Group 4 Metal Complexes of Benzynes, Cycloalkynes, Acyclic Alkynes, and Alkenes

STEPHEN L. BUCHWALD* and RALPH B. NIELSEN

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Contents

I. Introduction

Transition metals have the ability to stabilize highly reactive organic fragments and also to activate stable molecules toward selective attack. A large number of transition-metal complexes of small organic molecules have been prepared, but syntheses of such species are frequently limited to a specific type of organic fragment bound to a particular metal system. Few general strategies lend themselves to the preparation of a wide variety of fragments bound to a specific metal or to a particular fragment bound to a wide variety of metals. As a result, few structure-reactivity relationships have been mapped in organometallic chemistry. This paper will discuss recent research into the preparation, characterization, and reactivity of two-carbon fragments (i.e., alkynes and alkenes) bound to a single group 4 (Ti, Zr, Hf) metal center, in the hope that the initial outlines of such structure-reactivity relationships will be discernible.

Of the many transition-metal complexes of alkynes, alkenes, aldehydes, and ketones which have been prepared, relatively few involve group 4 metals. Strategies for the preparation of later transition-metal complexes of such molecules usually involve the direct combination of the unsaturated organic fragment and a coordinatively unsaturated metal center. However, low-valent, coordinatively unsaturated group 4 species are unstable and difficult to prepare. When such metal centers bind alkynes, alkenes, or thioaldehydes, the high degree of π-back-bonding from the metal to the organic fragment often makes the resulting complex behave more like a metallacyclopropene, metallacyclopropane, or metallathiirane. These complexes have been studied for a number of reasons, including intrinsic interest in their structure and reactivity, the desire to model catalytic processes such as Fischer–Tropsch chemistry and hydrogenation, and because such species may be of practical use as vehicles for olefin and acetylene polymerization and for achieving selective transformations of use in organic synthesis.

SCHEME 1
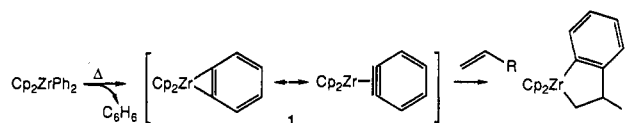
Much of this paper will deal with our work at MIT where we have developed a relatively general route to complexes of a variety of organic fragments bound to a single metal system, zirconocene.[1] Our goals in this area have been the understanding of structure-reactivity relationships and the development of reagents for organic synthesis. Due to space limitations, the studies of aldehyde, ketone, ketene, and thioaldehyde complexes carried out by Erker,[2] Floriani,[3] and Grubbs[4] and in our laboratory[1c,h] will not be discussed. Also, the related chemistry of group 5 metals (i.e., the niobium–imine complexes of Pedersen[5] or the tantalum–alkyne complexes of Schrock[6]) will not be covered. The chemistry of η^4-diene complexes of group 4 metals (which can also be formulated as metallacyclopent-3-enes) has been extensively studied and reviewed[7] and will also not be dealt with in this paper.

II. Alkyne Complexes

A. Complexes of Benzynes

Numerous examples of the reductive coupling of two unsaturated organic molecules to yield metallacyclic compounds using high-energy group 4 metal species such as zirconocene, Cp_2Zr ($Cp = \eta^5\text{-}C_5H_5$), have been reported.[8] This is a useful approach for the coupling of two identical fragments to form symmetrical metallacycles, but several limitations of this approach are apparent. First, intermolecular cross-coupling reactions (i.e., involving two different alkynes) are not practical. Second, in essentially all of the cases reported, the coupling of terminal alkynes is precluded due to the basicity of the organometallic reagents. Third, it has proven difficult to effect cross-coupling between alkyne complexes and heteroatom-containing organic substrates.

In contrast, there are few reports of the generation and coupling reactions of discrete alkyne or olefin π-complexes. One particularly important example is Erker's ground-breaking study on the generation and trapping of zirconocene complexes of benzyne.[9] The benzyne complex is formed without generating free zirconocene, and subsequent coupling with an excess of an olefin produces the zirconaindan products shown in Scheme 1.

The ability to prepare discrete π-complexes of this sort and an understanding of their reactivity can po-
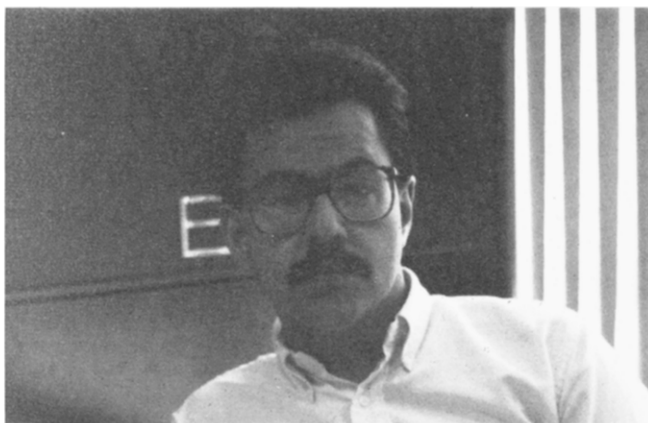
Stephen L. Buchwald was born in Bloomington, IN, in 1955. He became hooked on chemistry while a participant in an NSF High School Summer Research Program during which time he worked in the laboratories of Professor Gary M. Hieftje at Indiana University. After high school he matriculated to Brown University where he received an Sc.B. Degree in chemistry in 1977. While at Brown he did undergraduate research with Professors Kathlyn A. Parker and David E. Cane and spent a summer in the laboratories of Professor Gilbert Stork at Columbia University. In 1977 he entered graduate school at Harvard University as an NSF Graduate Fellow. At Harvard he worked with Professor Jeremy R. Knowles performing research to unravel the mechanisms of phosphoryl transfer reactions. After receiving his Ph.D., he went west to the California Institute of Technology where he spent $2^{1}/_{2}$ years as a Myron A. Bantrell Postdoctoral Fellow in the laboratories of Professor Robert H. Grubbs. In 1984, he moved back to Cambridge to join the faculty at MIT, where he is currently the Firmenich Assistant Professor of Chemistry. He is a Dreyfus Grantee for Newly Appointed Faculty in Chemistry, an American Cancer Society Junior Faculty Research Awardee, an Eli Lilly Grantee, an Alfred P. Sloan Research Fellow, and a participant in the 1988 Union Carbide Innovation Recognition Program. While not engaged in chemistry, his hobbies are sports, food, and cats.
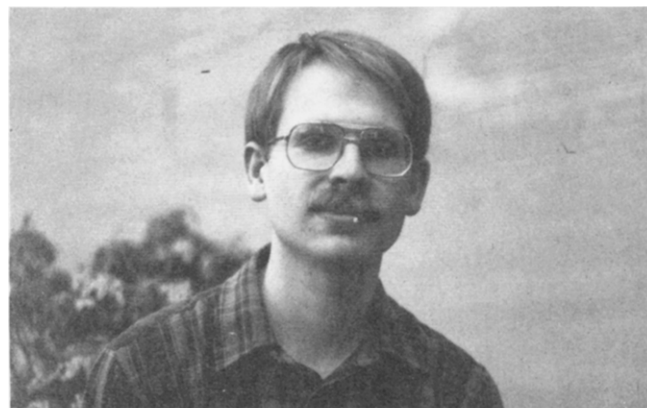
Ralph B. Nielsen was born in Logan, UT, in 1960, and he grew up in Baton Rouge, LA. He became interested in chemistry while working for two summers during high school in the laboratories of Professor William H. Daly at Louisiana State University. He then attended Brigham Young University in Provo, UT, where he received a Bachelor's degree in 1983 and a Master's degree in 1984. At BYU he worked on the synthesis of functionalized crown ethers with Professor Jerald S. Bradshaw. Since 1984 he has been working toward a doctoral degree in Professor Stephen L. Buchwald's laboratories at MIT, and he has been aided financially by graduate fellowships from the National Science Foundation and Arthur D. Little Inc. After graduation from MIT he will begin work in the Polymer Science and Technology Laboratory at Eastman Kodak in Rochester, NY.

tentially overcome several of the difficulties encountered in reductive coupling reactions using low-valent metal species such as Cp$_2$Zr. The selective coupling of two different groups (such as benzyne with an olefin)
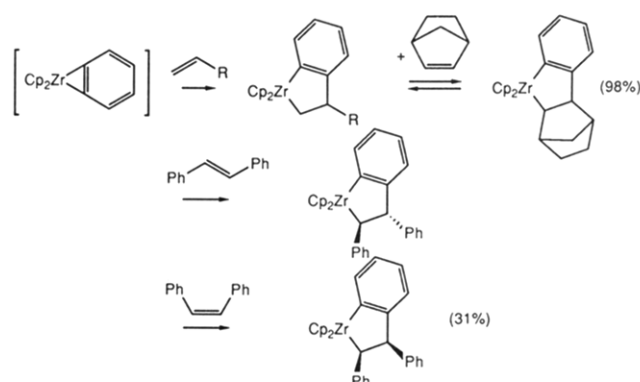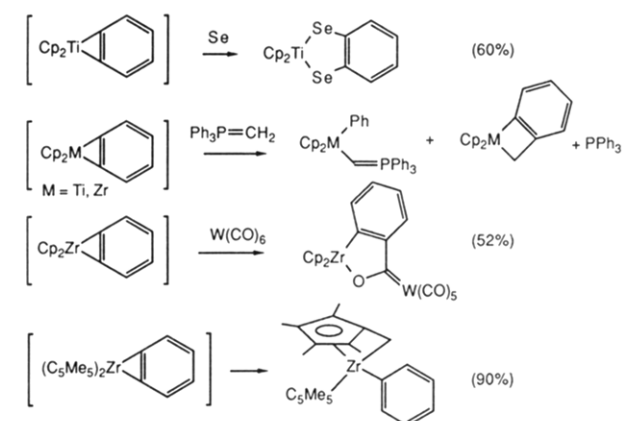
SCHEME 2
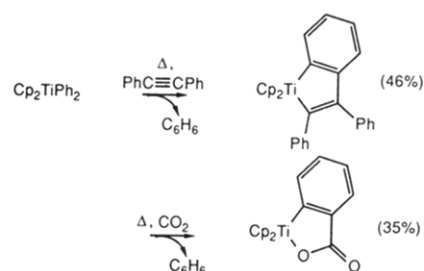
SCHEME 3
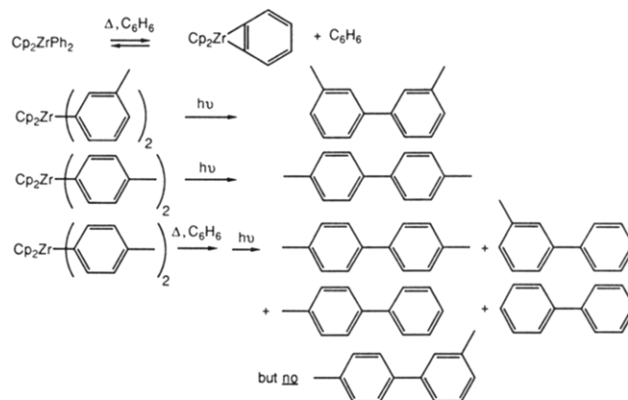
SCHEME 4

SCHEME 5

should be possible. Milder reaction conditions may be developed which tolerate sensitive functionality. Also, in some cases the reductive coupling of unstable organic fragments such as benzynes or thioaldehydes might be possible without having to generate the unstable species in the free state.

As early as 1963,[10] unusual reactivity of group 4 di-arylmetallocene derivatives was noted. Heating di-phenyltitanocene with diphenylacetylene leads to the loss of a molecule of benzene and formation of the ti-tanium metallacycle shown in Scheme 2. It was somewhat later that the intermediacy of a titanocene–benzyne complex was proposed by Vol'pin,[11] who showed that the benzyne complex couples carbon di-oxide and other unsaturated molecules. Initial kinetic investigations by Teuben and co-workers[12] estimated a value for $\Delta G^{\ddagger}$ of 29 kcal/mol for formation of the benzyne intermediate, and they also showed that deu-terium labels are scrambled between the phenyl ligands, the Cp ligands, and the solvent.

The elegant study by Erker[9a] of the reactivity of di-phenyl- and ditolylzirconocene derivatives demon-strated the intermediacy of benzyne complexes and suggested that the benzynes form by a concerted elim-ination of benzene and not by a β-hydride elimina-tion/reductive elimination sequence. As outlined in Scheme 3, Erker established that the benzyne complex and substituted benzyne complexes reversibly activate benzene solvent to re-form diarylzirconocene complexes. He also showed that photolysis of ditolylzirconocenes gives high yields of dimethylbiphenyl products which reflect the substitution pattern of the diarylzirconocene precursors. He then showed that heating di-p-tolyl-zirconocene in benzene solvent followed by photolysis gives 4,4'-dimethylbiphenyl, 4-methylbiphenyl, 3-methylbiphenyl, and, after an induction period, un-substituted biphenyl. However, no 3,4'-dimethylbi-phenyl is formed. All of the observed products are what should be expected from reaction of a 4-methylbenzyne complex with the solvent. However, since the entire thermal process is reversible, a mechanism which in-volves a β-hydride elimination to form a zirconocene 4-methylbenzyne hydrido p-tolyl intermediate is dis-counted because it predicts that a reversible hydro-zirconation should form p-tolyl-m-tolylzirconocene, which is not produced.

Erker also showed that the benzyne complex reduc-tively couples olefins to form zirconaindan derivatives.[9b] This reaction, too, is reversible, as shown. Heating the metallacycles with alkenes scrambles to olefin frag-ments. The coupling of *cis*- and *trans*-stilbene was shown to be stereospecific[13] for the formation of cis- and trans-substituted metallacycles. Subsequent reactions of these zirconaindan species with CO have also been studied (Scheme 4).[14]

In addition to the reactions of benzyne complexes with olefins and alkynes,[15] various other reactions of in situ generated benzyne complexes have been discovered (Scheme 5). Reaction with elemental selenium can yield the diselenametallacycles shown.[16] Methylene-triphenylphosphorane reacts with the zirconocene–benzyne complex to give a new phenylzirconocene-substituted ylide as the only product, but the titanocene derivative gives a 2:1 mixture of the ylide and the me-tallacyclobutene shown.[17] Tungsten hexacarbonyl re-acts to form a metallacyclic Fischer carbene.[18] Zirco-nocene benzyne complexes with substituted Cp ligands have also been shown to undergo intramolecular C–H bond activation.[19,20] Even the possible activation of dinitrogen by benzyne complexes has been suggested to explain the formation of low yields (<2%) of aniline
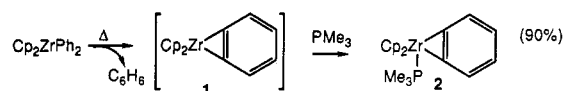
SCHEME 6

SCHEME 7

R = Me, Ph, n-Pr, i-Pr, vinyl,
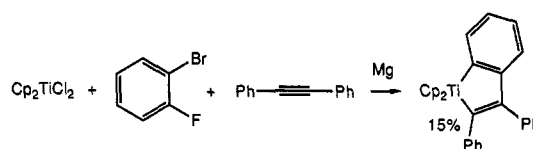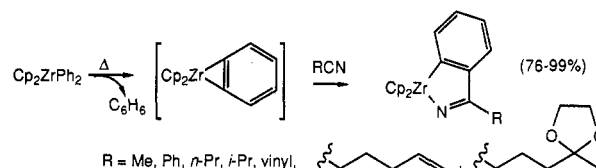
SCHEME 8

and toluidene by heating diaryltitanocenes under a nitrogen atmosphere.[21]

In at least one case, the titanocene–benzyne complex appears to have been prepared by a completely different route. Vol'pin reports[22] that treatment of a mixture of titanocene dichloride, o-bromofluorobenzene, and di-phenylacetylene with magnesium metal at low tem-perature leads to formation of modest amounts of the benzyne-derived metallacycle shown in Scheme 6. This apparent simultaneous generation of free titanocene and free benzyne is intriguing, but the rather harsh reaction conditions and the low yield suggest that this approach has limited synthetic utility.

Our efforts in this area stemmed from a desire to extend Erker's work with the zirconocene complex of benzyne to determine the feasibility of coupling other functional groups, especially aldehydes, ketones, and nitriles. Of these, only nitriles can be successfully em-ployed as substrates. This reaction produces a high yield of metallacycles as shown in Scheme 7.[1e]

As will be discussed later, we found that we could prepare and isolate a stable trimethylphosphine adduct of a closely related zirconocene–cyclohexyne complex.[1b] This success led us to immediately probe whether we could utilize similar methodology to prepare and isolate the trimethylphosphine adduct of the zirconocene–benzyne complex. As shown in Scheme 8, this is effi-ciently accomplished by heating a benzene solution of diphenylzirconocene in the presence of a large excess of trimethylphosphine.[1a] The thermal stability of 2 is attested to by the fact that it survives conditions of its formation, refluxing in benzene for 24 h. With this reaction, 2 can be isolated in ~90% yield as an air- and moisture-sensitive solid. The X-ray crystal structure of 2 shown in Figure 1 was determined by John Huff-man at Indiana University. A high level of back-bonding from zirconium to the π^*-orbital of benzyne is evidenced by the fact that all the carbon–carbon bonds in the ring of the benzyne fragment are identical in length, within experimental error. Compared to the two other structurally characterized transition-metal-benzyne complexes, this is similar to what is seen in Bennett's nickel–benzyne complex[23] but contrasts that manifested in Schrock's tantalum complex.[6]
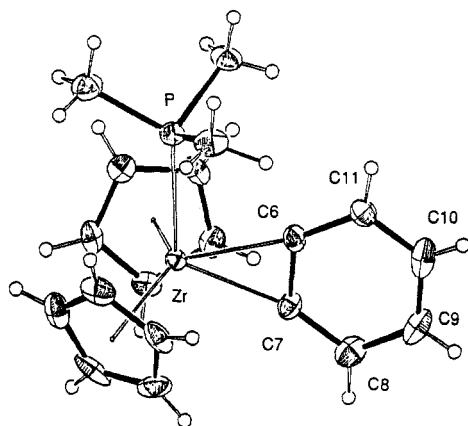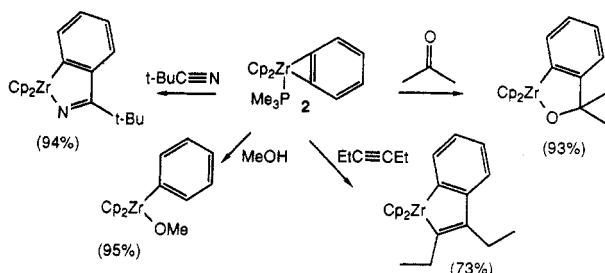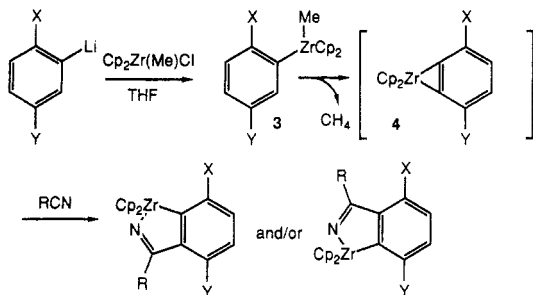
Figure 1. X-ray crystal structure of **2**. Bond distances (Å): Zr–C6, 2.267 (5); Zr–C7, 2.228 (5); C6–C7, 1.364 (8); C7–C8, 1.389 (8); C8–C9, 1.383 (9); C9–C10, 1.380 (9); C10–C11, 1.377 (9); C11–C6, 1.406 (8); Zr–P, 2.687 (3). Bond angles (deg): C6–Zr–C7, 35.33 (19); Zr–C6–C7, 70.8 (3); Zr–C7–C6, 73.9 (3); C6–C7–C8, 122.1 (5); C7–C6–C11, 120.2 (5).
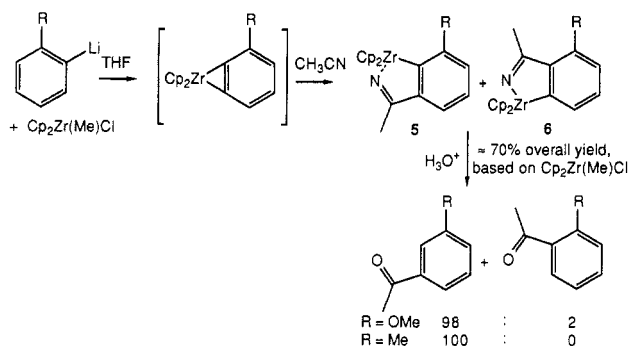
SCHEME 9

SCHEME 10

Unlike the in situ generated benzyne intermediate **1**, complex **2** undergoes clean, high-yield reactions upon treatment with a number of reagents as shown in Scheme 9.

Encouraged by these initial results, we sought to expand the utility of this chemistry by preparing substituted derivatives of **2**. Erker described the inability to prepare the di-o-tolylzirconocene precursor to the 3-methylbenzyne complex, presumably due to unfavorable steric interactions.[9a] We sought a method that would allow us to prepare zirconocene complexes of highly substituted benzynes and at the same time eliminate the need for 2 equiv of the substituted aromatic precursor. We found that the addition of a lithiated aromatic species to zirconocene methyl chloride produces **3**, which upon heating to 70 °C in benzene smoothly loses methane to yield **4** (Scheme 10).[1g] Complex **4**, formed in situ, can be coupled with various substrates to form metallacycles, which in turn can be converted into useful organic products without the need for their isolation or purification.

SCHEME 11

SCHEME 12
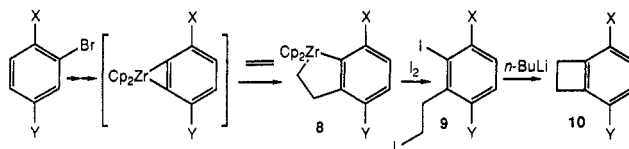
X	Y	Isolated Yield of 10 (based on aryl bromide)
OMe	H	50%
Me	OMe	69%
OMe	OMe	70%
Me	H	65% (estimated by ^{1}H NMR)

Although we had no a priori predictions about the regiochemical outcome of these coupling reactions, we found that conversion of a 2-substituted phenyllithium to the benzyne complex, followed by coupling with a nitrile and hydrolysis, leads almost exclusively to the non-Friedel–Crafts isomer of the resulting phenone (Scheme 11). We first used 2-lithio-1-methoxybenzene as the substrate and initially attributed the ∼50:1 ratio of the regioisomeric metallacycles **5** and **6** obtained by coupling **4** with acetonitrile to a chelation of a lone pair on the oxygen to the oxophilic zirconocene fragment.[24] However, changing the substituent from methoxy to methyl has little effect on the product ratio, and we now believe that the regiochemical preferences are steric in origin. Below are shown the proposed intermediate complexes immediately before insertion. Since the R–R' interaction in **7** is far worse than the analogous R'–H interaction in **7'**, it follows that **7'** is converted into
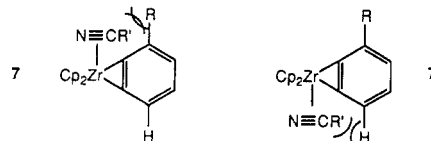
the regioisomer which predominantes. Thus, high levels of regioselectivity can be achieved in a predictable manner, based on the relative size of the substituents at carbons 2 and 6. This regiochemical outcome has also been previously observed in the coupling reaction of alkynes with the titanocene–2-methylbenzyne complex.[15a]

The substituted metallacycles obtained by coupling the benzyne complex with a nitrile can be readily converted to both simple aromatic ketones and iodoaromatic ketones, upon hydrolysis or iodination/hydrolysis.[1g] Some of our results obtained from coupling acetonitrile with benzyne complexes derived from several aryl halide precursors are outlined in Chart I.

If the benzyne complexes are generated under an atmosphere of ethylene, high yields of zirconaindans **8**

CHART I

Precursor	Workup	Regioisomer A	Regioisomer B	Isolated Yield
OMe, Br	H₃O⁺	(98)	(2)	86%
Me, Br	H₃O⁺	(100)	(0)	62
MeO, Br	H₃O⁺	(50)	(50)	74
Me, Br, OMe	H₃O⁺	(89)	(11)	47
OMe, Br	I₂→H₃O⁺	(100)	(0)	61
Me, Br	I₂→H₃O⁺	(100)	(0)	67

SCHEME 13

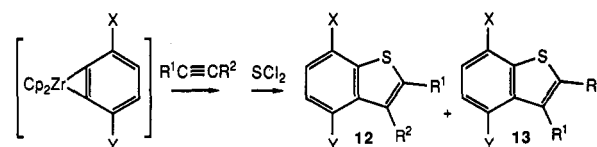| R	X	Y	Isolated Yield of 11 (based on aryl bromide)
Me	H	H	83% (yield based on isolated metallacycle)
Me	Me	H	59%
Me	OMe	H	25%
n-Pr	OMe	OMe	52%

are formed, as Erker found for the unsubstituted case. Treatment of 8, without isolation, with excess iodine produces diiodide 9, which upon exposure to n-BuLi at −78 °C cleanly yields substituted benzocyclobutenes 10 in good overall yield,[41] as shown in Scheme 12.

In addition to providing novel routes for the synthesis of carbocyclic and substituted aromatic compounds, benzyne-derived metallacycles can be used as precursors to sulfur-containing heterocycles. An efficient "metallacycle transfer" reaction of zirconacycles using dihalides of main-group metals and chalcogens has been reported by Nugent and Fagan.[26] Using this approach, we have derived general methods for the synthesis of benzisothiazoles and benzothiophenes as shown in Schemes 13 and 14.

Treatment of the azametallacycles derived from nitrile coupling with sulfur monochloride yields benzisothiazoles 11 (Scheme 13). In all examples studied to data, only one isomer has been observed. This represents a general entry to these heterocycles that have not been studied in detail, due to a lack of convenient methods for their synthesis.[27]

The generation and in situ coupling of the nascent benzyne complex with a nonterminal alkyne, followed by treatment of the zirconaindene intermediate with freshly distilled sulfur dichloride, provide good to excellent yields of the benzothiophenes indicated (Scheme 14).[28] Although one previous report of the coupling of trimethylsilyl-substituted alkynes with a benzyne complex indicated that the silyl substituent prefers the
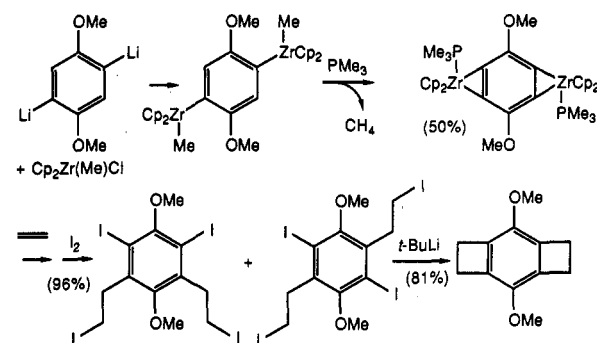
SCHEME 14

Entry	R1	R2	X	Y	12:13 Ratio	Isolated Yield (based on aryl bromide)
1	Et	Et	H	H	100:0	91% (yield based Cp₂ZrPh₂)
2	TMS	Me	H	H	100:0	92% (yield based Cp₂ZrPh₂)
3	Me	Me	Me	H	100:0	72%
4	TMS	Me	Me	H	100:0	69%
5	Et	Et	OMe	H	100:0	71%
6	Et	Et	OMe	H	100:0	80%
7	TMS	Me	OMe	H	95:5	71%
8	Me	Me	Me	Me	100:0	78%
9	Et	Et	Me	Me	100:0	67%
10	TMS	Me	Me	Me	100:0	75%
11	Me	Me	OMe	OMe	100:0	60%
12	TMS	Me	OMe	OMe	100:0	69%

TMS = SiMe₃

SCHEME 15

SCHEME 16
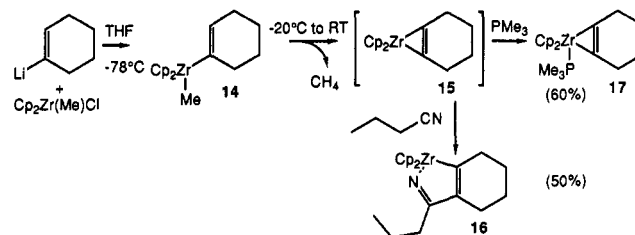
α-position of the metallacyclic intermediate,[15b] it is interesting to note entries 2, 4, 7, 10, and 12 where almost complete regioselectivity is seen, both with respect to the substituents of the benzyne and with those of the alkyne.

The X-ray crystal structure of the (trimethylphosphine)zirconocene–benzyne complex indicates that there was not an undue amount of ring strain present. This observation encouraged us to prepare a zirconocene–benzdiyne complex, as shown in Scheme 15.[1f] The benzdiyne complex was characterized by X-ray crystallography, and each zirconocene–benzyne fragment of the molecule is structurally quite similar to the simple benzyne complex. The reactivity of this complex is also similar, as shown by the ethylene coupling/iodination sequence shown to give a mixture of tetraiodides, which can be converted in high yield to the tricyclic compound shown.

B. Complexes of Cyclohexyne and Other Cycloalkynes

As an outgrowth of our studies on trapping the zirconocene–benzyne complex with nitriles, we queried whether our methodology could be extended to allow
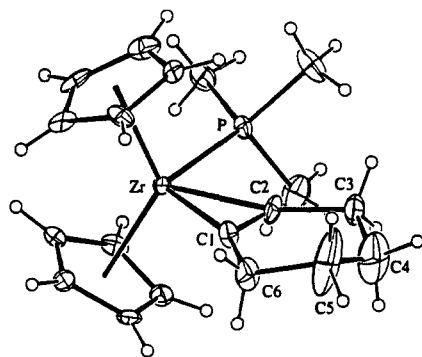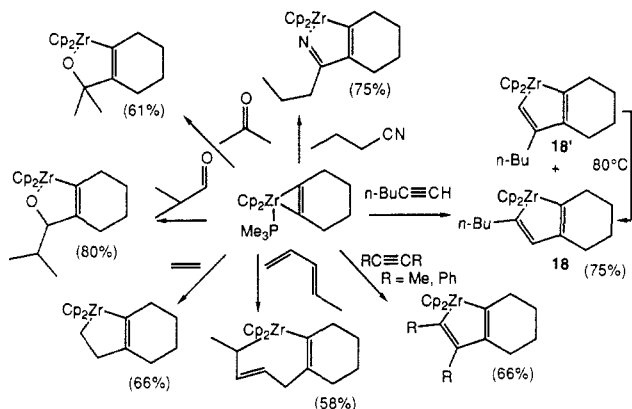
Figure 2. X-ray crystal structure of 17. Bond distances (Å): Zr–C1, 2.165 (13); Zr–C2, 2.244 (12); C1–C2, 1.295 (25); C2–C3, 1.532 (18); C1–C6, 1.519 (19); Zr–P, 2.689 (3). Bond angles (deg): C1–Zr–C2, 34.1 (0.5); C1–C2–C3, 126.0 (1.2); C6–C1–C2, 125.2 (1.2).
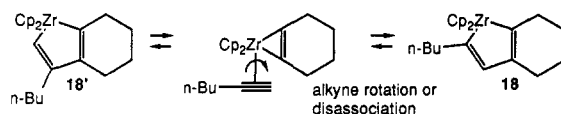
SCHEME 17

for the synthesis of zirconocene complexes of cyclo-alkynes. In our initial experiments, we attempted to prepare cyclohexenylmethylzirconocene (14) (Scheme 16). However, 14 could not be isolated at room temperature, due to its partial decomposition. Since formation of the zirconocene–benzyne complexes requires temperatures of 60–80 °C to proceed at a reasonable rate, it is surprising that the transformation of 14 to 15 takes place at 25 °C. This was confirmed by allowing a solution of 14, prepared at low temperature, to react with butyronitrile at 25 °C to form a quantitative yield (¹H NMR) of the azametallacycle 16. This transformation is also somewhat surprising in that it shows complete selectivity for activation of the sp² β-hydrogen over the sp³ β-hydrogens of the cyclohexenyl ligand. We were pleased to find that addition of excess trimethylphosphine to 14 at low temperature, followed by warming to room temperature and recrystallization from ether, allowed the isolation of the compound 17, a stable trimethylphosphine adduct of the cyclohexyne complex. This "one-pot" procedure can readily be used to prepare 6–8 gs of analytically pure 17 in ~60% isolated yield, based on bromocyclohexene.¹ᵇ

The X-ray crystal structure of 17 (Figure 2), determined by John Dewan, has several interesting features. First, the C1–C2 bond length of 1.295 (25) Å indicates a bond order substantially closer to 2 than to 3. Moreover, the C1–C2–C3 bond angle of 126.0 (1.2)°, again, is much closer to the 120° value expected for a sp²-hybridized carbon than to the 180° value expected for a sp-hybridized carbon. Taken together, these values reflect the high degree of back-bonding from the Cp₂Zr(PMe₃) moiety to the π*-orbital of the cyclo-

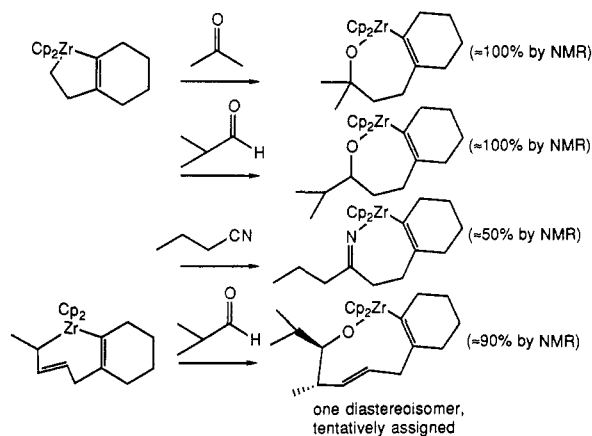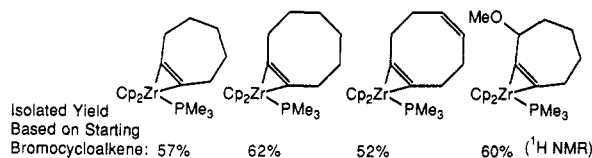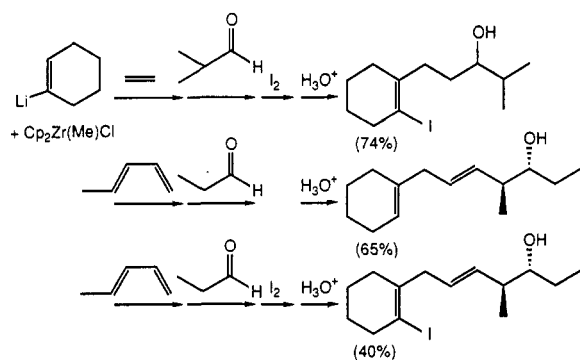**SCHEME 18**

SCHEME 19

CHART II

hexyne unit and indicate that this complex is best described as a metallacyclopropene. The stability of 17 is dependent on this back-bonding, since it stabilizes both the highly strained cyclohexyne fragment and the high-energy Cp₂Zr unit.

Complex 17 reacts readily with a wide variety of unsaturated organic compounds, including nitriles, ketones, aldehydes, ethylene, both internal and terminal alkynes, and dienes, as shown in Scheme 17. Of particular interest is the coupling reaction between 17 and 1-hexyne. At room temperature a ~3:2 mixture of regioisomers 18 and 18′ is formed. Heating the reaction mixture for 20 h at 80 °C causes isomerization to only one isomer, tentatively assigned as 18.²⁹ As depicted in Scheme 18, isomerization of the metallacycle must involve carbon–carbon bond cleavage of metallacycle 18′. Since this reaction is relatively rapid at 80 °C, it implies that the cyclohexyne intermediate is relatively strain-free. Related isomerization reactions of metallacyclopentanes (or pentenes) has been reported in a number of cases,⁹ᵇ,³⁰,³¹ but little is known about the mechanism of this low-energy carbon–carbon bond cleavage reaction.
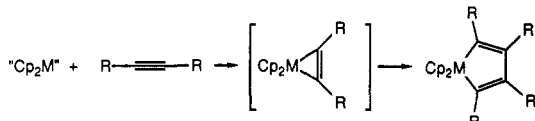
Using a similar synthetic strategy, we have been able to prepare the additional cycloalkynes in Chart II, and we are currently investigating their reaction chemistry.³²

Metallacycles formed by coupling ethylene or 1,3-dienes with 15 undergo chemoselective reactions to insert aldehydes, ketones, and nitriles, specifically into the sp³ carbon–zirconium bond as shown in Scheme 19.²⁹ Free cyclohexyne complex 15, generated in an in situ manner in the presence of ethylene or a 1,3-diene, is converted into a metallacycle which can be further treated with an aldehyde followed by hydrolysis or an iodinolysis–hydrolysis workup to produce organic
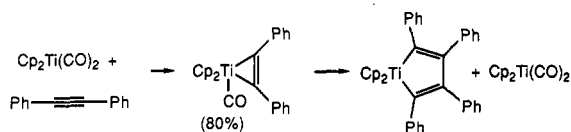
SCHEME 20

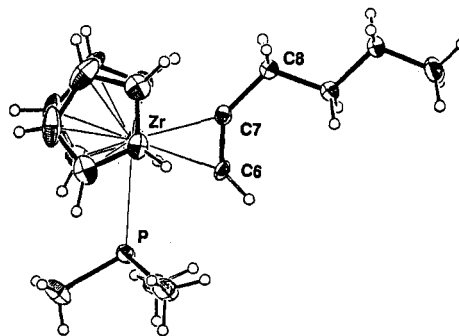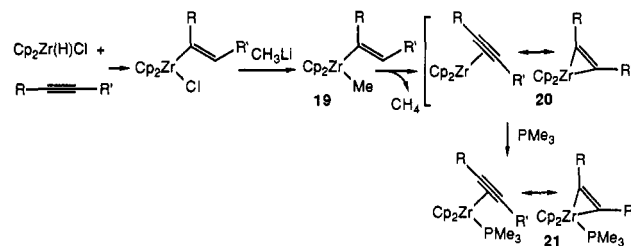**SCHEME 21**

SCHEME 22

Figure 3. X-ray crystal structure of **22**. Bond distances (Å): Zr–P, 2.6576 (11); Zr–C6, 2.244 (3); Zr–C7, 2.211 (3); C6–C7, 1.286 (5); C7–C8, 1.491 (5). Bond angles (deg): C6–C7–C8, 135.8 (3); Zr–C6–C7, 71.81 (19); Zr–C7–C6, 74.64 (20).
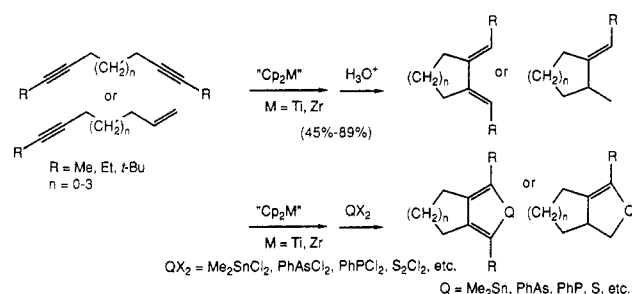
SCHEME 23

C. Complexes of Acyclic Alkynes

For some time it has been known that free metallocene or its equivalent (i.e., Cp₂M, M = Ti, Zr, Hf) can reductively couple two alkynes to give symmetrically tetrasubstituted metallacyclopentadiene products, and it has been generally assumed[33a] that a metallocene-alkyne complex is an intermediate in this process (Scheme 21). A remarkably large number of examples of this reaction type using diphenylacetylene have been reported, yielding the very stable tetraphenylmetallacyclopentadienes. Methods for generating "Cp₂M" include the following: TiCl₄ and 4 equiv of sodium cyclopentadienide,[33b] photochemically induced reductive elimination of Cp₂MR₂,[2d,34] thermal or photochemical reactions of Cp₂M(CO)₂,[35,36] reduction of Cp₂MCl₂ with sodium naphthalide[37] or magnesium/mercuric chloride,[8,22] and ligand displacement from Cp₂M(diene) complexes,[2d] which are generated from Cp₂MCl₂ and (butadiene)magnesium. This reaction has even been documented for a polymer-bound titanocene fragment.[38] There are a few examples where similar chemistry has been extended to other symmetric internal alkynes such as 2-butyne, 3-hexyne, or dimethyl acetylenedicarboxylate.[8,36] Alkynes have also been reported to induce reductive elimination of RH from Cp₂M(H)R, to give metallacyclopentadiene products.[39] However, discrete alkyne complexes have been observed or isolated in relatively few cases. Floriani reported the preparation[40] and X-ray crystal structure[41] of Cp₂Ti(CO)(diphenylacetylene), which is formed from Cp₂Ti(CO)₂ and the alkyne (Scheme 22). The complex is thermally unstable and disproportionates to form Cp₂Ti(CO)₂ and the metallacyclopentadiene. Replacing the CO with PMe₃ has been reported to enhance the stability of the alkyne complex.[36] The complexes Cp*₂Ti(2-butyne), Cp*₂Ti(diphenylacetylene), and Cp*₂Zr(diphenylacetylene) (Cp* = η⁵-C₅Me₅) have been briefly mentioned[30] as stable, isolable compounds. In the same report, the complex Cp*₂Ti(1-propyne) was implicated as in intermediate in the thermal decomposition of bis(1-propenyl)permethyltitanocene. Negishi and co-workers recently reported[42] the isolation and X-ray structure of Cp₂Zr(PMe₃)(diphenylacetylene), which was obtained by treating Cp₂Zr(PMe₃)₂ with the alkyne. The compound is structurally quite similar to Floriani's titanocene complex. Unfortunately, this is the only alkyne complex that can be prepared by using their methodology.

Rausch and co-workers found that reaction of Cp₂Ti(PMe₃)₂ with acetylene, propyne, phenylacetylene, or diphenylacetylene leads to formation of metallacyclopentadienes, and the intermediate Cp₂Ti(PMe₃)(alkyne) complexes can be observed spectroscopically.[43] This is the first report of such reductive-coupling chemistry using terminal alkynes.

We have found that the methods we used to prepare the zirconocene–cyclohexyne complex can be readily extended to the preparation of zirconocene complexes of both mono- and disubstituted acyclic alkynes as shown.[1d] Using the hydrozirconation methodology for alkynes developed by Schwartz,[44] followed by the addition of methyllithium, produces vinylmethylzirconocene **19**. Methane loss occurs smoothly at room temperature to produce alkyne complex **20**,[45] which, in the presence of trimethylphosphine, is transformed into complex **21** (Scheme 23). In this manner the trimethylphosphine adducts of the zirconocene complex of 1-hexyne **22** and of 3-hexyne **23** can be isolated in ~70% yield. This result suggests that the previously reported alkyne-induced "reductive elimination" of Cp₂Zr(H)Me[39] is likely to proceed via hydrozirconation of the alkyne to form the same vinylmethylzirconocene

SCHEME 24

R = Me, Et, t-Bu
n = 0-3

QX_2 = Me_2SnCl_2, $PhAsCl_2$, $PhPCl_2$, S_2Cl_2, etc.

Q = Me_2Sn, PhAs, PhP, S, etc.

SCHEME 25

X = $SiMe_3$, $SnMe_3$, alkyl, aryl, alkenyl
Y = $(CH_2)_n$, alkylidene, RN, etc.

SCHEME 26

intermediate which we observe.

An X-ray crystal structure of the 1-hexyne complex **22**, determined by John Huffman, at Indiana University, is shown in Figure 3. The C1-C2 bond distance is 1.286 (5) Å, while the C1–C2–C3 bond angle of 135.8 (3)°. This should be compared with the corresponding angles of 126.0 (1.2)° and 122.1 (5)° in the cyclohexyne **17** and the benzyne complex **2**, respectively. The C–C "triple bond" distance in **22** is identical, within experimental error, with that found for the cyclohexyne complex. This suggests that the 135.8 (3)° value more accurately reflects the bond order in these complexes and that the lower value observed for the cyclohexyne complex is due to some ring strain which prohibits the bond angles from splaying further outward. That the 1-hexyne complex **22** is essentially unstrained and still displays a zirconacyclopropene structure indicates that back-bonding significantly stabilizes the $Cp_2Zr(PMe_3)$ unit, in which the zirconium prefers to be in the +4 rather than in the +2 oxidation state.

Although the structures of several symmetric tetrasubstituted metallacyclopentadienes have been substantiated by isolating 1,3-dienes[8,33b,42] and 1,4-dihalo-1,3-dienes[34] obtained after hydrolysis of halogenation, the synthetic utility of "Cp_2M"-induced reductive couplings of alkynes has been very limited until recently. Three problems in particular have made this an unattractive reaction for synthetic applications. First, both "Cp_2M" and the reagents used in its generation (Mg, Na, etc.) react with functional groups such as terminal alkynes, oxygen-containing groups, or alkyl halides. Second, the attempted cross-coupling of two different alkynes (or an alkyne and another unsaturated group) usually leads to a mixture of cross- and self-coupled products. Third, even if cross-coupling could be efficiently controlled, ambiguities still exist in the regiochemical positioning of the metallacyclic product. Many of these problems have been overcome to some degree in the recent work of Nugent and Fagan[26,46] and Negishi,[47] who have developed relatively mild conditions for the intramolecular coupling of diynes and enynes, and from our development of routes to discrete alkyne complexes for intermolecular cross-coupling,[1d] and our study of the reversibility of reductive coupling.[48]

Nugent's initial work on the coupling of diynes and enynes is shown in Scheme 24.[46a-c] The intramolecular coupling of several diynes and one enyne (typically with a reagent prepared from sodium amalgam, titanocene dichloride, and methyldiphenylphosphine) followed by hydrolysis gave reasonable yields of carbocycles with only the E-exocyclic olefins as products. Alternatively, the intermediate metallacycles can be treated with dihalides of sulfur, phosphorus, or main-group metals
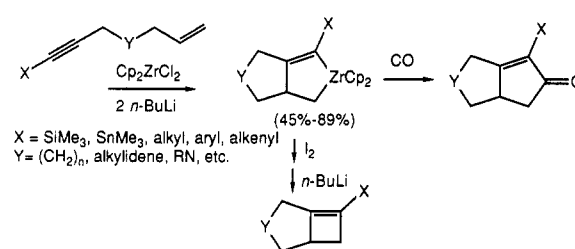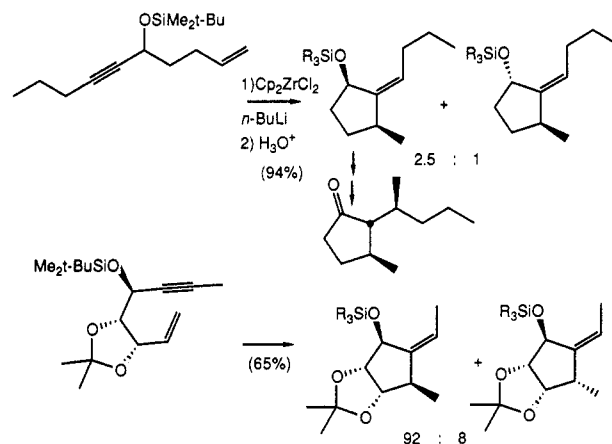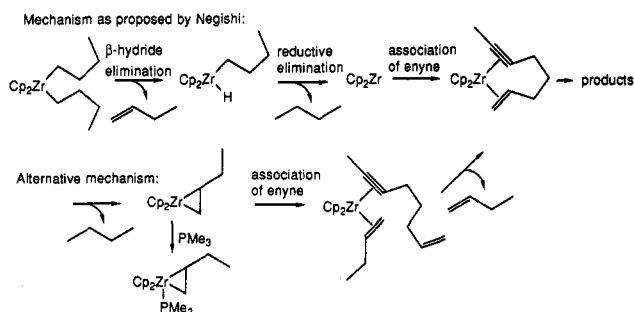
such as arsenic and tin to yield zirconocene dihalide and the corresponding thiophene, phosphole, or main-group metallacycle.[26]

Negishi's related cyclization of enynes initially[47a] employed Farona's conditions[8a] but later milder conditions were discovered by using a reagent prepared from zirconocene dichloride and 2 equiv of n-butyllithium (Scheme 25).[47b-d] Cyclization of enynes gives good yields of the metallacyclopentenes, which can be hydrolyzed to give exocyclic olefins, can be halogenated to give diiodides which are useful precursors to bicyclic cyclobutenes, or can be carbonylated to give cyclopentenones. Two apparent shortcomings of this procedure are that neither terminal enynes nor enynes with di- or polysubstituted double bonds give cyclized products.[47c]
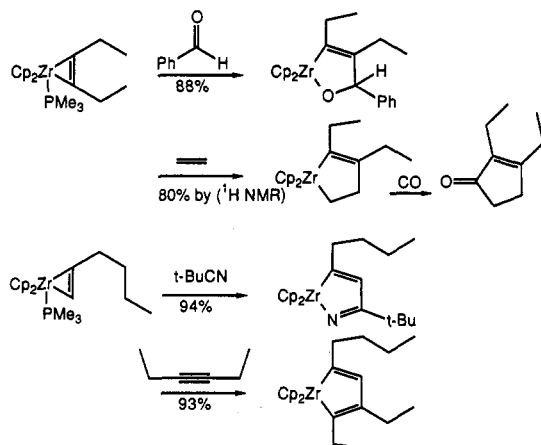
Very recent work by Nugent, Rajanbabu, and Taber[46d] using the Cp_2ZrCl_2/n-BuLi regent has extended this reaction to some very highly functionalized enynes, as shown in Scheme 26. The major stereoisomer from the first example was converted in several steps to the cyclopentanone shown, which is an intermediate in a previous synthesis of the fire-ant queen pheromone invictolide.[49] The second example shows the successful cyclization of an enantiomercially pure, highly oxygenated enyne obtained in several steps from a sugar.

The Cp_2ZrCl_2/n-BuLi reagent is very useful, and it is worthwhile to briefly examine how it induces bicyclization. Negishi showed that $Cp_2Zr(n\text{-}Bu)_2$ is formed rapidly at -78 °C and that this dialkyl undergoes first-order decomposition at 20 °C at a rate independent of the enyne concentration.[47d] When the bicyclization reaction is monitored by NMR, signals for the metallacyclic products appear as signals for $Cp_2Zr(n\text{-}Bu)_2$ disappear. Since the byproducts of the decomposition of dibutylzirconocene are n-butene and 1-butene, Negishi proposes that the $Cp_2Zr(n\text{-}Bu)_2$ must undergo β-hydride elimination with loss of butene as
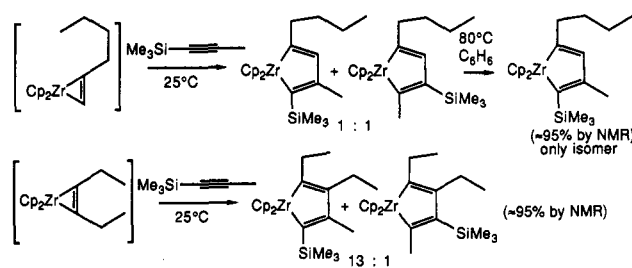
SCHEME 27

Mechanism as proposed by Negishi:

Alternative mechanism:

SCHEME 28

SCHEME 29

SCHEME 30

R^1	R^2	R^3	R^4	Reagent	Yield	(based on the
n-C_4H_9-	H-	n-C_2H_5-	n-C_2H_5-	S_2Cl_2	69%	vinyl(chloro)-
n-C_4H_9-	H-	CH_3-	CH_3-	S_2Cl_2	65%	zirconocene
n-C_4H_9-	H-	CH_3-	$SiMe_3$-(H-)	SCl_2	80%	precursor)
n-C_4H_9-	H-	Ph-	Ph-	SCl_2	54%	"
n-C_2H_5-	n-C_2H_5-	n-C_2H_5-	n-C_2H_5-	S_2Cl_2	90%	"
n-C_2H_5-	n-C_2H_5-	CH_3-	CH_3-	S_2Cl_2	63%	"
n-C_2H_5-	n-C_2H_5-	CH_3-	$SiMe_3$-(H-)	S_2Cl_2	75%	"
n-C_2H_5-	n-C_2H_5-	Ph-	Ph-	S_2Cl_2	70%	"
n-C_4H_9-	H-	n-C_2H_5-	n-C_2H_5-	S_2Cl_2	60%	(based on Cp_2ZrHCl)
n-C_4H_9-	H-	CH_3-	CH_3-	S_2Cl_2	53%	"

shown to give $Cp_2Zr(H)(n$-$Bu)$, which rapidly reductively eliminates butane to generate free Cp_2Zr, which he believes is the active metal species (Scheme 27). However, some evidence suggests that a zirconocene-diyne or -enyne complex can be formed without the need to generate free Cp_2Zr. First, simple alkyl hydrides of zirconocene such as $Cp_2Zr(H)(Me)$ do not always rapidly reductively eliminate alkane, even in strongly coordinating solvents such as THF.[50] Second, we have reported[1d] the observation and isolation of $Cp_2Zr(1$-butene)(PMe_3) as the major product formed by warming $Cp_2Zr(n$-$Bu)_2$ in the presence of PMe_3, indicating that butane is eliminated from $Cp_2Zr(n$-$Bu)_2$ *before* butene is lost. Therefore, a more plausible mechanism involves the initial loss of butane to give a zirconocene–butene complex which undergoes associative ligand exchange with the enyne.

The isolated 1-hexyne and 3-hexyne complexes that we have prepared (and in many instances, the complexes prepared in situ without the need for PMe_3) react with unsaturated organic functional groups such as nitriles, alkynes, aldehydes, ketones, and ethylene to give metallacyclic compounds in high yield, as shown in Scheme 28.[1d]

It would be synthetically interesting to be able to selectively cross-couple two different unsymmetrical alkynes with complete regiocontrol. However, one limitation of this chemistry is that neither the 1-hexyne or the 3-hexyne complex couples cleanly with a second terminal alkyne, which would give the largest steric difference between the ends of the alkyne. Therefore, we decided to investigate the coupling of the 1-hexyne complex with 1-(trimethylsilyl)propyne. Unfortunately, when carried out at room temperature, the reaction is not selective, leading to a 1:1 mixture of regioisomers as shown in Scheme 29. However, we found that
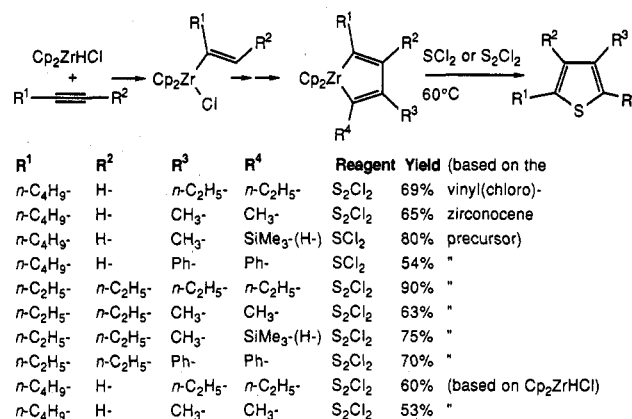
heating this mixture to 80 °C for 24 h in benzene leads to complete conversion to the regioisomer in which the silyl substituent occupies the α-position of the metallacycle.[28] The analogous coupling reaction of the in situ generated 3-hexyne complex leads to a 13:1 mixture of the two metallacycles as shown in the scheme. Heating this mixture to 80 °C leads to a slight diminution of this ratio.[48]

With this measure of regiocontrol in the coupling reactions described above, we sought to devise methodology to convert these metallacyclic intermediates into useful organic products. Our ultimate goal here is to develop one-pot procedures for the conversion of simple precursors into the final organic products without needing to manipulate or isolate organometallic intermediates.

One example of this approach is the very general synthesis of thiophenes outlined in Scheme 30. Treatment of the intermediate zirconacyclopentadienes, obtained by the selective intermolecular cross-coupling of two alkynes, with SCl_2 (freshly distilled) or S_2Cl_2, in tetrahydrofuran produces good to excellent yields of the polysubstituted thiophenes.[26,28] The overall transformation is to selectively combine two different alkynes and a sulfur atom to form the thiophene, with good control over the regiochemical placement of the four substituents. As can be seen from the examples, shown, di-, tri-, and tetrasubstituted thiophenes can be prepared by using this methodology. The disubstituted thiophenes are readily available via protodesilylation of initially formed trimethylsilyl-substituted thiophenes.[51] This synthesis can be carried out conviently as a one-pot procedure starting with Cp_2ZrHCl.
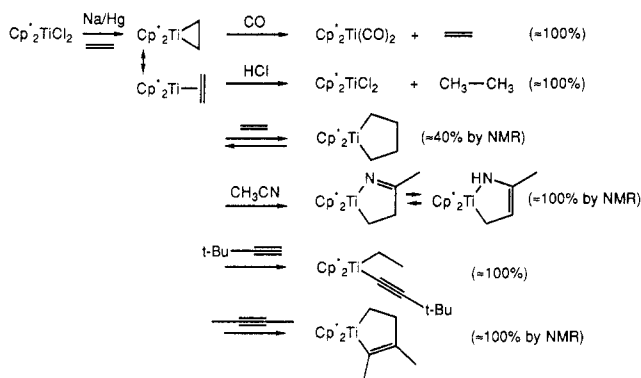
III. Alkene Complexes

Compared to the number of alkyne complexes that have been reported, very few simple mononuclear al-

SCHEME 31
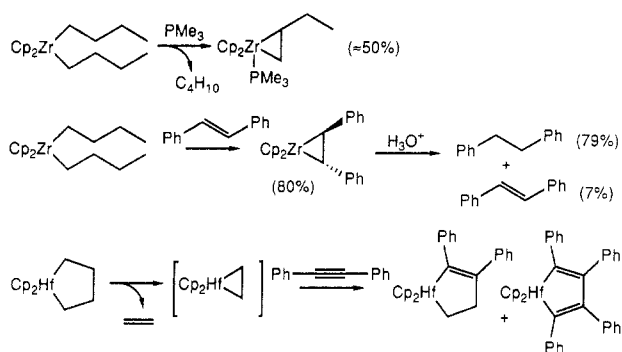
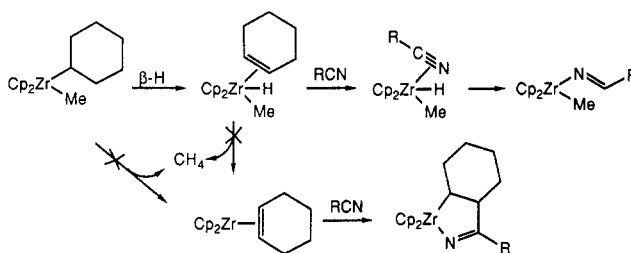**SCHEME 32**

SCHEME 33

SCHEME 34

kene complexes of group 4 metals have been prepared. One binuclear olefin complex has been reported by Erker[52] in which a styryl fragment and a chloride ligand bridge two zirconocene centers. The styryl ligand is σ-bound to one metal and η^2,π-bound to the other. A related binuclear zirconocene complex with an η^2-arene ligand has been prepared by a tedious procedure and in low yield by Pez and Stucky.[53] This complex contains bridging hydride and naphthyl ligands, and the X-ray crystal structure shows that the arene fragment is π-bound to one metal center.

Three examples of mononuclear alkene complexes are shown in Scheme 31. Compared to the corresponding alkyne complexes, these alkene complexes are more likely to participate in ligand exchange reactions which lead to loss of free alkene, and they participate in fewer reductive coupling reactions. The zirconocene–1-butene complex which we have prepared[1d] has already been mentioned in the acyclic alkyne section. Negishi has reported the preparation of the zirconocene–stilbene complex shown.[47d] Treatment of this complex with aqueous acid leads to formation of a mixture of 1,2-diphenylethane and stilbene. Erker has shown that metallacyclopentanes, such as the hafnocene example above, decompose to form an intermediate ethylene complex.[31,54] These complexes undergo both ligand exchange and reductive coupling reactions, depending on the particular reaction conditions.

The most extensively studied group 4 metal olefin complex is the permethyltitanocene–ethylene complex reported by Bercaw.[30,55] This complex is prepared from $Cp*_2TiCl_2$ by reduction with sodium amalgam under an atmosphere of ethylene. The X-ray crystal structure of this complex indicates that there is roughly equal contribution of both the Ti(II) π-ethylene and the Ti-(IV) metallacyclopropane resonance forms. As shown
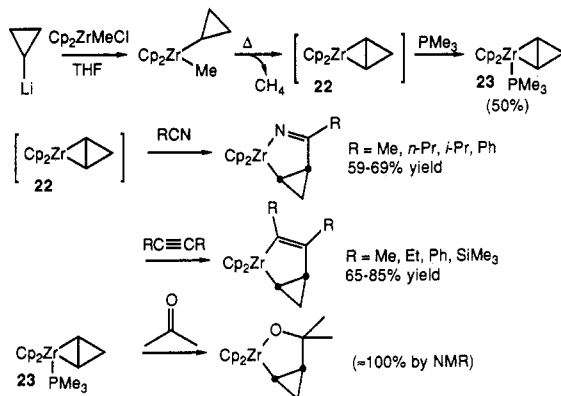
in Scheme 32, the complex reacts with a variety of substrates, with loss of bound ethylene in some cases and reductive coupling or C–H bond activation in others.

We were interested in determining whether the same strategies we employed to generate zirconocene–alkyne complexes could be extended to alkene complexes. In our initial efforts, we attempted to prepare the zirconocene complex of cyclohexene and to couple it with a nitrile, as shown in Scheme 33. Instead of the metallacyclic product, however, the N-metalated imine was produced in good yield.[56] Presumably, this is formed from the exchange of the bound cyclohexene with nitrile and subsequent insertion of the nitrile into the Zr–H bond. Hydrozirconation of nitriles is well-precedented,[57] and it is interesting to note that ligand exchange and insertion are faster than reductive elimination of methane from the cis alkyl hydride.

With this result in mind, we reasoned that a bound cyclopropene ligand would be less likely to be displaced, as it possesses ~54 kcal/mol ring strain.[58] The ready availability of cyclopropyllithium[59] allowed the generation of cyclopropene complex 22 (Scheme 34). Nitriles and internal alkynes are coupled by 22 to give the unique bicyclo[3.1.0]metallacycles,[29] but terminal alkynes give mixtures of regioisomeric metallacycles, and carbonyl compounds fail to react cleanly. If 22 is generated in the presence of excess trimethylphosphine, complex 23 can be isolated. Despite a good deal of experimentation, no reliable route to 23 of acceptable purity (>95%) has been found, although occasional batches are produced in a pure state, and we have been able to successfully obtain an elemental analysis for the compound. Compound 23 couples cleanly with ketones (but not other carbonyl compounds) to form metallacyclic products as shown. The bicyclic metallacycles obtained from 22 or 23 can also be converted into a number of cis-1,2-disubstituted cyclopropanes via hy-

SCHEME 35
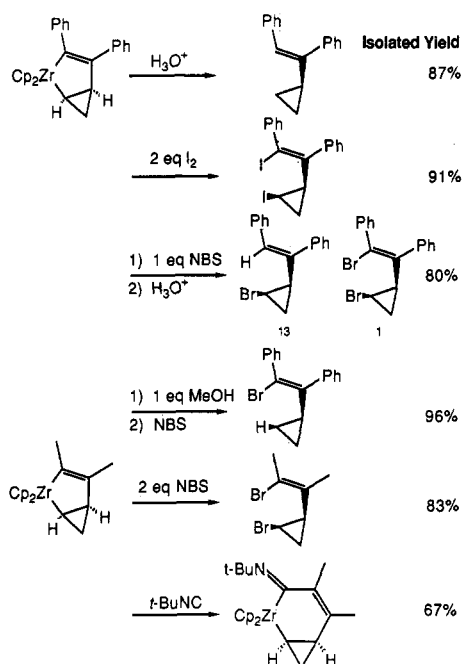
drolysis or halogenation, as indicated (Scheme 35).

IV. Conclusion

It is clear that there are both interesting structural features and useful reactivity associated with the group 4 metal complexes which have been discussed. As more examples are uncovered, it should be possible to make further predictions about the stability and reactivity which such π-complexes will exhibit. Considerable progress has been made in the past 3 years in extending the use of these complexes in organic synthesis, primarily through the development of milder reagents and reaction conditions for the generation of reduced metal species and through the preparation of discrete π-complexes for chemoselective cross-coupling reactions. There have also been major advances in understanding the regiochemical and stereochemical outcome of these reductive coupling reactions and in the development of methods for converting the metallacyclic products into a variety of organic molecules. With this information, the application of reductive coupling methodology can become a powerful tool in the synthesis of a wide range of organic compounds of pharmaceutical interest.

V. Acknowledgment

VI. References and Notes

(1) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (c) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590. (d) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (e) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. *Tetrahedron Lett.* **1987**, *28*, 3245. (f) Buchwald, S. L.; Lucas, E. A.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4396. (g) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137. (h) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3191.
(2) (a) Erker, G.; Czisch, P.; Schlund, R.; Angermund, K.; Krüger, C. *Angew. Chem.* **1986**, *98*, 356. (b) Erker, G.; Dorf, U.; Czisch, P.; Peterson, J. L. *Organometallics* **1986**, *5*, 668. (c) Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. (d) Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15. (e) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. (f) Erker, G.; Kropp, K.; Krüger, C.; Chiang, A. P. *Chem. Ber.* **1982**, *115*, 2447. (g) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29. (h) Rosenfeldt, F.; Erker, G. *Tetrahedron Lett.* **1980**, *21*, 1637.
(3) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269.
(4) (a) Waymouth, R. M.; Clauser, K. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6385. (b) Meinhart, J. D.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318. (c) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427. (d) Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050. Ho, S.C.H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. (e) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (f) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499.
(5) (a) Roskamp, E. J.; Pederson, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 3152. (b) Roskamp, E. J.; Pederson, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551.
(6) (a) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697.
(7) (a) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (b) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (c) Erker, G.; Krüger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.
(8) (a) Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65. (b) Sabade, M. B.; Farona, M. F. *J. Organomet. Chem.* **1986**, *310*, 311.
(9) (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659.
(10) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750.
(11) Kolomnikov, I. S.; Lobeeva, T. S.; Gorbachevskaya, V. V.; Aleksandrov, G. G.; Struckhov, Yu. T.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1971**, 972.
(12) (a) Boekel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *81*, 371. (b) Boekel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *102*, 161.
(13) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246.
(14) (a) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (b) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45.
(15) (a) Rausch, M. D.; Mintz, E. A. *J. Organomet. Chem.* **1980**, *190*, 65. (b) Mattia, J.; Humphrey, M. B.; Rogers, R. D.; Atwood, J. L.; Rausch, M. D. *Inorg. Chem.* **1978**, *17*, 3257.
(16) (a) Erker, G.; Mühlenbernd, T.; Benn, R.; Rufinska, A.; Tainturier, G.; Gautheron, B. *Organometallics* **1986**, *5*, 1023. (b) Gautheron, G.; Tainturier, G.; Pouly, S. *Organometallics* **1984**, *38* 1495.
(17) (a) Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310. (b) deBoer, H. J. R.; Akkerman, O. S.; Bickelhaupt, F.; Erker, G.; Czisch, P.; Mynott, R.; Wallis, J. M.; Krüger, C. *Angew. Chem.* **1986**, *98*, 641.
(18) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 572.
(19) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232.
(20) Erker, G.; Mühlenbernd, T. *J. Organomet. Chem.* **1987**, *319*, 201.
(21) Berkovich, E. G.; Shur, V. B.; Vol'pin, M. E.; Lorenz, B.; Rummel, S.; Wahren, M. *Chem. Ber.* **1980**, *113*, 70.

(22) Shur, V. B.; Berkovich, E. G.; Vol'pin, M. E.; Lorenz, B.; Wahren, M. *J. Organomet. Chem.* **1982**, *228*, C36.

(23) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(24) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-zirconium and -hafnium Compounds*; Wiley: New York, 1986.

(25) To our knowledge the only similarly substituted benzocyclobutenes to be reported are (a) with X = Y = OMe; Watabe, T.; Oda, M. *Chem. Lett.* **1984**, 1791 and (b) X = H, Y = Me; Riemann, J. M.; Trahanovsky, W. S. *Tetrahedron Lett.* **1977**, 1863.

(26) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(27) Pain, D. L.; Pearl, G. J.; Wooldridge, K. R. H. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Pergamon: Oxford, 1984; Vol. 6, pp 131–175 and references therein.

(28) Buchwald, S. L.; Fang, Q., submitted for publication.

(29) Buchwald, S. L.; Lucas, E. A.; Lum, R. T., unpublished results.

(30) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

(31) Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138.

(32) Buchwald, S. L.; LaMaire, S. J., unpublished results.

(33) (a) Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1178. (b) Vol'pin, M. E.; Dubovitskii, V. A.; Nogina, O. V.; Kursanov, D. N. *Dokl. Akad. Nauk. SSSR* **1963**, *151*, 1100.

(34) (a) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. (b) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299. (c) Alt, H.; Rausch, M. *J. Am. Chem. Soc.* **1974**, *96*, 5936.

(35) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5079.

(36) Demerseman, B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1981**, 665.

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

(38) Lau, C.-P.; Chang, B.-H.; Grubbs, R. H.; Brubaker, C. H. *J. Organomet. Chem.* **1981**, *214*, 325.

(39) Yoshifuji, M.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *153*, C15.

(40) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 66.

(41) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398.

(42) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623.

(43) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 3717.

(44) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.

(45) This reaction appears to be one of only a few examples of activation of a sp^2 β-hydrogen followed by reductive elimination of methane. Cf. ref 30.

(46) (a) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. (b) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (c) Parshall, G. W.; Nugent, W. A.; Chan, D. M.-T.; Tam, W. *Pure Appl. Chem.* **1985**, *57*, 1809. (d) RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J., submitted for publication in *J. Am. Chem. Soc.*

(47) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (c) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. (d) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(48) Buchwald, S. L.; Nielsen, R. B., unpublished results.

(49) Rocca, J. R.; Tumlinson, J. H.; Glancey, B. M.; Lofgren, C. S. *Tetrahedron Lett.* **1983**, *24*, 1893.

(50) (a) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E. *Organometallics* **1987**, *6*, 1041. (b) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405.

(51) Eaborn, C.; Jenkins, I. D.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 596.

(52) Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555.

(53) Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933.

(54) (a) Erker, G.; Szisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. (b) Dorf, U.; Engel, K.; Erker, G. *Angew. Chem.* **1982**, *94*, 916.

(55) (a) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

(56) Buchwald, S. L.; Watson, B. T., unpublished results.

(57) Fromberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343.

(58) Meinwald, J.; Meinwald, Y. C. *Adv. Alicycl. Chem.* **1966**, *1*, 1.

(59) Marino, J. P.; Browne, L. J. *J. Org. Chem.* **1976**, *41*, 3629.