18** permit the conclusion that it is indeed an antiaromatic ring. Not only does it have the same color as the isoelectronic, antiaromatic pentaphenylcyclopentadienyl cation (**19**) [30], but its ^{11}B signal at 55 ppm is only slightly shifted from that of trivinylborane (56 ppm), indicating that there is little C–B π-bonding or π-electron density buildup on boron. In resonance terms, **18** and **18a** are more important contributors than **18b**. This lack of aromatic stabilization is equally manifest in its chemical reactivity: (1) **18** is instantly oxidized in air (**11b**, by contrast, is relatively stable) and is decolorized to yield furan **20**; (2) acetolysis of **18** produces diene **21**; and (3) **18** undergoes Diels–Alder adduct formation with the normally unreactive diphenylacetylene rapidly at 20°C to give **22** [29] (Scheme 6).

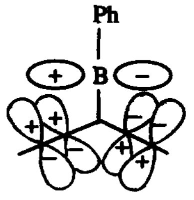


The spectral and chemical properties of 7-borabicyclo[2.2.1]heptadiene (**22**), by itself, provided unexpectedly a wealth of information about the ways in which an empty boron $2p_z$-orbital can interact with π-electrons within the molecule [31–33]. First of all, the long-wavelength absorption of **22** at 318 nm undergoes a hypsochromic shift to a shoulder at 278 nm when complexed with pyridine. This indicates that the free boron $2p_z$-orbital overlaps with the *cis*-stilbene π-bonds in **22** in a homoconjugative manner. In this view, **22** is a bis-homoborirene. Secondly, the ^{11}B NMR signal at



Scheme 6.

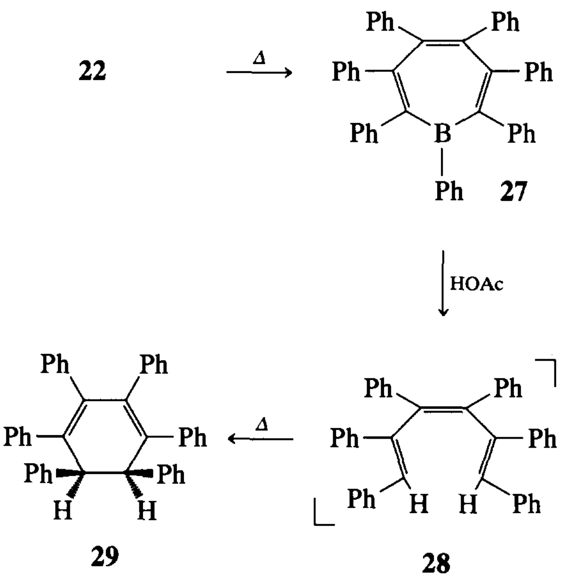
−5.0 ppm must be considered extraordinarily shifted upfield. Even the pyridine complex of **22**, a tetracoordinate boron, has its ^{11}B NMR signal downfield at 5.0 ppm and all tricoordinate R_3B structures exhibit their ^{11}B signals downfield at 68–87 ppm. Both spectral observations are in accord with the orbital interactions in **22** increasing the π-delocalization and electron density around boron (phenyl groups omitted for clarity, **23**).



23

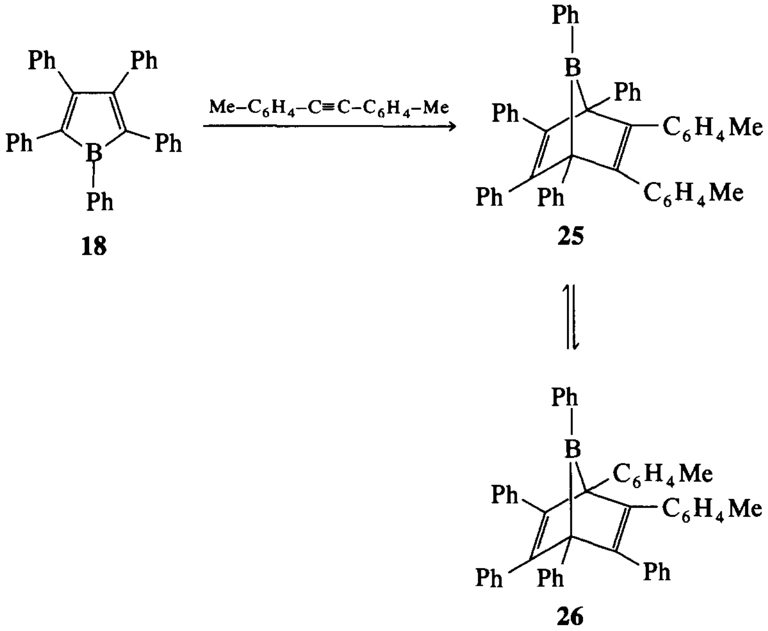
The importance of such proposed orbital interactions is even more evident in the thermal behavior of such bicyclic systems: they undergo a whole array of facile and profound skeletal rearrangements. One of the most rapid of such rearrangements is a 1,3-allylic shift occurring above 25°C and observable when **18** is allowed to react with a different alkyne, such as di-*p*-tolylacetylene (**24**). In addition to the expected adduct (**25**, one methyl group in the ^{1}H and ^{13}C spectra), the isomeric adduct **26** is formed as well (two different methyl groups) (Scheme 7). This shows that the first-formed **25** has equilibrated with **26** by an allylic rearrangement.

Finally, when **22** is heated in refluxing toluene the colorless solution of **22** turns lime green; acetolysis of the mixture gives *cis*-1,2,3,4,5,6-hexaphenyl-1,4-dihydrobenzene, thought to arise from **22**, and *cis*-1,2,3,4,5,6-hexaphenyl-1,2-dihydrobenzene (**29**), likely to have arisen from **27** via **28** (Eq. (2)).

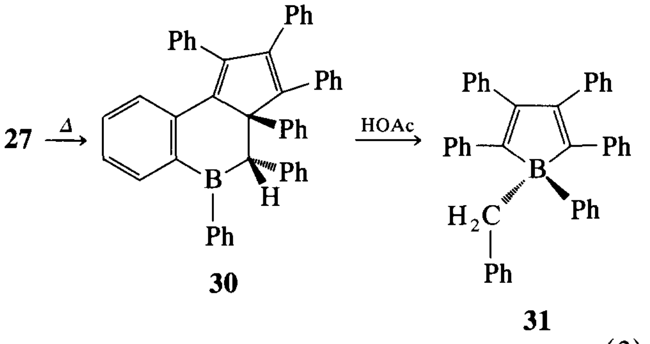


(2)

Borepin **27** could not be isolated in the pure state because in refluxing toluene it isomerized further to a fluorescent, chartreuse-green solid **30**, whose acetolysis produced 5-benzyl-1,2,3,4,5-pentaphenylcyclopentadiene (**31**) (Eq. (3)).



Scheme 7.



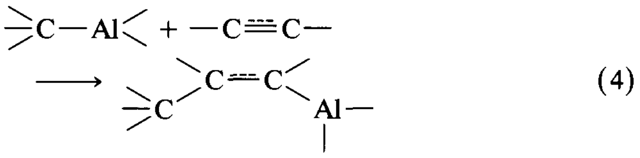
(3)

The structure of **30** was determined by XRD analysis; clearly, intuitional structure assignment would never have sufficed to track the series of remarkable rearrangements leading from **22** to **30**. From the transient intermediacy of borepin **27** in this overall transformation, it is evident that whatever aromatic stabilization **27** has as a 6-π-electron Hückel system is inadequate to protect it from further rearrangement. Most likely, the chief destabilizing feature in **27**, which greatly reduces any π-electron stabilization is the steric repulsion of adjacent phenyl groups in a planar seven-membered ring. Such repulsion can be minimized by an allowed disrotatory ring closure to nonplanar and nonaromatic **32**. Structure **32** can then pass through a number of thermally allowed pericyclic reactions (allylic shift to **33**; disrotatory ring opening to **34**; and an ene-reaction which finally leads to **30** (Scheme 8). In all of these fascinating rearrangements, the interaction of the B $2p_z$-orbital with the π-electron cloud plays a significant role.

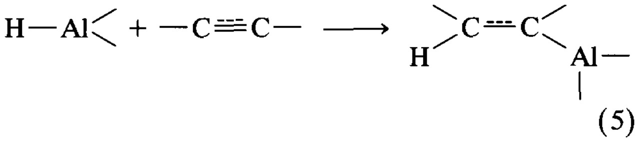
Further details and experimental evidence on the structure and reactivity of these boracyclopolyenes can be found both in a comprehensive survey [34] and in a very recent review [35].

6. Mechanisms of the carbalumination and hydroalumination of unsaturated hydrocarbons

Our investigations into the mechanisms of Ziegler's organoaluminum reactions with hydrocarbons were more straightforward: we strove to elucidate what kinetic factors determined the ease of adding C–Al bonds (Eq. (4)) or H–Al bonds (Eq. (5)) to olefins and acetylenes. Employing principally dimeric triphenylaluminum (**35**) for the carbalumination additions and trimeric diisobutylaluminum hydride (**36**) for hydroalumination reactions, we established that both reactions had several kinetic features in common. First of all, the empirical rate laws, **37** [36] and **38** [37,38], were consistent with



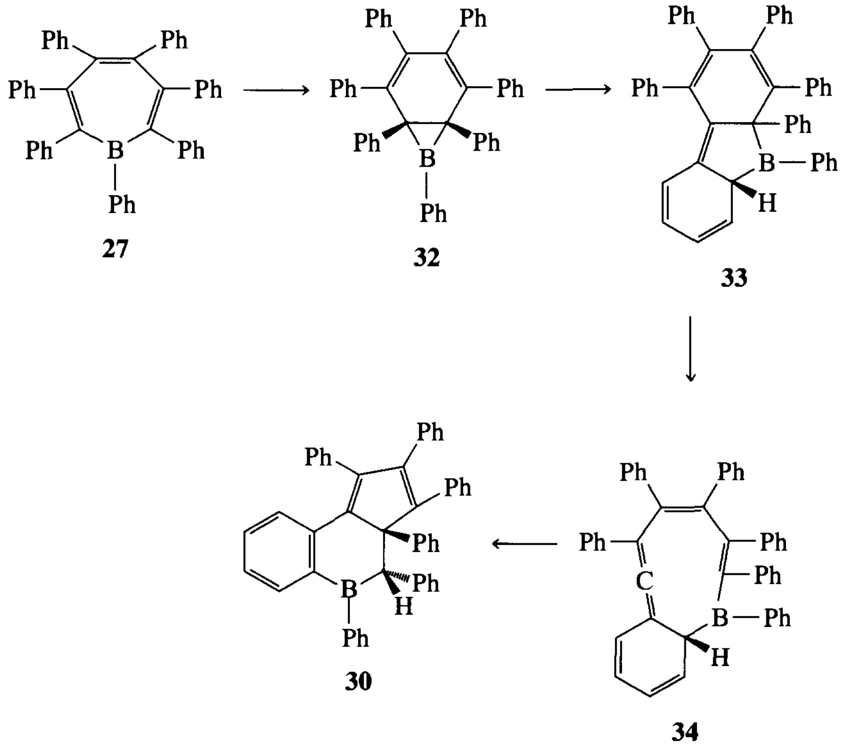
(4)



(5)

$$v = k[\mathbf{35}]^{0.5}\,[\text{Acetylene}] \qquad v = k[\mathbf{36}]^{0.33}\,[\text{Acetylene}]$$

37 **38**



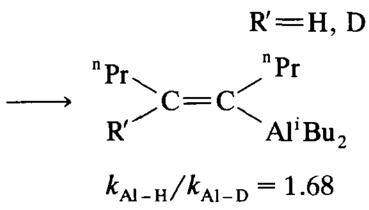
Scheme 8.

the attack of the monomeric Ph_3Al or monomeric Bu^i_2AlH on the unsaturated substrate, R–C≡C–R′ (**39**), in the rate-determining step. Secondly, such additions proceeded most rapidly in hydrocarbon media and donor solvents retarded such additions (ether) or prevented them altogether (amines). These two observations support the hypothesis that tricoordinate, unsolvated R''_2AlR''' (**40**, R″ = Ph, Bu^{i}′, R‴ = Ph, H) attacks the π-electron cloud of **39** in an electrophilic manner, forming a transition state **41** that resembles a π-complex (Scheme 9). Reorganization of **41** in the product-determining step can occur in two competing ways, **42a** and **42b**, whose relative energies will control the ratio of products, **43a** and **43b**.

The bridging in transition states **42a** and **42b** is postulated to be very similar to that of the bridging of the methyl groups in $(Me_3Al)_2$, where the methyls are also suspended between two positively polarized centers.

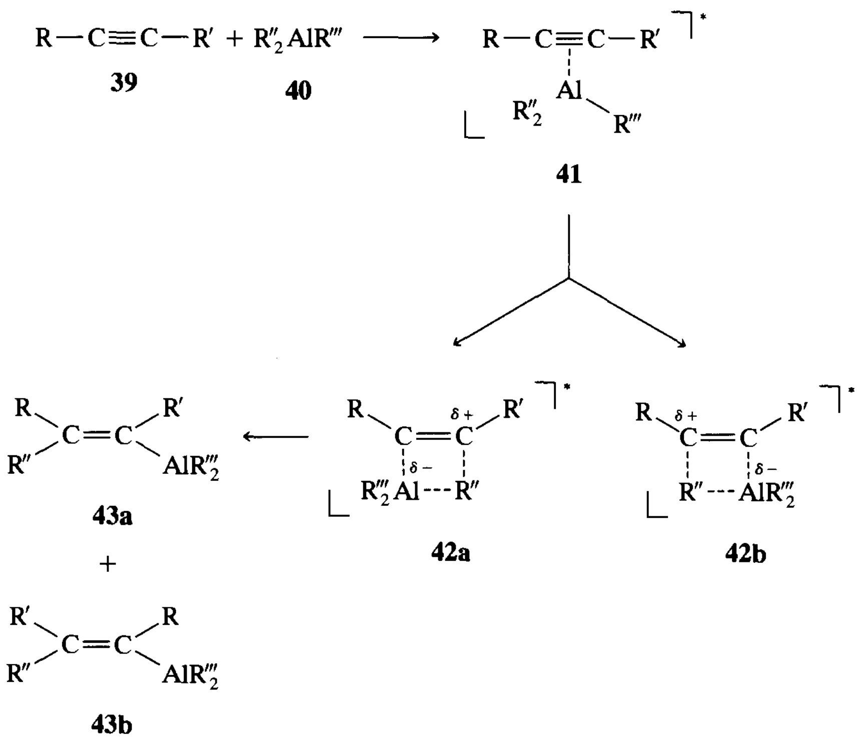
From kinetic results with the hydroalumination of acetylenes, there are several reasons to favor transition state **41** or π-complex formation as the highest energy barrier to reaction. Transition states **42a** and **42b**, in which the Al–H bond is significantly stretched and the acetylene unit, R–C≡C–R′, significantly distorted from linearity, would have to lie lower than **41** for two cogent reasons. First, if attainment of **42a** and **42b** were the rate-determining step, then the attendant Al–H bond stretching should manifest itself in a marked isotope effect. However, $^iBu_2Al$–H adds to 4-octyne at 30°C only 1.7 times faster than $^iBu_2Al$–D (Eq. (6)) [37]. This isotope effect cannot be considered as a primary effect, that is as one operative in the rate-determining step.

$$^nPr{-}C{\equiv}C{-}Pr^n + {}^iBu_2Al{-}R' \quad R'{=}H, D$$



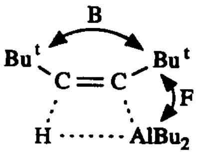
$$k_{Al-H}/k_{Al-D} = 1.68 \qquad (6)$$

A second argument against transition states **42a** and **42b** being of higher energy than transition state **41** stems from relative reactivities of R–C≡C–R′, as determined from initial rates (k at time 0) [39]. Di-t-butylacetylene (**44**), for example, undergoes hydroalumination some 20 times more rapidly than di-n-butylacetylene (**45**) at 35°C. If as much change in the alkyne's configuration were to have occurred in the rate-determining step as indicated in transition states **42a** and **42b**, then the transition states **46** and **47** would differ significantly in F- and B-steric repulsions. Indeed, such repulsions should make transition states **46** lie higher than transition states **47** and thus make **44** less reactive than **45**. Since transition states **46** and **47** cannot explain the



Scheme 9.

small $k_{H/D}$ isotope effect, nor can they rationalize the reactivities of **44** and **45**, a preferable transition state is



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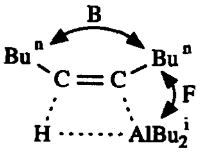

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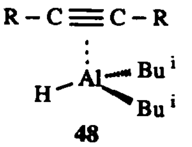
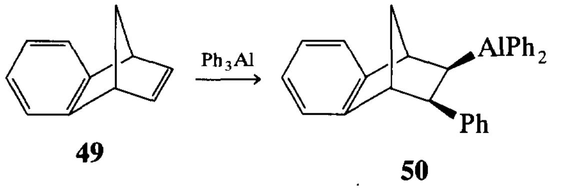


48

the π-complex-like **48**, where the Al–H bond has undergone little stretch and the R–C≡C–R is still essentially linear, thereby minimizing F- and B-repulsions. With this transition state model, the greater reactivity of the t-butyl-acetylene (**44**) over the n-butyl-acetylene (**45**) can be attributed to the greater electron-release of the t-butyl group over that of the n-butyl group, as measured by Taft polar substituent constants σ^* [40]. The pertinent values are $\sigma^*_{\mathrm{Bu^t}} = -0.300$ and $\sigma^*_{\mathrm{Bu^n}} = -0.130$.

In addition to these kinetic similarities, the carbalumination and hydro-alumination of both olefins and acetylenes share a kinetically determined, *syn*-mode of addition (Eqs. (7–10)) [41–44]. Such *syn*-addition is consistent with the electrophilic attack of R_3Al or R_2AlH on the π-cloud of the substrate.



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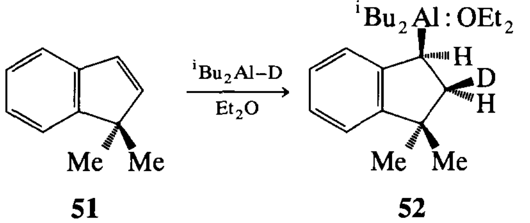

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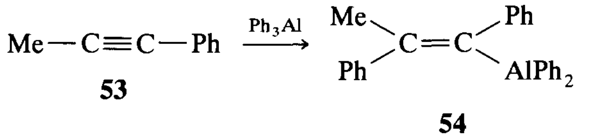

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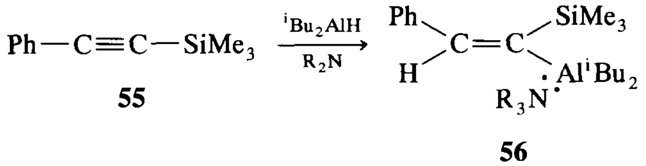
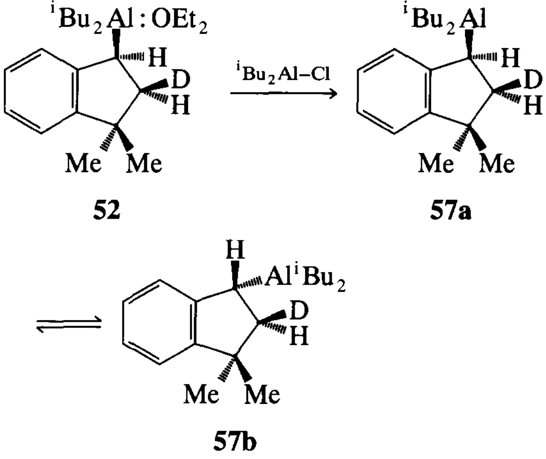
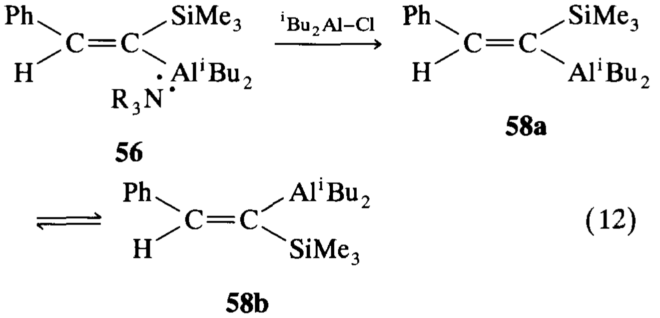


(10)

In addition to the *syn*-stereochemistry uniformly observed, note that the regioselectivity with unsymmetrical acetylenes is also very high: regioadduct **54** is > 95% and regioadduct **56** is > 99% of the product. Furthermore, stereoisomers **52** and **56** are kinetically stable only as complexes with ethers or amines. In the absence of such donor molecules, both systems rapidly undergo stereoisomerization (Eqs. (11–12))



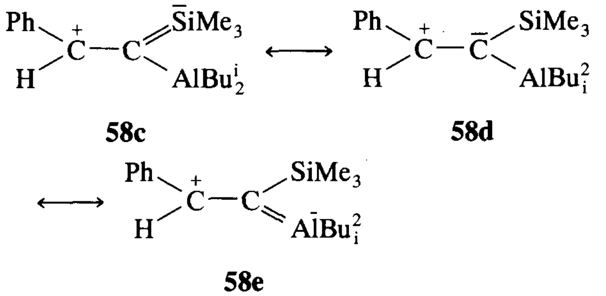
(11)



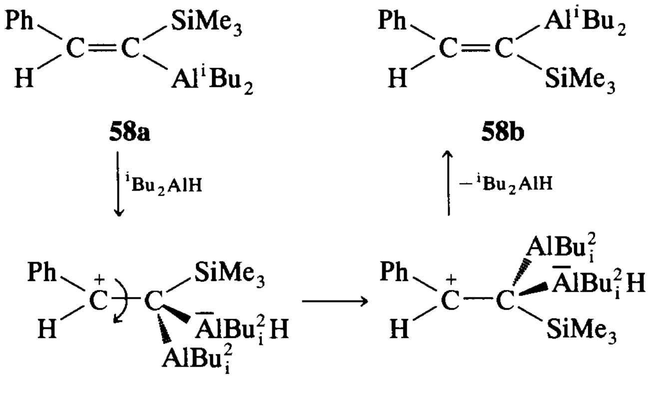
(12)

At equilibrium, the ratio of **57a** : **57b** is 50 : 50 and that of **58a** : **58b** is < 5 : 95.

What is truly remarkable about the α-trimethylsilylvinylalanes **58a** and **58b** is that they rapidly interconvert at temperatures as low as −5.0°C. This configurational lability stands in stark contrast to the thermal stability of ordinary vinylalanes to prolonged heating at 50°C. We suggest that synergistic p_π–Sid_π (**58c**) and p_π–Alp_π (**58e**) effects operative in the ground state of **58a** (or **58b**) decrease the π-bonding of the C=C group and increase the π-electron density alpha to the Si and Al substituents (**58d**) [44].

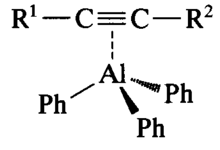


Although such contributions are important in describing the ground states of **58a** and **58b**, they may not by themselves facilitate the interconversion of the isomers. Rather the buildup of π-electron on C_α (**58d**) may permit a second Lewis acid (**58** or $^i Bu_2AlH$) to complex and catalyze the isomerization in an electrophilic manner (Scheme 10).

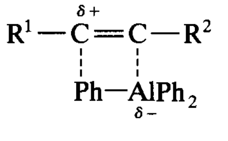


Scheme 10.

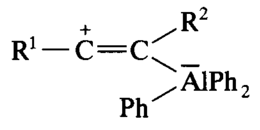
Finally, some consideration should be given to transition state models for the carbalumination of alkynes by Ph_3Al in light of available kinetic information. A priori, three models appear possible: (1) a π-complex transition state **59**, which is similar to **41**; (2) a bridging complex **60**, which resembles **42a** and **42b**; and (3) a σ-complex **61**, which is reminiscent of **4**. In terms of charge separation, the models become less polar in the sequence: **61** > **59**. Steric factors involving transfer of a phenyl group from Ph_3Al to the unsaturated carbon should also be important in any of these transition states and that is in fact observed: t-butyl(phenyl)acetylene (**62**) produces one regioisomer (**63**) (Eq. (13)) [45]. The phenyl group clearly is introduced onto the vinylic carbon that is sterically more accessible.



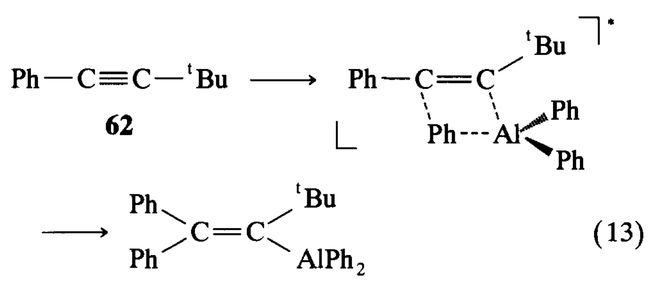
59



60

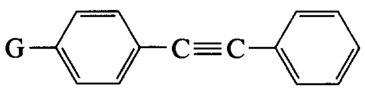


61

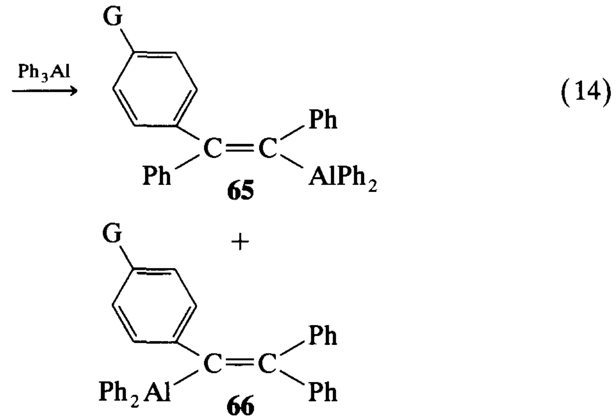


63

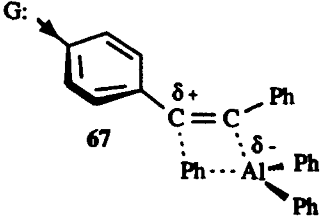
The polar nature of the transition state in carbalumination was studied by measuring the rates of addition and the distribution of regioisomers **65** and **66** formed from *p*-substituted diphenylacetylenes (**64**) and Ph_3Al (Eq. (14)) [36,46]. Where substituent G was a Lewis basic site, as with G = Me_2N, MeO and MeS, no straightforward kinetic data could be obtained (due to complexation with Ph_3Al), but where G = Cl, H and Me, the kinetic data gave overall relative carbalumination rates of (Cl) 0.80, (H) 1.00 and (Me) 1.23. Thus, replacing a *para*-H in **64** with Cl lowered the rate by 12% and a similar substitution by Me raised the rate by 23%. That the electron-donating Me gave a moderate rate increase and the electron-withdrawing Cl led to a modest rate decrease is consistent with electrophilic attack by Ph_3Al on **64** but only with a moderately polar transition state, **60** rather than **61**.



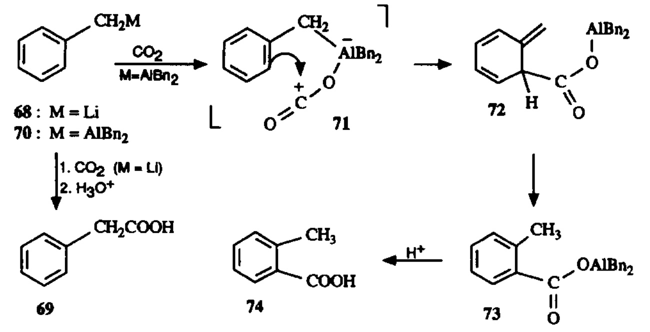
64



Likewise, the experimentally determined ratio of regioisomers **65** and **66** (actually the triarylethenes resulting from hydrolysis), where G = Me_2N, MeO, Me, MeS and Cl, taken as their logarithm, was found to correlate linearly with Hammett σ_{para} values, giving a slope (ρ-value) of −0.713 having a standard deviation of ±0.012. This finding is consistent with the relative stabilization of the transition state **67** leading to regioisomer isomer **65** by electron-donating groups. But since the ρ-value is relatively small, such electron donation is not of large importance in determining the ratio of **65** : **66**. Hence, again the less polar transition state **60** accords better with the facts than **61**.



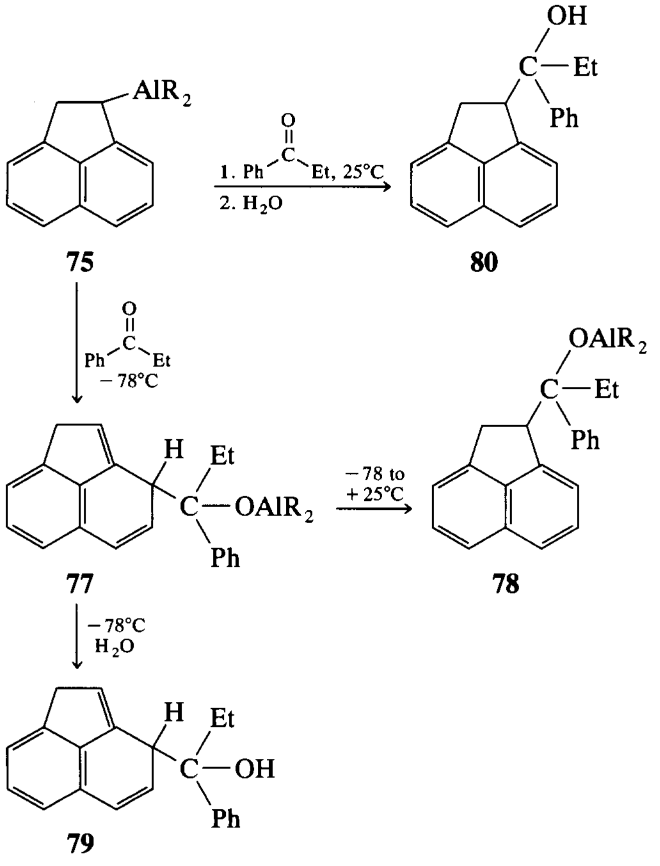
Not only is the electrophilic mechanism of attack applicable to the additions of R_3Al or R_2AlH to olefins and acetylenes, but also to the reactions of allylic



Scheme 11.

aluminums with carbonyl substrates. In contrast to the action of CO_2 on benzyllithium (**68**), which produces phenylacetic acid (**69**) on hydrolysis, CO_2 reacts with tribenzylaluminum (**70**) to yield only *o*-toluic acid (**74**) [47]. As will be evident subsequently, there is reason to consider this outcome to proceed via **71–73** (Scheme 11).

A remarkable example of such intramolecular electrophilic attack induced by the Al center is shown in Scheme 12. Depending upon the temperature of reaction and workup, **75** reacts with propiophenone (**76**) to give a high yield of either **79** or **80** (Scheme 12) [48]. Adduct **77** is first formed by kinetically controlled electrophilic attack (cf. **71**), but rearranges upon warming to the thermodynamically stable product **78**. Further aspects of electrophilic mechanisms for organoaluminum compounds have been reviewed elsewhere [49,50].

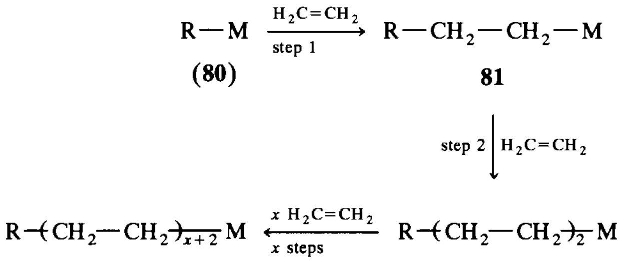


Scheme 12.

7. Investigations into the initiation of Ziegler–Natta polymerization

After about two decades of research devoted to understanding the bonding and reaction mechanisms of organoboron and organoaluminum compounds, our group began in 1976 a serious study of Ziegler–Natta polymerization catalysis. Feeling reluctant and unqualified to undertake a study of the various heterogeneous catalysts then in use, we chose the homogeneous titanocene dichloride-alkylaluminum chloride catalyst system (**80**), which was discovered almost simultaneously by Breslow and Newbury [51] and by Natta's group [52] in 1957 to initiate the polymerization of ethylene in solution to yield linear polyethylene. Subsequent studies by Long [53] and by Fink and Rottler [54] established that the titanium and aluminum components formed a number of complexes, but the structure and the role of such complexes in polymerization was unknown. As early as 1960 Zafirova and Shilov speculated upon the existence of Cp_2Ti^+Me cations in such systems [55] and in 1965 Dyachkovskii adduced evidence for such ions by an electrodialysis method [56]. However, in a review of the field published in 1979 [8], Boor discussed theories on the nature of the active site which encompassed: (1) solely the transition metal; (2) solely the aluminum alkyl; and (3) some undefined combination of the transition metal and aluminum components. Thus in 1976 nothing definite was known about the organometallic chemistry of such ethylene polymerization catalysts.

The prevailing assumption for the initiation and growth of the polymer chain, however, was that a carbon–metal bond (R–M) (where the metal might in **80** be titanium, aluminum or a complex of both metals) underwent repeated insertions of ethylene units (Scheme 13). We reasoned that if we could limit the reaction of **80** to the insertion of one unsaturated unit (as in **81**), we might be able to isolate **81**, determine its structure and from this information deduce what the nature of the active site in **80** might be. Achieving the isolation of **81**



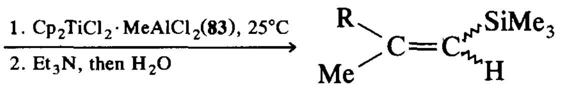
Scheme 13.

is impossible, of course, because a second insertion (Scheme 13, step 2) and further insertions of ethylene are too rapid.

In order to stop reaction of **80** after one insertion, we had to employ an unsaturated surrogate for ethylene. Thus, we needed an olefin or acetylene reactive enough to insert once to form an adduct, which for steric reasons would then undergo no further insertions. After evaluating the suitability of disubstituted olefins and acetylenes, norbornenes and vinylsilanes, we found that 1-alkynylsilanes, R–C≡C–$SiMe_3$ (**82**), underwent such a single insertion with > 95% conversion. As our specific Breslow–Natta combination, a 1 : 1 mixture of Cp_2TiCl_2 and $MeAlCl_2$ (**83**) in CH_2Cl_2 solution proved most efficient. (The alternative aluminum components, Me_3Al and Me_2AlCl, gave more rapid reduction of Cp_2TiCl.) Treatment of alkyne **82** with **83**, followed hydrolysis in the presence Et_3N (to prevent generated HCl from cleaving the C–Si bond in (**84**)), gave high yields of just one regioisomer, **84** [56,57] (Eq. (15)). This demonstrated that indeed just one insertion of **82** had occurred in a highly regioselective manner. The stereochemistry of the hydrolyzed product **84**, however, was seemingly unselective ($E : Z \sim 1 : 1$) but this aspect of the reaction proved to be misleading (cf. infra). Also, it is noteworthy that where $R = {}^tBu$ in **82**, the alkyne failed to insert.

$R{-}C{\equiv}C{-}SiMe_3$

82

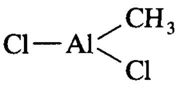


84

(15)

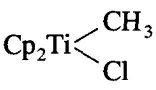
R = 1-hexyl, cyclohexyl, 1-cyclohexenyl, phenyl

That such alkylative additions yielding **84** are due to the combined reagent **83** and not due to the individual components is seen in the failure of either **85** alone or **86** alone to produce any **84** at 25°C. Clearly, their M–CH_3 bonds are unable, by themselves, to undergo insertion of **82**.



$Cl{-}Al(CH_3)Cl$

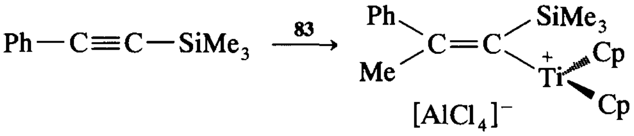
85



$Cp_2Ti(CH_3)Cl$

86

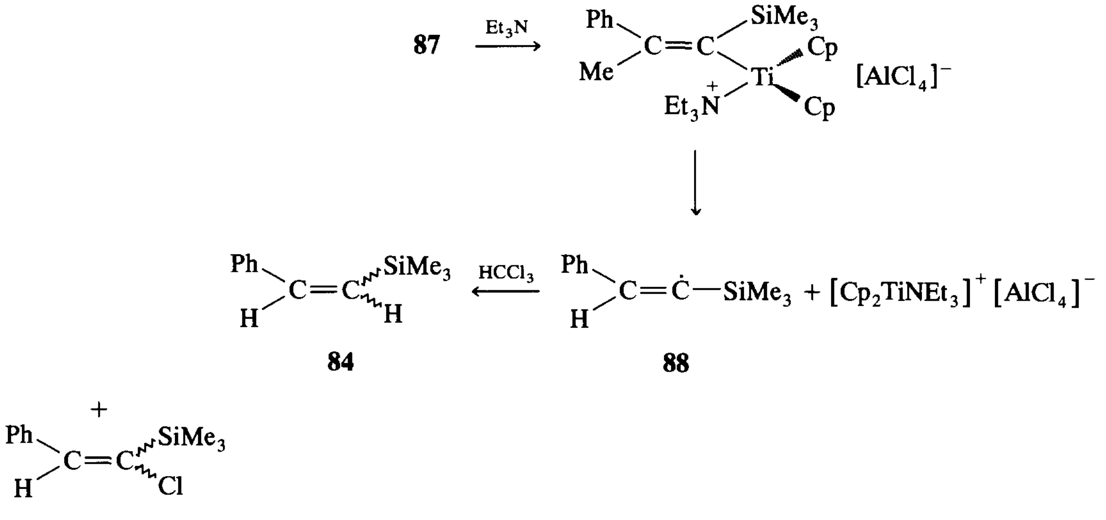
Insight into such insertions came from the direct isolation of the adduct formed from **82** (R = Ph) and **83** and an XRD analysis of its crystal structure (**87**) (Eq. (16)) [59]. The structure is that of the ion pair, bis(cyclopentadienyl)(*E*-2-methyl-2-phenyl-1-trimethylsilylethenyl)titanium(IV) tetrachloroaluminate (**87**).



87

(16)

The positioning of the titanium and the methyl groups on the C=C bond *syn* to each other does not agree with the lack of stereoselectivity in the hydrolysis product **84**. This unselective stereochemistry in **84** was shown to be caused by the Et_3N, which triggered a homolysis of the carbon–titanium bond in **87**. Such homolysis was demonstrated by adding Et_3N–D_2O to **87** in $CHCl_3$: no deuteriated **84** was found but only **84** and its chloro derivatives **89**. This shows that radical **88** abstracts H and Cl atoms from the solvent (Scheme 14) [60]. Apparently the full positive charge on Ti in **87** stabilizes the C–Ti bond.

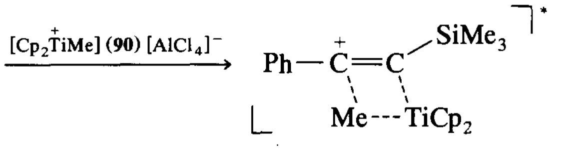


Scheme 14.

With the structure of **87** well-defined, we can then propose that **82** inserts in a *syn*-manner into the C–Ti bond of the bis(cyclopentadienyl)methyltitanocenium ion **90** (Eq. (17)).

$Ph-C\equiv C-SiMe_3$

82 (R = Ph)

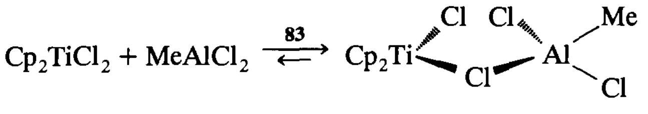


89

$\longrightarrow$ **87** (17)

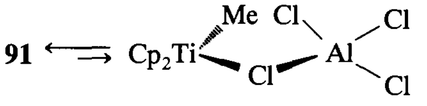
The *syn*-addition is readily understandable in terms of electrophilic attack by Cp_2Ti^+Me and the high regioselectivity (which is contrary to the expected steric influence) can be attributed to C–Si σ-bond hyperconjugation which stabilizes the positive charge in transition state **89** on the carbon beta to silicon [59,61].

The origin of **90** could be the straightforward result of the following equilibria (Eqs. (18–20)) [62]. The equilibrium in Eq. (18) is known to be shifted to the right, because complex **91** has been isolated and its structure determined by XRD analysis [59]. The equilibrium in Eq. (19) must be shifted far to the left, because neither **92** nor **93** can be detected by NMR analysis. The last equilibrium indicated, Eq. 20, can be considered as that between a contact ion-pair **92** and solvent-separated ion-pair **93**. This kind of equilibrium has been observed at low temperatures for the closely related complex, $Cp_2TiCl_2 \cdot AlCl_3$ [62]. As expected, such an equilibrium would be expected to be shifted to the right by at least two factors: (1) greater dilution, favoring two particles over one; (2) a more polar solvent, favoring charge separation. By these same criteria, a decision can be reached on whether the contact ion-pair (**92**) or the solvent-separated ion-pair (**93**) is the active site in catalyst **83**. Our finding that the polymerization activity of **83** increases upon dilution or upon using a more polar solvent (CH_2Cl_2 in place of toluene) leads us to conclude that **93** is the most active site in these Breslow–Natta catalysts [62].



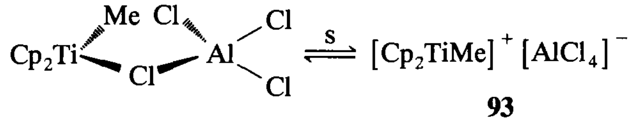
91

(18)



92

(19)



92 **93**

(20)

Thus, as in organoaluminum reaction mechanisms, electrophilic attack by an electron-deficient center upon an unsaturated hydrocarbon has proved to be the key to understanding the initiation of Ziegler–Natta polymerizations. The great electrophicity of a positively charged metal center over that displayed by neutral R_3Al is immediately apparent. Subsequent to our work, Jordan and co-workers have demonstrated the applicability of this metal cation concept to zirconium polymerization catalysts [63] and Ewen and coworkers have postulated the formation of metallocenium cations as active sites with their soluble isospecific [64] and syndiospecific [65] catalyst systems for the production of stereoregular polypropylenes.

8. Evolution of organometallic reaction mechanisms

From the foregoing account of our past research, it is evident that experimental data forced us to change our view that organometallics generally react in a carbanionic manner. Experience has now persuaded us that, possibly excepting organometallics of Groups 1 and 2, the majority of the known organometallics act as metallic electrophiles. Thus our mechanistic *Weltanschauung* has undergone a complete *Umpolung*, to use, in memory of Karl Ziegler, two weighty German words. But as a wary mechanistic chemist, I realize the dangers of taking too dogmatic view of reaction mechanism. Without experimental evidence one cannot dismiss the possibility of the intrusion of free-radical or single-electron-transfer processes [66] in organometallic reactions. These uncertainties are what keep mechanistic studies exciting and challenging.

Acknowledgments

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