*Bull. Chem. Soc. Jpn.*, *71*, 755—769 (1998)

## *Accounts*

# Alkene and Alkyne Complexes of Zirconocene. Their Preparation, Structure, and Novel Transformations

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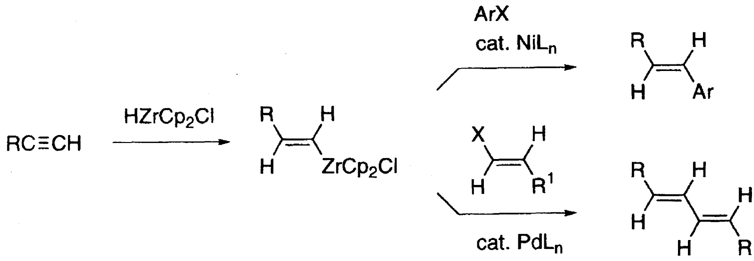
(Received October 13, 1997)

Dialkylzirconocenes in situ generated such as $Cp_2Zr(n\text{-}Bu)_2$, $Cp_2ZrEt_2$, and $Cp_2Zr(t\text{-}Bu)(i\text{-}Bu)$ are thermolyzed to afford zirconocene-alkene complexes. In the cases of $Cp_2Zr(n\text{-}Bu)_2$ and $Cp_2Zr(t\text{-}Bu)(i\text{-}Bu)$, $Cp_2Zr$-alkene complexes generated from them tend to act as a "$Cp_2Zr$" equivalent, since the initially generated alkene is often replaced by another π-bond containing compound. In the presence of alkynes, for example, alkyne complexes may be generated. On the other hand, $Cp_2Zr$(ethylene) tends to serve as an intermediate since the ethylene moiety is often incorporated in the final organic products. Ring expansion and contraction, ligand substitution, transmetallation, migratory insertion, stereoisomerization, regioisomerization, oxidative addition involving these $Cp_2Zr$-alkene and $Cp_2Zr$-alkyne complexes as well as their structures are reviewed.

Over the past two to three decades, metals and metal derivatives used as reagents and intermediates have significantly revamped and improved the art of organic synthesis.1,2) Even if twenty or so actinides and heavier elements are excluded from consideration, there are roughly 26 main group metals, 24 *d*-block transition metals, and 15 lanthanides. Collectively, these metallic elements account for roughly 60% of all elements known today. At the time the authors became interested in explorations of organometallic chemistry for organic synthesis, the widespread use of metals in organic synthesis was limited to a few alkali metals, e.g., Li, Na, and Mg, although several others, e.g., Zn, B, Al, Si, and Sn, appeared to be destined to attain a similar status. Aside from some specific uses of transition metals, e.g., catalytic hydrogenation with late transition metals, oxidation with Cr and Mn compounds, and Ti-mediated alkene polymerization, Cu was about the only transition metal which began showing its wide-range synthetic utility.3) From a historical perspective, it was a very attractive notion to explore the chemistry of other potentially useful metals with the goal of incorporating them into an integrated part of organic synthesis, and a dozen or so *d*-block transition metals, including Ti, Cr, Mn, Fe, Co, Ni, Zr, Mo, Ru, Rh, and Pd, along with some lanthanides appeared to be particularly promising. For a combination of reasons, the authors began investigating the organometallic chemistry involving Ti, Zr, Ni, and Pd in the mid-1970's.

Zirconium is relatively abundant (roughly as abundant as carbon) and relatively inexpensive ($11 per mole of 98% pure $ZrCl_4$, Strem Chemicals). Although discovered in 1824,4) the use of Zr and organozirconium compounds in organic synthesis had been virtually unknown until the mid-1970's with the exception of occasional uses of Zr salts as somewhat exotic Lewis acid catalysts in the Friedel–Crafts reaction5) and generally inferior substitutes for Ti salts in the Ziegler–Natta polymerization.6) One significant breakthrough was Schwartz' systematic investigation7) of hydrozirconation of alkenes and alkynes with $HZrCp_2Cl$ initiated in 1974 based on earlier preparation of $HZrCp_2Cl$8) and observation of its addition to alkenes and alkynes by Wailes, et al.9) Noting that hydrozirconation permits generation of synthetically attractive stereo- and regio-defined alkenylmetals but that the alkenylmetal derivatives of Zr are rather unreactive in a conventional sense,7b) we thought of their reaction with organic halides with Ni and Pd catalysts10,11) and discovered that Ni or Pd complexes containing phosphines were indeed very effective catalysts (Scheme 1). Our discovery was soon followed by that of Ni-catalyzed conjugate addition by Schwartz.12) Some other noteworthy breakthroughs include our discovery and development of Zr-catalyzed carboalumination of alkynes13) and Kaminsky's use of $Cp_2ZrCl_2$ and methyaluminoxanes as catalysts for alkene polymerization.14)

All of the reactions mentioned above involve $Cp_2Zr^{IV}$ derivatives. In principle, Zr compounds may also contain $Zr^{II}$ or $Zr^{III}$. It was therefore very striking that the first comprehensive monograph on organozirconium chemistry by Wailes,



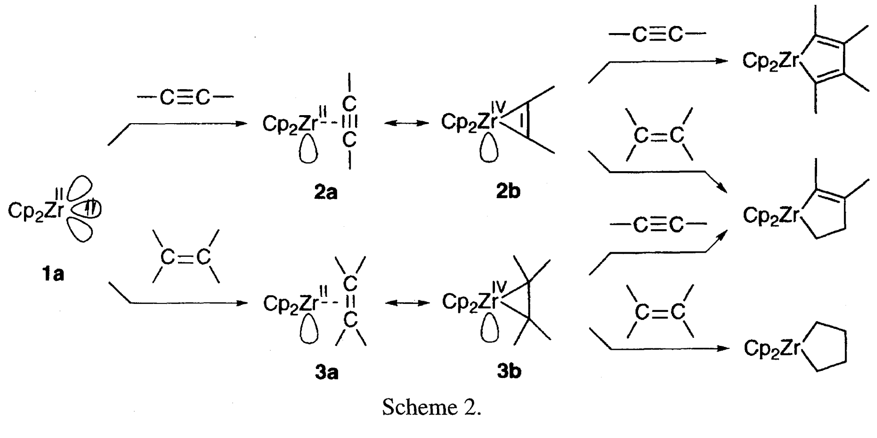
Scheme 1.

Courtts, and Weigold published in 1974[15] allocated less than a page on $Cp_2Zr^{II}$ chemistry. We became interested in exploring the chemistry of $Cp_2Zr^{II}$ derivatives with Schemes 2 and 3 in mind. Although essentially unknown, the parent $Cp_2Zr$ should be a 14-electron $Zr^{II}$ species, i.e., **1a** or **1b** (Chart 1). In its singlet form, i.e., **1a**, it should be capable of strongly interacting with a wide variety of compounds in concerted manners similar to the reactions of singlet carbenes. Thus, its reaction with alkynes and alkenes should produce the corresponding $\eta$-complexes **2a** and **3a**, respectively, or zirconacyclopropenes (**2b**) and zirconacyclopropanes (**3b**). The $\eta$-complexes **2a** and **3a** may be considered as $Cp_2Zr^{II}$ derivatives, while zirconacyclopropenes (**2b**) and zirconacyclopropanes (**3b**) may be viewed as $Cp_2Zr^{IV}$ species. Unless these exist a pair of two discrete isomeric species, which can be represented by **2a** and **2b** (or **3a** and **3b**), it is reasonable to view **2** and **3** as resonance hybrids in which **2a** and **2b** as well as **3a** and **3b** serve as resonance structures, respectively. It might be useful to equate **3a** and **3b**, respectively, to the Walsh model[16] and the more usual bent $\sigma$-bond structure of cyclopropane. All these considerations suggest that either of the two formalisms, i.e., $\eta$-complexes and three-membered metallacycles, may be used interchangeably. Inasmuch as these compounds are generated through reduction of $Cp_2Zr^{IV}$ species, we may arbitrarily view **2** and **3** as $Cp_2Zr^{II}$ derivatives. Complexation of **1a** with alkenes was expected to proceed stereospecifically with retention of configuration (vide infra). Significantly, the complexation products **2** and **3** with its second empty valence-shell orbital remaining intact should be capable of interacting with a second $\pi$ compound (compound containing $\pi$-orbitals) to undergo formal cyclic carbometallation to give the corresponding five-membered zirconacycles. We were especially attracted by the possibility that the reaction of $Cp_2Zr$ (**1**) with enynes would produce the corresponding zirconabicycles (Scheme 3) and that their carbonylation would give the corresponding ketones. At the time we initiated this investigation, the Pauson–Khand reaction[17] using $Co_2(CO)_8$ was known. Presumably due to the fact that $Co_2(CO)_8$ is coordinatively saturated 18-electron species, high reaction temperatures (100—200 °C) were typically employed. We reasoned that the simple MO considerations summarized in Scheme 3 should be applicable to practically all transition metals including Zr and that 14- and 16-electron species would allow the desired intramolecular cyclization under much milder conditions.

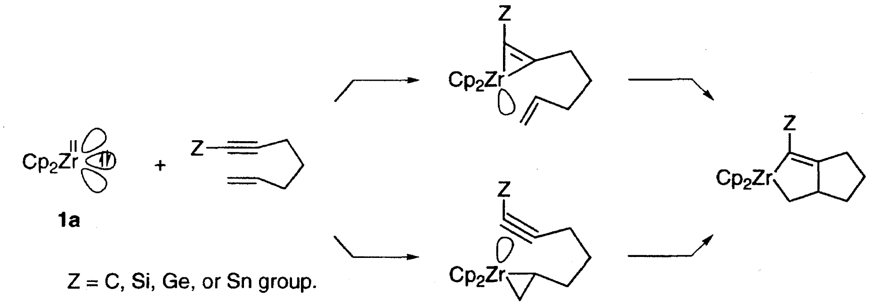
**1a** **1b**

Chart 1.

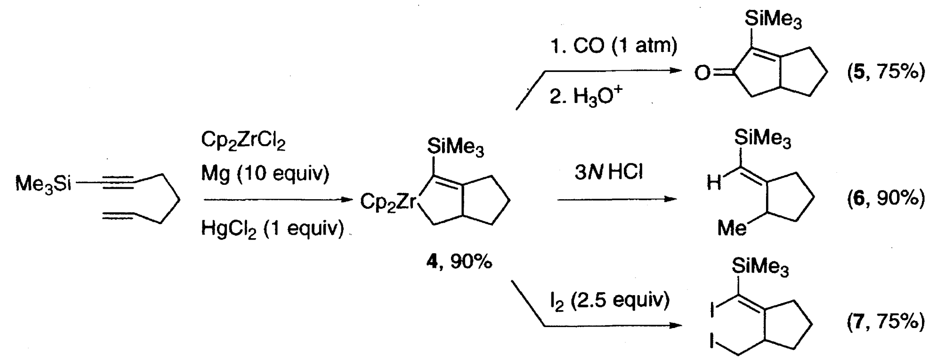
With the assumptions presented above in mind, we set out to devise a $Cp_2Zr$-promoted intramolecular cyclization of enynes and indeed found that 7-trimethylsilyl-1-hepten-6-yne reacted with a reagent generated in situ by treating $Cp_2ZrCl_2$ with Mg (10 molar amounts) and $HgCl_2$ to produce at 25 °C the desired zirconabicycle **4** in 90% yield.[18] The products showed two distinct singlets for the two Cp protons at 6.78 and 6.82 ppm in toluene-$d_6$. Its treatment with 1 atm of CO at 0 °C for 2 h gave **5** in 75% yield based on the starting enyne. Protonolysis of **4** with 3 M HCl (1 M = 1 mol dm$^{-3}$) provided **6** in 90% yield, while its iodinolysis with $I_2$ afforded **7** in 75% yield (Scheme 4). These highly satisfactory results prompted us to undertake a systematic



Scheme 2.



Scheme 3.



Scheme 4.

investigation of the chemistry of $\mathrm{Cp_2Zr^{II}}$ compounds, especially alkyne and alkene complexes of $\mathrm{Cp_2Zr}$. Prior to our study, some pioneering investigations by other workers in the late 1970's and early 1980's, notably those by Bercaw,[19] Erker,[20] Farona,[21] Nakamura,[22] Rausch,[23] and Schwartz[24] had contributed to the earlier development of this area. Over the past ten or a dozen years, we have presented several reviews of the chemistry of $\mathrm{Cp_2Zr^{II}}$ complexes with emphasis on their reactions, especially ring expansion and ring contraction.[25—31] In this Account, an overview of the preparation of the alkyne and alkene complexes of $\mathrm{Cp_2Zr}$ and their structure will be presented along with a brief discussion of some novel aspects of their reactions with the hope that, together with earlier reviews, a more complete and wholesome picture of the chemistry of $\mathrm{Cp_2Zr^{II}}$ derivatives would emerge.

## 1. Methods of Preparation of Alkyne and Alkene π-Complexes of Zirconocene

**14-Electron Zirconocene. Reality or Fiction?** An attempt to prepare $\mathrm{Cp_2Zr}$ by treating $\mathrm{Cp_2ZrCl_2}$ with Na-naphthalene was reported as early as 1966,[32] but the product was not identified. Later studies have shown that reduction of $\mathrm{Cp_2ZrCl_2}$ with metals, e.g., Na and Mg, in the presence of $\mathrm{PhC{\equiv}CPh}$[33] and bipyridine[34] can give $\mathrm{Cp_2Zr(PhC{\equiv}CPh)_2}$ and $\mathrm{Cp_2Zr(bpy)}$, respectively. Presumably, 14-electron $\mathrm{Cp_2Zr}$ or a loosely ligand-stabilized derivative was generated and trapped by the added reagent. Other derivatives of $\mathrm{Cp_2Zr}$, e.g., $\mathrm{Cp_2Zr(PR_3)_2}$, where $\mathrm{PR_3}$ is a phosphine, were also prepared.[35] Although these results may point to the generation of the parent $\mathrm{Cp_2Zr}$ as a transient species, its isolation and direct characterization do not appear to have been reported. Furthermore, the use of restricted amounts of trapping agents in the above reactions or thermal treatment of $\mathrm{Cp_2Zr^{II}L_2}$, e.g., $\mathrm{Cp_2Zr(PMe_2Ph)_2}$, can lead to the formation of much more stable dimeric $\mathrm{Zr^{III}}$ complexes **8** via C–H activation and dehydrogenation (Chart 2).[24b] While very interesting from structural and purely organometallic viewpoints, these dimeric species are rather unreactive and hence unattractive from the viewpoint of organic synthesis. Despite some ambiguities, it now appears reasonable to state that, contrary to our naive assumption, the parent 14-electron $\mathrm{Cp_2Zr}$ may well be much too reactive to be synthetically useful. Nor is it necessary to generate such a species. More realistic and desirable is to generate loosely ligand-protected 16-electron species which can serve as $\mathrm{Cp_2Zr}$ equivalents.

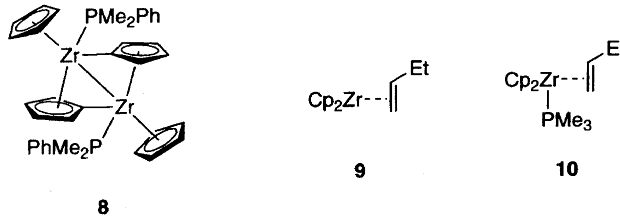


Chart 2.

**Alkene and Alkyne π-Complexes of Zirconocene as Reagents and Intermediates.** In our initial investigation of $\mathrm{Cp_2Zr}$-promoted enyne intramolecular cyclization, a combination of an excess of Mg and $\mathrm{HgCl_2}$ was used for reduction of $\mathrm{Cp_2ZrCl_2}$.[18] In search for a more convenient and favorable reagent, we used 2 molar amounts of $n$-BuLi[35] and obtained very favorable results.[36] This reagent has since been widely used not only by us but also by Nugent[37] and others, as detailed in our earlier reviews[26—30] and pertinent papers therein. As detailed later, the reaction of $\mathrm{Cp_2ZrCl_2}$ with $n$-BuLi produced $\mathrm{Cp_2Zr}$(1-butene) (**9**) acting as a "$\mathrm{Cp_2Zr}$" equivalent. Although we first thought mistakenly that treatment of **9** with $\mathrm{PMe_3}$ would produce $\mathrm{Cp_2Zr(PMe_3)_2}$[35] on the basis of the presence of two overlapping doublets for the Cp groups which was mistaken as a triplet, we soon noted that the product was actually $\mathrm{Cp_2Zr}$(1-butene)($\mathrm{PMe_3}$) (**10**).[36b] In addition to $\mathrm{Cp_2Zr}$(1-butene), a few other alkene-$\mathrm{ZrCp_2}$ complexes, e.g., $\mathrm{Cp_2Zr}$(ethylene)[38] and $\mathrm{Cp_2Zr}$(isobutylene),[39] have also been developed. Collectively, they serve as reagents that are synthetically equivalent to $\mathrm{Cp_2Zr}$

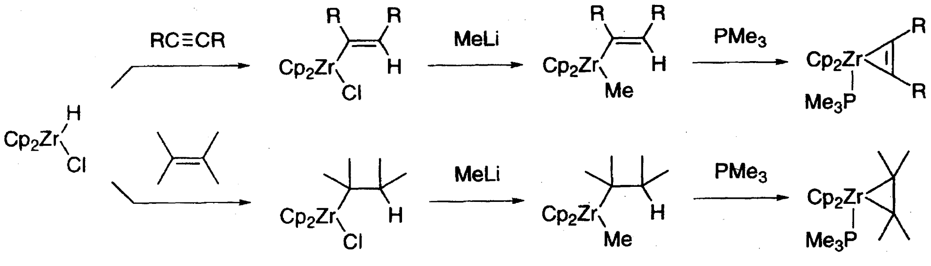
and alkene-providing intermediates (Negishi–Takahashi protocol, hereafter). Shortly after our initial publications, Buchwald et al. began publishing a series of papers[40] reporting related but different methods for the preparation of alkyne (and benzyne) complexes of $Cp_2Zr$ as intermediates based on earlier investigation by Erker[20] (Erker–Buchwald protocol, hereafter).

In the original Erker procedure,[20a] diphenylzirconocene was thermolyzed to induce $\beta$C–H activation leading to the formation of $Cp_2Zr$(benzyne). One of the two phenyl groups is lost as benzene. Since the aryl group is usually incorporated in the final organic products, loss of 50% of the aryl group as an arene could be a significant problem. Buchwald has provided a couple of potentially practical solutions to this problem, as summarized in Schemes 5 and 6.[40b,40c] It would be very desirable to be able to avoid the use of expensive and rather toxic $PMe_3$. Also desirable would be to develop more convenient routes to $HZrCp_2Cl$ and $MeZrCp_2Cl$ than the currently available ones. In the Erker–Buchwald protocol, the alkyne and alkene moieties of three-membered zirconacycles are introduced either via hydrozirconation or in the form of organolithiums.

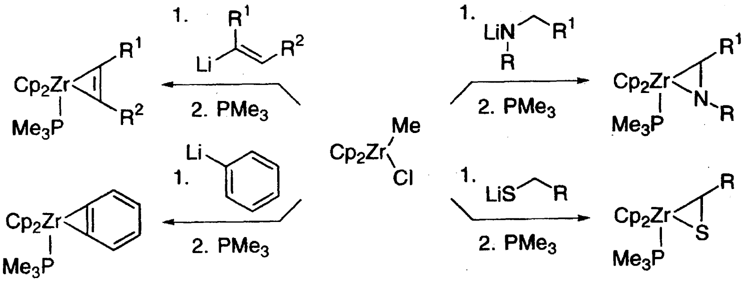
In the Negishi–Takahashi protocol, some readily available dialkylzirconocenes, e.g., $Cp_2Zr(n\text{-Bu})_2$, $Cp_2ZrEt_2$, and $Cp_2Zr(t\text{-Bu})(i\text{-Bu})$, are in situ generated and thermolyzed to generate alkene-zirconocene complexes in the presence of alkenes and alkynes (Schemes 7, 8, and 9). In cases where the initially generated alkene is replaced by another $\pi$ compound, as is often the case with $Cp_2Zr(n\text{-Bu})_2$ and $Cp_2Zr(t\text{-Bu})(i\text{-Bu})$, $Cp_2Zr$-alkene complexes act as reagents. On the other hand, the ethylene moiety of $Cp_2Zr$(ethylene) is often incorporated in the final organic products. Thus, $Cp_2Zr$(ethylene) acts as an intermediate.

It should be noted that the two main protocols discussed above are often complementary with each other. Although operationally somewhat elaborate, the Erker–Buchwald procedure is applicable to even those cases where $\eta$-ligands are highly unstable, e.g., benzyne and cycloalkynes. The contrasting behavior of $Cp_2Zr(n\text{-Bu})_2$ and $Cp_2ZrEt_2$ should also be clearly noted. Typically, it is not practical to generate $Cp_2Zr$-alkyne complexes using $Cp_2Zr(n\text{-Bu})_2$, because homodimerization of the alkynes used is usually the dominant path. It thus requires the use of a phosphine to achieve stepwise cross dimerization of two different alkynes.[41] On the other hand, $Cp_2ZrEt_2$ can be converted to zirconacyclopentenes in high yields, which can subsequently be treated with a different alkyne to achieve alkyne cross dimerization[42] (Scheme 10). In this reaction, ethylene acts as an inexpensive, convenient, and nontoxic substitute for phosphines.

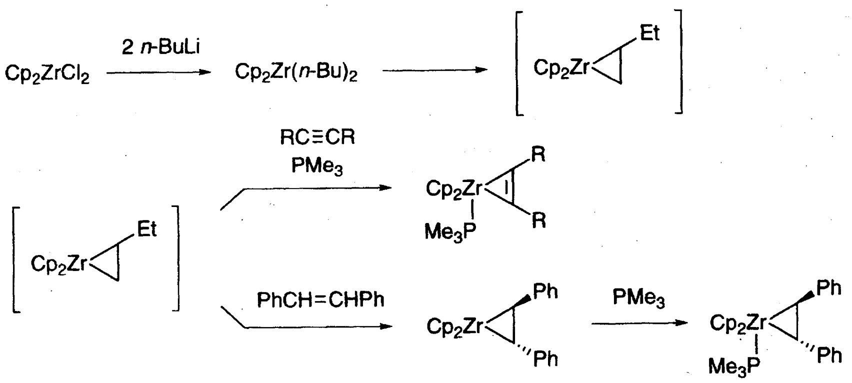
Unlike $Cp_2Zr$-alkene $\eta$-complexes, $Cp_2Zr$-alkyne $\eta$-complexes are generally unsuitable as $Cp_2Zr$ equivalents, because the alkyne



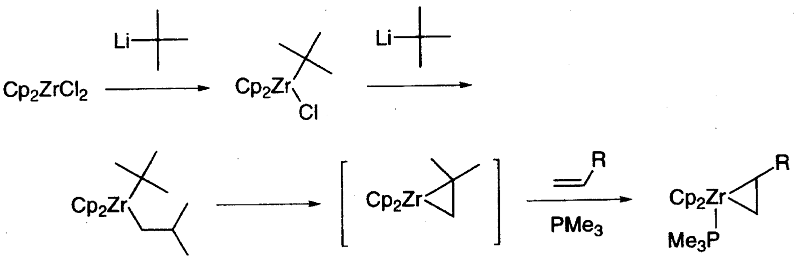
Scheme 5.



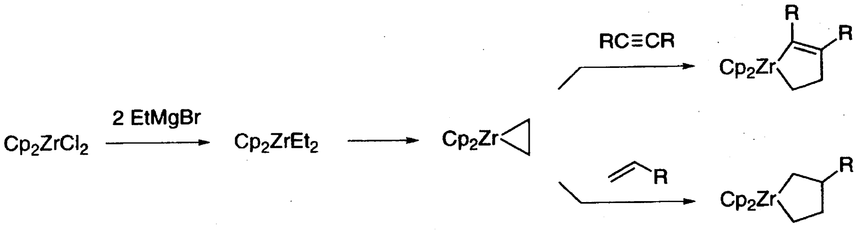
Scheme 6.



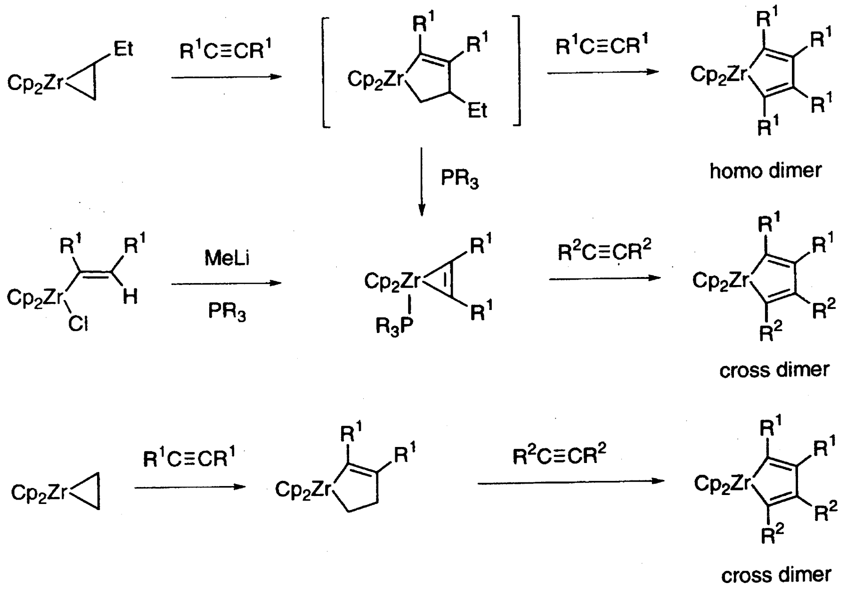
Scheme 7.



Scheme 8.



Scheme 9.

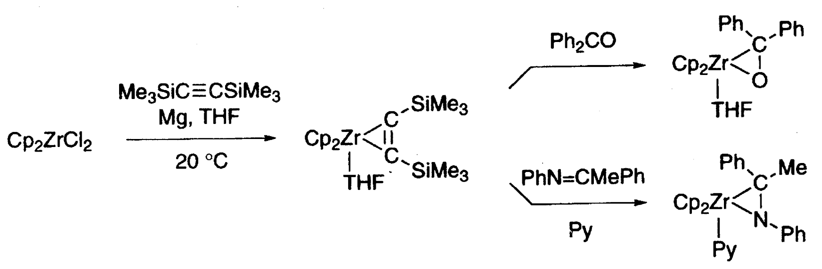


Scheme 10.

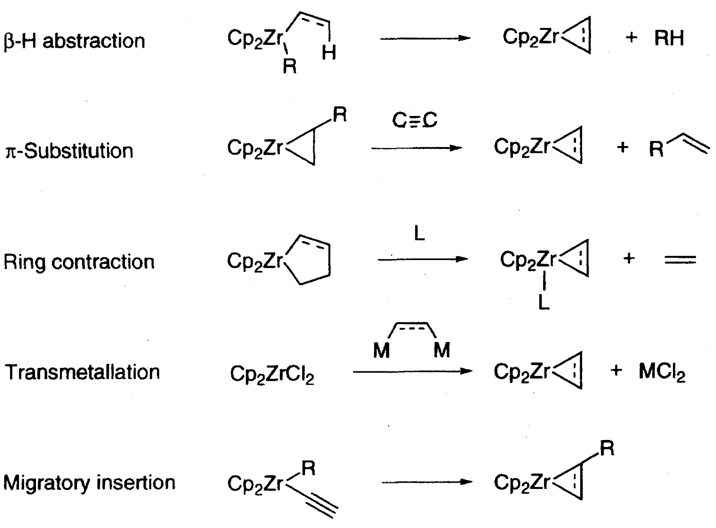
moiety is usually incorporated in the organic products. Recent studies by Rosenthal,[43] however, have shown that $Me_3SiC{\equiv}CSiMe_3$ does not homodimerize and that it can be readily displaced by other π-compounds. Consequently, $Cp_2Zr(Me_3SiC{\equiv}CSiMe_3)(THF)$ can serve as a "$Cp_2Zr$" equivalent,[44] even though the current synthetic scope is rather limited (Scheme 11).

## 2. Transformations Generating Alkene and Alkyne π-Complexes of Zirconocene

Over the past decade or two, several processes leading to the formation of alkene and alkyne η-complexes of zirconocene summarized in Scheme 12 have been found and investigated. As indicated in the preceding section, β-H



Scheme 11.

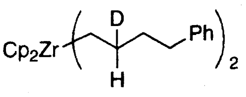


Scheme 12.

abstraction and π-substitution (an exchange of unsaturated compounds) are currently the two most important and widely employed processes. In this section, some detailed aspects of these processes are discussed.

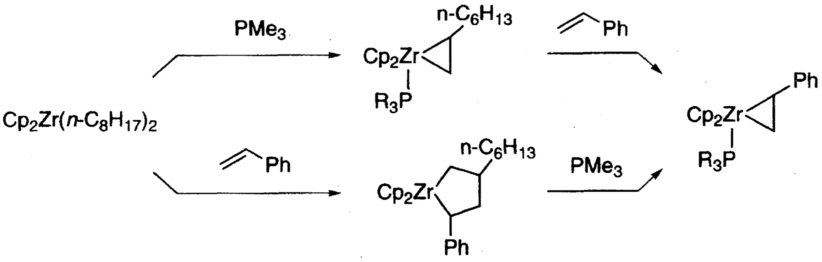
***β*-H Abstraction.** Thermal decomposition of diorganylzirconocenes containing one or more *β*-H atoms is a critically important process in both Negishi–Takahashi and Erker–Buchwald protocols discussed earlier. A detailed investigation of the thermal decomposition of dialkylzirconocenes indicates the following. First, it is a first-order non-dissociative process in which free 14-electron $Cp_2Zr$ is not generated at any moment. Thus, conversion of $Cp_2Zr(\textit{n}\text{-}C_8H_{17})_2$ into $Cp_2Zr$(1-octene)($PMe_3$) in the presence of $CD_2{=}CH(CH_2)_5CH_3$ and $PMe_3$ at −10 °C proceeded much faster than incorporation of $CD_2{=}CH(CH_2)_5CH_3$. At the point of 50% conversion, less than 5% of the dideuterated alkene was incorporated, even though a nearly 50 : 50 mixture of the deuterated and nondeuterated products were eventually obtained.[45] An earlier study[35] indicated that $PMe_3$ does not interact with diorganylzirconocenes. Nor does it affect the reaction rate. Its only role is to trap $Cp_2Zr$-alkene complexes. Similarly, thermal decomposition of $Cp_2Zr(\textit{n}\text{-}C_8H_{17})_2$ in the presence of styrene and $PMe_3$ initially produces only $Cp_2Zr$(1-octene)($PMe_3$), even though it is eventually converted to thermodynamically more favorable $Cp_2Zr$(styrene)($PMe_3$)[45] (Scheme 13). Second, the relative rates of *β*-H abstraction of $Cp_2ZrMeR$ as a function of R have been shown to be: *s*-Bu > *t*-Bu≈Et > *n*-Bu > *i*-Bu.[46] Clearly, the rates do not correlate well with the overall bulk of the R group, but they do correlate well with the degree of substitution at the *β*-carbon atom. Thus, the rates decrease in the order: *β*-methyl (i.e., *s*-Bu, *t*-Bu, and Et) > *β*-methylene (i.e., *n*-Bu) > *β*-methine (i.e., *i*-Bu). Third, a significant kinetic isotope effect of $k_H/k_D = 5.7$ has been observed with **11** (Chart 3).[46] All of these results indicate that the *β*-H abstraction reaction is a nondissociative process in which *β*-agostic interaction represented by **12** plays a crucial role. A concerted process involving direct conversion via intramolecular acid-base interaction may be proposed, although the intermediacy of **13** cannot be ruled out at this time (Scheme 14).

**π-Substitution via Ring Expansion and Ring Contraction.** Alkene and alkyne *η*-complexes of zirconocene are 16-electron species with one valence-shell empty orbital. They can therefore interact with alkenes and alkynes. Two major courses of the reaction are carbometallative ring expansion to produce the corresponding five-membered zirconacycles, as discussed in detail in previous reviews,[25—31] and *η*-ligand substitution involving substitution of the original π-compound with the added free π-compound. Some

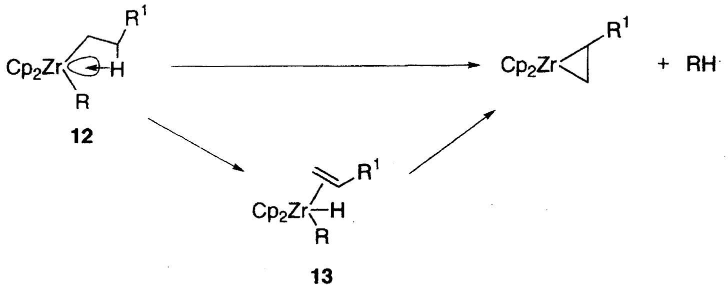


**11**

Chart 3.



Scheme 13.



Scheme 14.

results of our kinetic and product studies including the effects of an excess of an alkene indicate that π-substitution proceeds associatively. Since it has been shown at least in some cases that the corresponding five-membered zirconacycles can produce the same three-membered zirconacycles at comparable rates, they most likely serve as intermediates. Thus, π-substitution on $Cp_2Zr$ must proceed by an addition-elimination process shown in Scheme 15. In accord with this mechanism, preformed five-membered zirconacycles can also serve as the starting compounds for the preparation of $Cp_2Zr$ η-complexes. This ring contraction method has been applied to the synthesis of $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$.[47] Facile equilibration among three-membered and five-membered zirconacycles also provides a reasonable explanation for skeletal rearrangements, such as that shown in Scheme 16.[48]

**Transmetallation.** The potential scope of the transmetallation route to alkene and alkyne η-complexes of zirconocene appears to be very broad. However, it has thus far been applied mainly to the synthesis of $Cp_2Zr$-diene complexes.[22] Clearly, this process deserves to be more systematically explored.

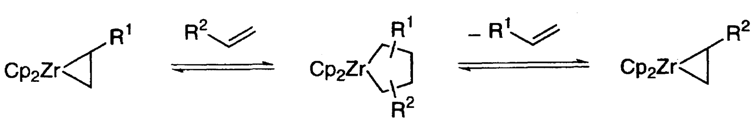
**Migratory Insertion.** This process represents yet another potentially general pattern for the synthesis of η-complexes of zirconocene. Indeed, migratory insertion of CO has been shown to be an attractive and potentially general route to $Cp_2Zr$ η-complexes with aldehydes and ketones.[49] The migratory insertion also appears to be useful for the synthesis of $Cp_2Zr$ η-complexes with imines and thiocarbonyl derivatives.[50]

We have found that even alkynyl groups can participate in a related migratory insertion reaction to give $Cp_2Zr$-alkyne complexes with a concomitant carbon-carbon bond formation[51] (Scheme 17). This reaction promises to provide a novel method for alkynyl-alkynyl coupling.

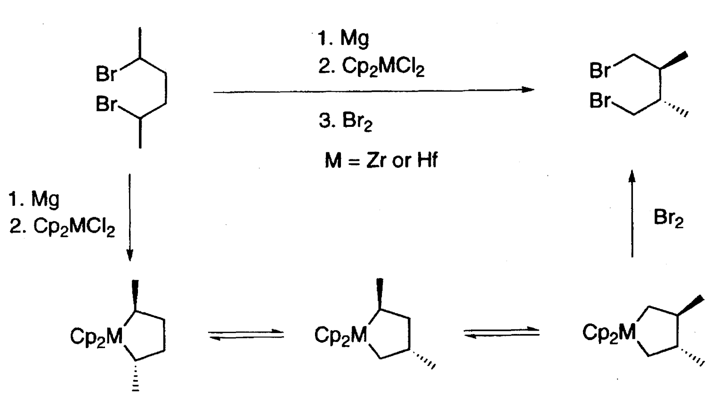
All of these several processes deserve to be further explored and investigated. Collectively, however, they provide even in the present forms satisfactory routes to a wide range of $Cp_2Zr$ η-complexes containing not only alkenes and alkynes but also carbonyl compounds and imines.

## 3. Structure of Alkene and Alkyne π-Complexes of Zirconocene

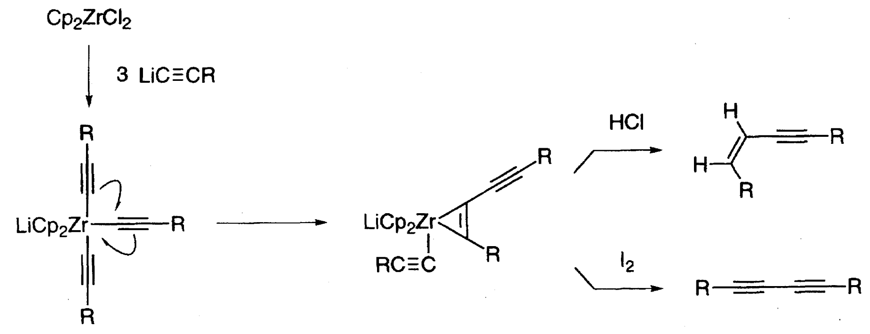
Aside from rather special cases of $Cp_2Zr$-diene complexes, e.g., $Cp_2Zr$ (*s-cis*-2,3-dimethylbutadiene),[52] $Cp_2Zr$-(*s-trans*-1,3-butadiene),[52] and $Cp_2Zr$(*s-trans*-1,4-diphenylbutadiene),[22b] the X-ray structures of alkene and alkyne η-complexes of zirconocene had not been obtained until 1986,[40a] even though some had been known since 1977[53] and characterized by NMR and other means. As we wrote a review of $Cp_2Zr$ chemistry,[25] we noted that full characterization and identification of η-complexes of zirconocene containing monoenes and monoynes had remained unknown



Scheme 15.



Scheme 16.



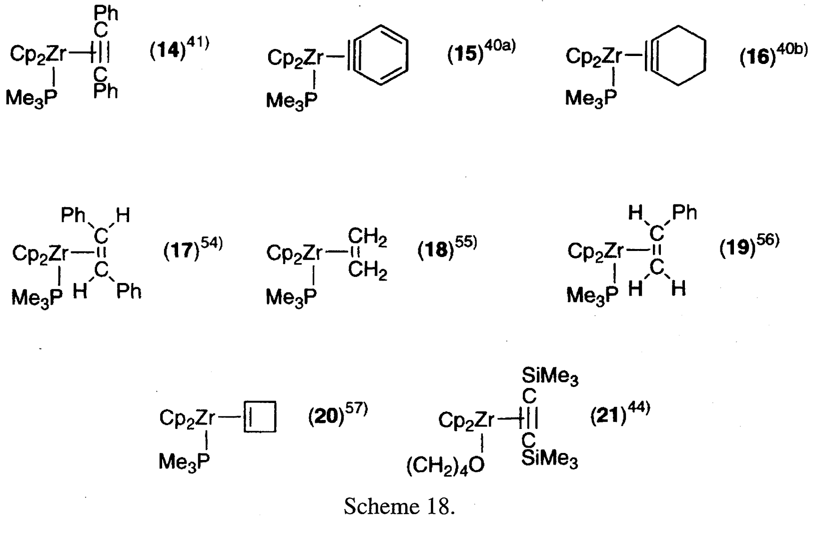
Scheme 17.

and began our efforts toward this goal. The reaction of PhC≡CPh with Cp$_2$Zr(*n*-Bu)$_2$ in the presence of PMe$_3$ according to Scheme 10 indeed gave the desired complex **14** as a crystalline compound, mp (decomp) 201—203 °C, which has been fully identified by elemental analysis, IR, $^1$H and $^{13}$C NMR, and X-ray analysis.[41] Although two other X-ray structures of Cp$_2$Zr-alkyne complexes, i.e., **15**[40a] and **16**,[40b] were reported during our investigation, our study demonstrated, for the first time, that free alkynes could react with "Cp$_2$Zr" and produce Cp$_2$Zr-alkyne complexes as discrete and fully identifiable species. We then prepared similarly Cp$_2$Zr(PhCH=CHPh)(PMe$_3$) (**17**) as the first example of crystalline Cp$_2$Zr-alkene complexes[54a] that can be isolated and fully identified and orally presented the results in the 13th International Conference on Organometallic Chemistry in Torino in September, 1988.[46] Shortly thereafter, the X-ray structure of Cp$_2$Zr(H$_2$C=CH$_2$)(PMe$_3$) (**18**) was reported by Alt.[55] The ORTEP structure of **17** is shown in Fig. 1 as the representative example. Since then a number of other X-ray structures of Cp$_2$Zr $\eta$-complexes with alkenes, alkynes, and their hetero analogues have been reported (Scheme 18). In cases where alkenes and alkynes are unsymmetrically substituted, mixtures of two possible stereoisomers in which sterically less encumbered distal isomers are favored over proximal isomers by a factor of roughly 5 to 10.[36b,56] Most of the crystalline complexes that have yielded their X-ray structures contain PMe$_3$. However, **21** contains THF as a stabilizing ligand.[44] X-Ray structures of 16-electron Cp$_2$Zr $\eta$-complexes with alkenes and alkynes appear to be unknown. Moreover, such complexes have been rarely characterized as such, even though they are undoubtedly synthetically most interesting and important. Formation of Cp$_2$Zr(PhCH=CHPh) in 80% yield was detected by $^1$H NMR ($\delta = 5.25$). In view of the X-ray structure of **21**, however, this complex too must be stabilized by THF used as a solvent.[41]

## 4. Novel Transformations of Akene and Akyne π-Complexes of Zirconocene

Once alkene and alkyne $\eta$-complexes of Cp$_2$Zr are generated, they can be subjected to a variety of synthetically interesting transformation. Their carbometallative ring expansion reactions with various π-compounds have been developed as useful synthetic processes and procedures. Since we have extensively reviewed the ring expansion reactions of three-membered zirconacycles,[26—31] their systematic discussion is not presented here. In this section, a variety of novel transformations of three-membered zirconacycles that can accompany and/or compete with the more usual ring expansion processes. These reactions are not only interesting in their own right but provide us with insights into various side reactions and unexpected observations encountered in the ring expansion reactions.

**Alkene Stereoisomerization. To What Extents Are the Reactions of Alkene and Alkyne π-Complexes of Zir-**



Scheme 18.

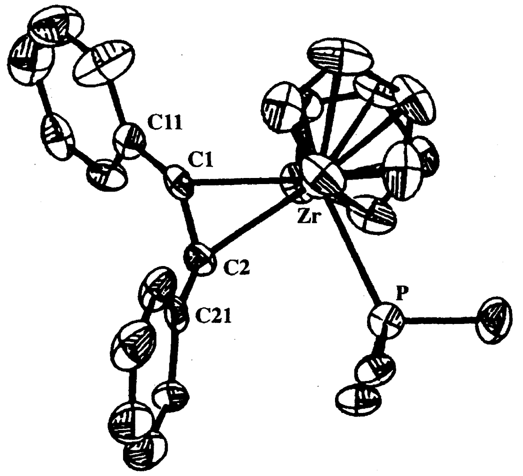
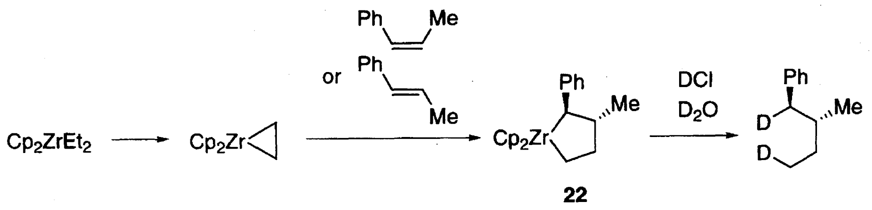
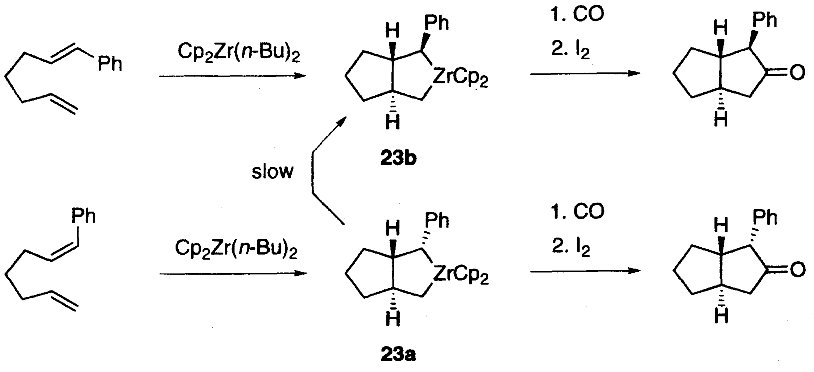


Fig. 1. Molecular structure and atom labeling scheme for $Cp_2Zr(PhCH{=}CHPh)(PMe_3)$. Selected bond length (Å) and angles (deg) are as follows. Zr–P = 2.715(5), Z–C1 = 2.361(15), Zr–C2 = 2.426(15), C1–C2 = 1.376(21), C1–C11 = 1.509(22), C2–C21 = 1.495(22), C1–Zr–C2 = 33.4(5), C11–C1–C2 = 127.2(14), C21–C2–C1 = 122.8(14), Zr–C1–C2 = 75.9(9), Zr–C2–C1 = 70.7(9), P–Zr–C1 = 114.5(4), P–Zr–C2 = 81.3(4), Zr–C1–C11 = 123.5(1), Zr–C2–C21 = 125.2(10).

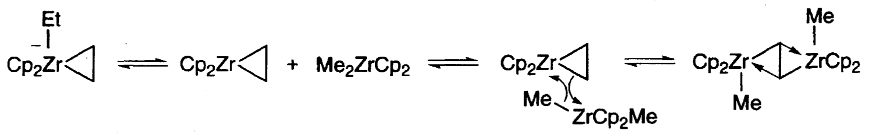
**conocene Concerted?** The reaction of $Cp_2Zr$(benzyne) with (*E*)- and (*Z*)-stilbene to give the corresponding zirconaindenes was reported to be stereospecific,[20c)] supporting the notion that ring expansion of three-membered zirconacycles and its microscopic reversal, i.e., ring contraction, are both stereospecific concerted processes. We were therefore surprised by our observation that either (*E*)- or (*Z*)-$\beta$-methylstyrene reacted with $Cp_2Zr$(ethylene) to give the identical *trans*-isomer of **22** even at −20 °C[58)] (Scheme 19). Although much slower, stereoisomerization of **23a** into **23b** was also observed[58)] (Scheme 20). It was also found that the formation of $Cp_2Zr$(stilbene) was stereoselective but nonstereospecific, producing only the *E*-isomer. In fact, (*Z*)-stilbene can be catalytically isomerized to the *E*-isomer by a catalytic amount of $Cp_2Zr$(stilbene).[58)] All of these results pointed to nonconcerted paths for some reactions of $Cp_2Zr$-alkene complexes. A detailed investigation has indicated that the stereoisomerization of stilbene occurs without any skeletal rearrangement. It is first-order in stilbene but second-order in the catalyst, i.e., $Cp_2Zr$(stilbene), and it is a polar (rather than radical) process in which a benzylic cation and zirconate anion play significant roles. Stilbene does not homodimerize on $Cp_2Zr$. Noting that many Lewis acid-catalyzed reactions, such as Friedel–Crafts reaction, often display second-order kinetics with respect to catalysts[5,59)] and that the 2 : 1 interaction of $Cp_2Zr$ with an alkene in a "sandwich" mode has been recently observed[60)] (Scheme 21), we proposed a mechanism shown in Scheme 22,[58)] which seem to accommodate all observed facts. We suggest that $Cp_2Zr$-alkene complexes can undergo nonconcerted polar processes and that they are more prone to doing so than the corresponding $Cp_2Zr$-alkyne complexes, which have not thus far displayed polar processes.



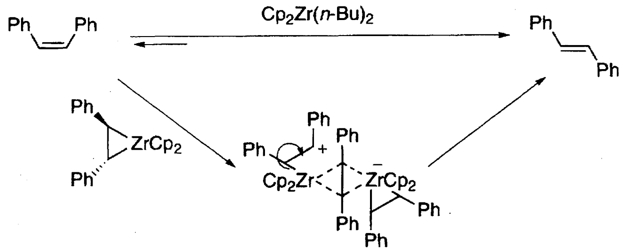
Scheme 19.



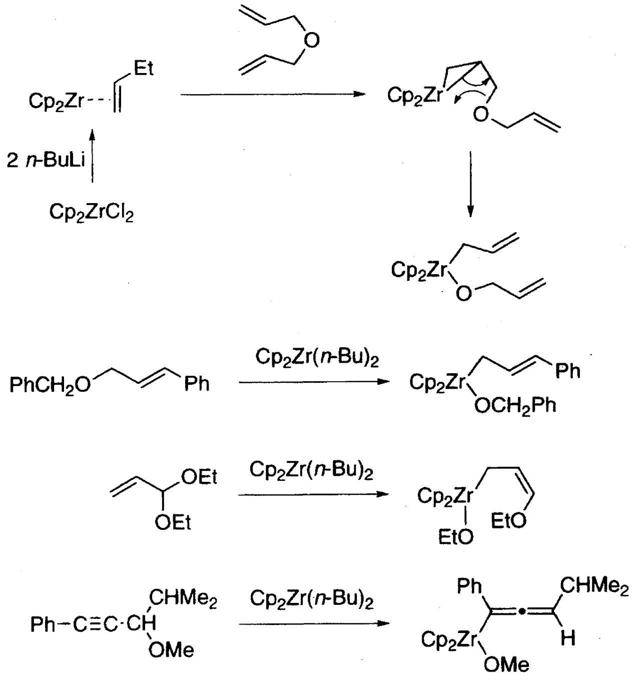
Scheme 20.



Scheme 21.



Scheme 22.



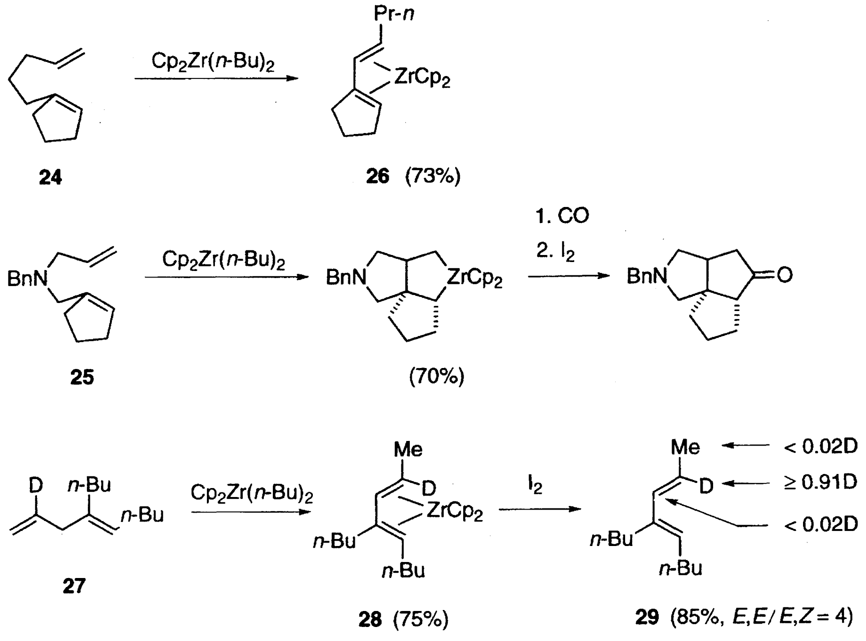
Scheme 24.

**Regioisomerization.** Zirconocene $\eta$-complexes with alkenes containing allylic hydrogens can additionally undergo regioisomerization in which the alkene and Cp$_2$Zr moieties migrate along carbon chains. We first noted it in unsuccessful attempts to intramolecularly cyclize 1-(4-pentenyl)-1-cyclopentene (**24**). Whereas its N analogue **25** underwent the desired intramolecular cyclization in 70% yield, **24** was converted only to a Cp$_2$Zr-diene complex **26** in 73% yield[61] (Scheme 23). In the reaction of 4-butyl-1,4-nonadiene-2*d* (**27**) with Cp$_2$Zr($n$-Bu)$_2$, **28** was obtained in 75% yield (Scheme 23). Its iodinolysis gave a 4 : 1 *E*, *E*/*E*, *Z* mixture of **29**, in which the D contents in the C1–C3 positions were $<0.02$, $\geq 0.91$, and $<0.02$, respectively.[61b] Thus, the D atom in the C2 position was not detectably scrambled, supporting the 1,3-H shift mechanism.

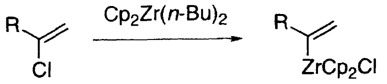
**Oxidative Addition of Allyl and Alkenyl Derivatives.** The stereo- and regioisomerization processes discussed above would be in most cases unwanted side reactions. In an attempt to observe Cp$_2$Zr-promoted intramolecular cyclization of diallyl ether, another unexpected side reaction was observed. Instead of producing the desired zirconabicycle, the reaction gave allyl(allyloxy)zirconocene via net oxidative addition of Cp$_2$Zr to diallyl ether, which must have proceeded by $\eta$-complexation-elimination[36d] (Scheme 24). This originally unwanted side reaction has proved to be a synthetically useful route to allylzirconocene derivatives, as eloquently demonstrated by Hanzawa and Taguchi.[62] A few additional examples of oxidative addition reported by them are also shown in Scheme 24.

Equally interesting is the oxidative addition reaction of Cp$_2$Zr(1-butene) with 2-chloro-1-alkenes[63] (Scheme 25). Further studies are clearly desirable to make this reaction synthetically useful.

**Effects of Countercations in Alkylating Agents.** As discussed in earlier sections, incorporation of alkyl groups into Cp$_2$Zr derivatives is most commonly achieved with al-



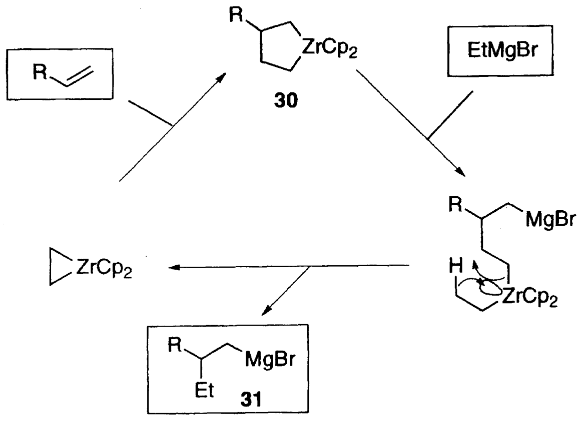
Scheme 23.



Scheme 25.

kylmetals containing Li, Mg, and Al. Although not yet widely used, those containing Zn may also prove to be useful. The alkylating ability of these alkylmetals decrease in the order: Li > Mg > Al. Zinc probably will be ranked between Mg and Al. Some significant differences among these metals have been observed. With most alkyllithiums, it is difficult to stop alkylation of $Cp_2ZrCl_2$ after introduction of one alkyl group to produce $RZrCp_2Cl$, where R is alkyl. Using just two molar amounts of alkyllithiums, dialkylzirconocenes can be obtained in high yields. Unlike Grignard reagents, however, alkyllithiums have not been very useful reagents for generating dialkylzirconocenes in Zr-catalyzed reactions. We have recently found that the third molar amounts of alkyllithiums can readily displace one of the two Cp groups from $Cp_2ZrR_2$ to produce $CpZrR_3$, where R is alkyl.[64)] Undoubtedly, this is at least partially responsible for the difficulty mentioned above.

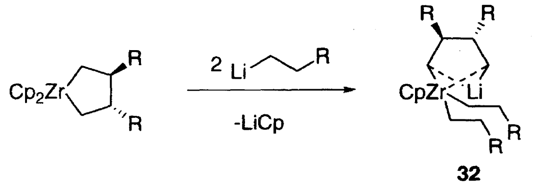
Grignard reagents, on the other hand, do not show this tendency, and $Cp_2ZrR_2$ can be generated in the presence of an excess of the Grignard reagent used. However, we have found that zirconacyclopentanes generated from $Cp_2ZrR_2$ and alkenes can react with the third molar amount of the Grignard reagent to undergo transmetallation or σ-bond metathesis to generate dialkylzirconocenes in which one of the alkyl groups contains Mg, which, in turn, can undergo $\beta$-H abstraction. Specifically, the reaction of $Cp_2ZrCl_2$ with just two molar amounts of EtMgBr and one equimolar amount of 1-alkene ($RCH{=}CH_2$) cleanly and selectively produces 3-alkyl-substituted zirconacyclopentane (**30**).[65)] If, on the other hand, the third molar amount of EtMgBr is present, it will react with **30** to undergo transmetallation followed by $\beta$-H abstraction to give 2-ethylalkylmagnesium bromide (**31**) and $Cp_2Zr$(ethylene), which can be trapped as its $PMe_3$ complex (Scheme 26). We then discovered[65)] that this entire sequence would amount to the mechanism of Dzhemilev's Zr-catalyzed ethylmagnesiation of 1-alkenes with ethylmagnesium derivatives.[66)] One can imagine how difficult the task of establishing this highly intricate and circuitous mechanism might have been, if the mechanistic clarification were the main goal and if one started only with the facts available in the original synthetic papers. We find it to be an eloquent example supporting the significance of serendipity and systematic basic investigations in science.



Scheme 26.

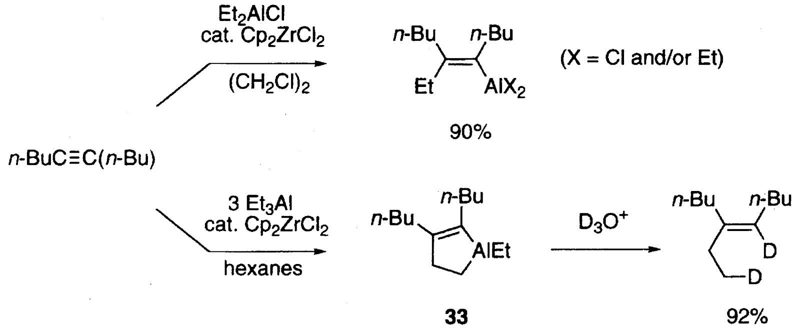
As might be expected, alkyllithiums can also react with zirconacyclopentanes, but their mode of reaction is different from that of Grignard reagent. Once again, it involves displacement of one of the two Cp rings, and a novel type of zirconate-like bimetallic species **32**, in which the 1,4-alkanediylidene moiety is fluxional on the NMR time scale[64)] (Scheme 27).

It should be noted that the reaction of $Cp_2ZrCl_2$ with just one molar amount of a Grignard reagent (RMgX) does not generally produce $RZrCp_2Cl$ in high yield, because the formation of $R_2ZrCp_2$ is very competitive. With some sterically hindered Grignard reagents, e.g., *t*-BuMgCl, however, it is feasible to prepare the corresponding $RZrCp_2Cl$, which can serve as convenient hydrozirconating agents.[67)] In sharp contrast, alkylaluminium compounds appear to be incapable of dialkylating $Cp_2ZrCl_2$. With one molar amount of $Me_3Al$ or $Et_3Al$, monoalkylation proceeds up to 60—70% without a sign of dialkylation.[13b,68,69)] We were therefore puzzled by the fact that the reaction of 5-decyne with $Et_2AlCl$ and $Et_3Al$ catalyzed by $Cp_2ZrCl_2$ proceeded in two totally different manners. Whereas the reaction of $Et_2AlCl$ must involve a straightforward carbometallation process, that of $Et_3Al$ has turned out to be cyclic. Interestingly, this cyclic process proceeded faster and more cleanly in hexanes than in 1,2-dichloroethane. On deuterolysis, one and two D atoms are incorporated, respectively (Scheme 28). The results strongly indicated that the cyclization product could be represented by an aluminacycle **33**.[69)] For the cyclic process with $Et_3Al$, we first considered a dialkylative and monometallic process in which $Cp_2Zr$(ethylene) and a zirconacyclopentene **34** might act as intermediate (Scheme 29), despite the fact that $Et_3Al$ does not dialkylate $Cp_2ZrCl_2$ to a detectable extent. We felt that this might be a case to which the Curtin–Hammett principle would apply. When a preformed, pure sample of **34** failed to initiate the reaction of 5-decyne with $Et_3Al$, our long and laborious search for the correct mechanism began. Detailed description of this aspect of our work may be found in a full paper[69)] and another review[31)] and therefore will not be repeated here. In short, $Cp_2ZrCl_2$ reacts with $Et_3Al$ to produce a relatively stable 1 : 1 complex **35** which undergoes only a straightforward ethylalumination with alkynes. If an excess of $Et_3Al$ is present, the second molar amount of $Et_3Al$ replaces $Et_2AlCl$ once in a while to generate **36**

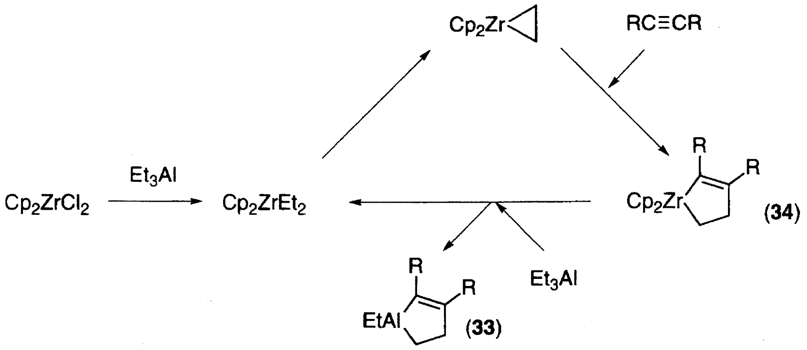


Scheme 27.

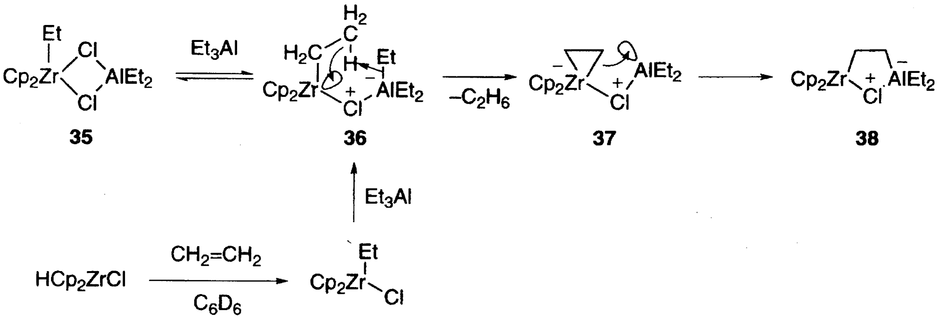
which undergoes a monoalkylative and bimetallic βC-H activation requiring (i) $Cp_2ZrEt$, (ii) $Et_3Al$ but not $Et_2AlCl$, and (iii) an active Cl that can bind Al and Zr to give **37** and eventually **38**. Formally, formation of **38** involves a σ-bond



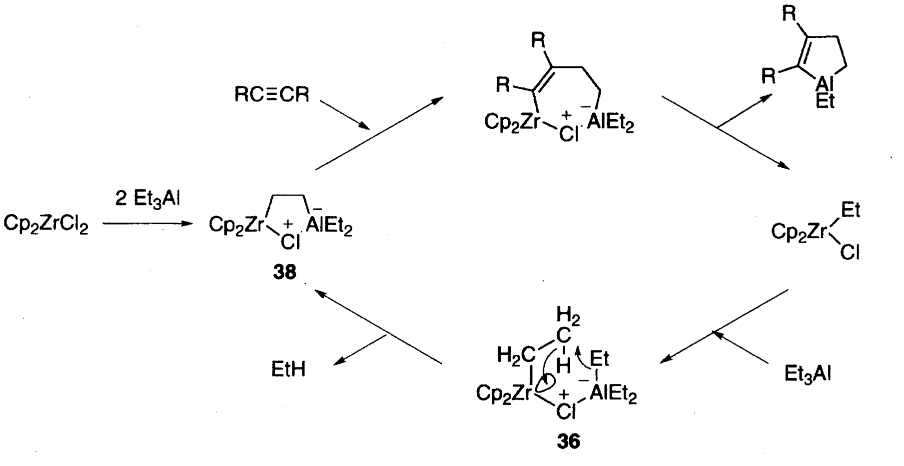
Scheme 28.



Scheme 29.



Scheme 30.



Scheme 31.

metathesis of $Cp_2Zr$(ethylene) and $Et_2AlCl$. As expected, **38** could be much more readily and cleanly generated by treatment of Al-free $EtZrCp_2Cl$ with $Et_3Al$ (Scheme 30).[69] The overall reaction mechanism has been established as shown in Scheme 31.[69] These results clearly indicate that alkylmetals are not mere alkylating agents and that significant and major differences can result depending on the countercations.

## 5. Conclusion

While $Cp_2Zr$, a monomeric 14-electron compound, remains to be an elusive species or perhaps a species to be avoided for synthetic purposes, its alkene and alkyne $\eta$-complexes can be generated as either 16- or 18-electron species. Many of them can be isolated as stable 18-electron species stabilized by phosphines and other 2-electron donors and characterized by spectroscopic methods including X-ray analysis. A few of the convenient methods for their generation involve in situ generation of diorganylzirconocenes followed by their $\beta$-H abstraction reaction, although several other different processes also offer attractive alternatives. Alkene and alkyne $\eta$-complexes of zirconocenes may be viewed as either $Cp_2Zr^{II}$ $\eta$-complexes or $Cp_2Zr^{IV}$-containing zirconacyclopropanes and zirconacyclopropenes. The currently available data suggest that their structures may be best represented by resonance hybrids of the two extremes mentioned above. Although not extensively discussed here, a variety of reactions of alkene and alkyne $\eta$-complexes of zirconocene, most notably their ring expansion reactions to produce five-membered zirconacycles, have been developed as synthetically useful processes. Concurrently, discoveries and investigations of their novel and often unexpected transformations have provided a more wholesome and realistic picture of the chemistry of $Cp_2Zr^{II}$ derivatives. Thus, various reactions including stereoisomerization proceeding via a nonconcerted polar process and regioisomerization via 1,3-H shift as well as skeletal rearrangement and oxidative addition can compete with their $\eta$-ligand substitution, ring expansion, and ring contraction processes. Another significant recent finding is that the counteractions of the organometals used to alkylate $Cp_2Zr$ derivatives have profound effects on the courses of both stoichiometric and catalytic reactions of $Cp_2Zr$ derivatives. It is hoped that these new findings will be exploited in further developing the chemistry of $Cp_2Zr$ derivatives.

### References

1) For a review of the use of the Main Group metals, see, for example: E. Negishi, "Organometallics in Organic Synthesis," John Wiley & Sons, New York (1980), Vol. 1, p. 532.

2) For a review of the use of the transition metals, see, for example: J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, CA (1987), p. 989.

3) a) G. H. Posner, *Org. React.*, **22**, 253 (1975); b) B. H. Lipshutz, in "Organometallics in Synthesis," ed by M. Schlosser, Wiley, New York (1994), p. 283.

4) J. J. Berzelius, *Ann. Chim. Phys.*, **26**, 43 (1824).

5) G. A. Olah, "Friedel–Crafts and Related Reactions," Interscience, New York (1963), Vol. 1, p. 1031.

6) J. Boor, "Ziegler–Natta Catalysis and Polymerization," Academic Press, New York (1978), p. 670.

7) a) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 8115 (1974); b) J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, **15**, 333 (1976).

8) P. C. Wailes and H. Weigold, *J. Organomet. Chem.*, **24**, 405 (1970).

9) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organomet. Chem.*, **27**, 373 (1971).

10) E. Negishi and D. E. Van Horn, *J. Am. Chem. Soc.*, **99**, 3168 (1977).

11) a) N. Okukado, D. E. Van Horn, W. L. Klima, and E. Negishi, *Tetrahedron Lett.*, **1978**, 1027; b) E. Negishi, N. Okukado, A. O. King, D. E. Van Horn, and B. I. Spiegel, *J. Am. Chem. Soc.*, **100**, 2254 (1978).

12) a) M. J. Loots and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 8045 (1977); b) M. J. Loots and J. Schwartz, *Tetrahedron Lett.*, **1978**, 4381.

13) a) D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.*, **100**, 2252 (1978); b) E. Negishi, D. E. Van Horn, and T. Yoshida, *J. Am. Chem. Soc.*, **107**, 6639 (1985).

14) a) W. Kaminsky, H.-J. Vollmer, E. Heins, and H. Sinn, *Makromol. Chem.*, **175**, 443 (1974); b) H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, **18**, 99 (1980).

15) P. C. Wailes, R. S. P. Courtts, and H. Wiegold, "Organometallic Chemistry of Titanium, Zirconium, and Hafnium," Academic Press, New York (1974), p. 302.

16) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

17) a) I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, and M. I. Foreman, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 977; b) N. E. Schore, in "Comprehensive Organic Synthesis," ed by L. A. Paquette, Pergamon Press, Oxford (1991), Vol. 5, p. 1037.

18) E. Negishi, S. J. Holmes, J. M. Tour, and J. A. Miller, *J. Am. Chem. Soc.*, **107**, 2568 (1985).

19) a) D. R. McAlister, D. K. Erwin, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 5966 (1978); b) J. E. Bercaw, D. H. Berry, A. J. Jircitano, and K. B. Mertes, *J. Am. Chem. Soc.*, **104**, 4712 (1982).

20) a) G. Erker and K. Kropp, *J. Am. Chem. Soc.*, **101**, 3659 (1979); b) G. Erker, J. Wicher, K. Engel, and C. Krüger, *Chem. Ber.*, **115**, 3300 (1982); c) K. Kropp and G. Erker, *Organometallics*, **1**, 1246 (1982).

21) S. Thanedar and M. F. Farona, *J. Organomet. Chem.*, **235**, 65 (1982).

22) a) H. Yasuda, Y. Kajihara, K. Mashima, K. Lee, and A. Nakamura, *Chem. Lett.*, **1981**, 519; b) For a review, see: H. Yasuda, K. Tatsumi, and A. Nakamura, *Acc. Chem. Res.*, **18**, 120 (1985).

23) H. G. Alt and M. D. Rausch, *J. Am. Chem. Soc.*, **96**, 5936 (1974).

24) a) K. I. Gell and J. Schwartz, *J. Chem. Soc., Chem. Commun.*, **1979**, 244; b) K. I. Gell, T. V. Harris, and J. Schwartz, *Inorg. Chem.*, **20**, 481 (1981).

25) E. Negishi and T. Takahashi, *Aldrichim. Acta*, **18**, 31 (1985).

26) E. Negishi, *Acc. Chem. Res.*, **20**, 65 (1987).

27) E. Negishi and T. Takahashi, *Synthesis*, **1988**, 1.

28) E. Negishi, *Chem. Scripta*, **29**, 457 (1989).

29) E. Negishi, in "Comprehensive Organic Synthesis," ed by L. A. Paquette, Pergamon Press, Oxford (1991), Vol. 5, p. 1163.

30) E. Negishi and T. Takahashi, *Acc. Chem. Res.*, **27**, 124 (1994).

31) E. Negishi and D. Y. Kondakov, *Chem. Soc. Rev.*, **26**, 417

(1996).

32) G. W. Watt and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **88**, 5926 (1966).

33) G. W. Watt and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **92**, 826 (1970).

34) P. C. Wailes and H. Weigold, *J. Organomet. Chem.*, **28**, 91 (1971).

35) E. Negishi, F. E. Cederbaum, and T. Takahashi, *Tetrahedron Lett.*, **27**, 2829 (1986).

36) a) E. Negishi, D. R. Swanson, F. E. Cederbaum, and T. Takahashi, *Tetrahedron Lett.*, **28**, 917 (1987); b) E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson, and T. Takahashi, *J. Am. Chem. Soc.*, **111**, 3336 (1989); c) D. R. Swanson, C. J. Rousset, E. Negishi, T. Takahashi, T. Seki, M. Saburi, and Y. Uchida, *J. Org. Chem.*, **54**, 3521 (1989); d) C. J. Rousset, D. R. Swanson, F. Lamaty, and E. Negishi, *Tetrahedron Lett.*, **30**, 5105 (1989); e) E. Negishi and S. R. Miller, *J. Org. Chem.*, **54**, 6014 (1989).

37) a) W. A. Nugent, D. L. Thorn, and R. L. Harlow, *J. Am. Chem. Soc.*, **109**, 2788 (1987); b) T. V. RajanBabu, W. A. Nugent, D. F. Taber, and P. J. Fagan, *J. Am. Chem. Soc.*, **110**, 7128 (1988).

38) a) T. Takahashi, N. Suzuki, M. Kageyama, Y. Nitto, M. Saburi, and E. Negishi, *Chem. Lett.*, **1991**, 1579; b) T. Takahashi, Y. Nitto, T. Seki, M. Saburi, and E. Negishi, *Chem. Lett.*, **1990**, 2259.

39) D. R. Swanson and E. Negishi, *Organometallics*, **10**, 825 (1991).

40) a) S. L. Buchwald, B. T. Watson, and J. C. Huffman, *J. Am. Chem. Soc.*, **108**, 7411 (1986); b) S. L. Buchwald, R. T. Lum, and J. C. Dewan, *J. Am. Chem. Soc.*, **108**, 7441 (1986); c) S. L. Buchwald, B. T. Watson, and J. C. Huffman, *J. Am. Chem. Soc.*, **109**, 2544 (1987); d) For a review, see: S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, **88**, 1047 (1988).

41) T. Takahashi, D. R. Swanson, and E. Negishi, *Chem. Lett.*, **1987**, 623.

42) a) T. Takahashi, M. Kageyama, V. Denisov, R. Hara, and E. Negishi, *Tetrahedron Lett.*, **34**, 687 (1993); b) Z. Xi, R. Hara, and T. Takahashi, *J. Org. Chem.*, **60**, 4444 (1995).

43) U. Rosenthal, A. Ohff, M. Michalek, H. Görls, V. V. Burlakov, and V. B. Shur, *Angew. Chem., Int. Ed. Engl.*, **32**, 1193 (1993).

44) A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V. V. Burlakov, and U. Rosenthal, *Synlett*, **1996**, 111.

45) E. Negishi, D. R. Swanson, and T. Takahashi, *J. Chem. Soc., Chem. Commun.*, **1990**, 1254.

46) E. Negishi, T. Nguyen, J. P. Maye, D. Choueiry, N. Suzuki, and T. Takahashi, *Chem. Lett.*, **1992**, 2367.

47) T. Takahashi, M. Tamura, M. Saburi, Y. Uchida, and E. Negishi, *J. Chem. Soc., Chem. Commun.*, **1989**, 852.

48) T. Takahashi, T. Fujimori, T. Seki, M. Saburi, Y. Uchida, C. J. Rousset, and E. Negishi, *J. Chem. Soc., Chem. Commun.*, **1990**, 182.

49) a) D. A. Straus and R. H. Grubbs, *J. Am. Chem. Soc.*, **104**, 5499 (1982); b) E. J. Moore, D. A. Straus, J. Armantrout, B. D. Santarsiero, R. H. Grubbs, and J. E. Bercaw, *J. Am. Chem. Soc.*, **105**, 2068 (1983); c) S. C. H. Ito, D. A. Straus, J. Armantrout, W. P. Schaefer, and R. H. Grubbs, *J. Am. Chem. Soc.*, **106**, 2210 (1984); d) R. M. Waymouth, B. D. Santarsiero, R. J. Coots, M. J. Bronikowski, and R. H. Grubbs, *J. Am. Chem. Soc.*, **108**, 1427 (1986).

50) J. M. Davis, R. J. Whitby, and A. Jaxa-Chamiec, *Tetrahedron Lett.*, **33**, 5655 (1992).

51) K. Takagi, C. J. Rousset, and E. Negishi, *J. Am. Chem. Soc.*, **113**, 1440 (1991).

52) G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, and C. Krüger, *J. Am. Chem. Soc.*, **102**, 6344 (1980).

53) G. Erker, *J. Organomet. Chem.*, **134**, 189 (1977).

54) a) T. Takahashi, M. Murakami, M. Kunishige, M. Saburi, Y. Uchida, K. Kozawa, T. Uchida, D. R. Swanson, and E. Negishi, *Chem. Lett.*, **1989**, 761; b) T. Takahashi, Y. Uchida, T. Uchida, and E. Negishi, "13th International Conference on Organometallic Chemistry," Torino, September 1988, Abstr., No. 187.

55) H. G. Alt, C. E. Denner, U. Thewalt, and M. D. Rausch, *J. Organomet. Chem.*, **356**, C83 (1988).

56) P. Binger, P. Müller, R. Benn, A. Rufinska, B. Gabor, C. Krüger, and P. Betz, *Chem. Ber.*, **122**, 1035 (1989).

57) R. A. Fisher and S. L. Buchwald, *Organometallics*, **9**, 871 (1990).

58) E. Negishi, D. Choueiry, T. B. Nguyen, D. R. Swanson, N. Suzuki, and T. Takahashi, *J. Am. Chem. Soc.*, **116**, 9751 (1994).

59) See, for example: F. A. Carey and R. J. Sundberg, "Advanced Organic Chemistry," Part A, 3rd ed, Plenum Press, New York (1990), p. 570.

60) T. Takahashi, K. Kasai, N. Suzuki, K. Nakajima, and E. Negishi, *Organometallics*, **13**, 3413 (1994).

61) a) J. P. maye and E. Negishi, *Tetrahedron Lett.*, **34**, 3359 (1993); b) E. Negishi, J. P. Maye, and D. Choueiry, *Tetrahedron*, **51**, 4447 (1995).

62) a) H. Ito, T. Taguchi, and Y. Hanzawa, *Tetrahedron Lett.*, **33**, 1295 (1992); b) H. Ito, T. Nakamura, T. Taguchi, and Y. Hanzawa, *Tetrahedron Lett.*, **33**, 3769 (1992); c) H. Ito, Y. Ikeuchi, T. Taguchi, and Y. Hanzawa, *J. Am. Chem. Soc.*, **116**, 5469 (1994); d) H. Ito, T. Nakamura, T. Taguchi, and Y. Hanzawa, *Tetrahedron*, **51**, 4507 (1995).

63) T. Takahashi, M. Kotora, R. Fischer, Y. Nishihara, and K. Nakajima, *J. Am. Chem. Soc.*, **117**, 11039 (1995).

64) D. Y. Kondakov and E. Negishi, *J. Chem. Soc., Chem. Commun.*, **1996**, 963.

65) a) T.Takahashi, T. Seki, M. Saburi, and E. Negishi, "XIVth International Conference on Organometallic Chemistry," Detroit, MI (1990), Abstr., No. B17; b) T. Takahashi, T. Seki, Y. Nitto, M. Saburi, C. J. Rousset, and E. Negishi, *J. Am. Chem. Soc.*, **113**, 6266 (1991).

66) a) U. M. Dzhemilev, O. S. Vostrikova, and R. M. Sultanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1983**, 219; b) For a review, see: U. M. Dzhemilev, O. S. Vostrikova, and G. A Tolstikov, *J. Organomet. Chem.*, **304**, 17 (1986).

67) E. Negishi, J. A. Miller, and T. Yoshida, *Tetrahedron Lett.*, **25**, 3407 (1984).

68) E. Negishi and T. Yoshida, *J. Am. Chem. Soc.*, **103**, 4095 (1981).

69) E. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai, and T. Takahashi, *J. Am. Chem. Soc.*, **118**, 9577 (1996).

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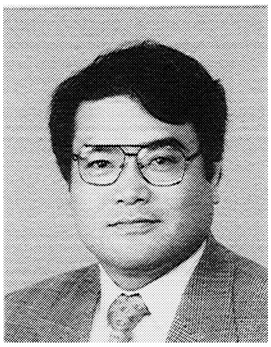

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