Pergamon

Tetrahedron Vol. 51, No. 15, pp. 4395-4406, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01128-1

Preparation and Reactions of Cyclic and Acyclic Allene Complexes of Zirconocene

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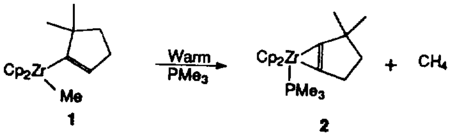
Abstract: The zirconocene π-complex of 3-methyl-1,2-butadiene (1,1-dimethylallene) cannot be prepared by simple ligand substitution due to rapid coupling of the initially formed complex with the unreacted allene. This problem was circumvented by generating the allene complex by β-hydrogen elimination from a pre-formed sigma complex. This appears to be a potentially general way to prepare allene complexes of zirconocene if the allene precursor has no cis-vinyl hydrogen. This method has been successfully used to prepare zirconocene complexes of 3-methyl-1,2-cycloheptadiene, 3-methyl-1,2-cyclohexadiene and 4-phenyl-1,2,3-cyclohexatriene. Attempts to prepare a complex of 3-methyl-1,2-cyclopentadiene failed. Selected reactions of two of these cumulene complexes and their coupling products are reported.

INTRODUCTION

For some years we have been interested in transition metal complexes of strained cyclic allenes[1] but have been unsuccessful in our attempts to prepare late transition metal complexes of rings with less than seven members.[1d,2] We therefore turned our attention to the early transition metals but discovered that although the chemical literature is replete with examples of late transition metal complexes of allenes,[1-5] when this work was initiated early transition metal complexes of allenes were unknown.[6,9] This prompted us to initiate a study to address this void with special interest in the possibility of preparing stable complexes of highly strained allenes and higher cumulenes.[5] Zirconocene was selected for our initial work for two reasons. First, zirconocene pi-complexes of alkenes and alkynes can be readily prepared by displacement of loosely bound ligands such as 1-butene[10]or trimethylphosphine.[10a,11] This type of reaction has been widely used for the preparation of allene complexes of late transition metals but, with a single exception[2] has been limited to stable allenes.

A second reason for selecting zirconocene for initial study is the propensity for dialkyl and divinyl sigma complexes of zirconocene to undergo β-hydrogen elimination to give alkene and alkyne complexes, (even when highly strained)[12] as exemplified in Buchwald's[12d] very impressive synthesis of 2. This type of reaction provides an inviting synthetic method for the preparation of cumulene complexes in cases where direct substitution is not feasible.

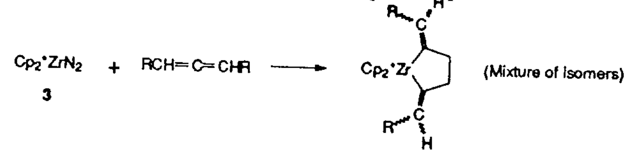


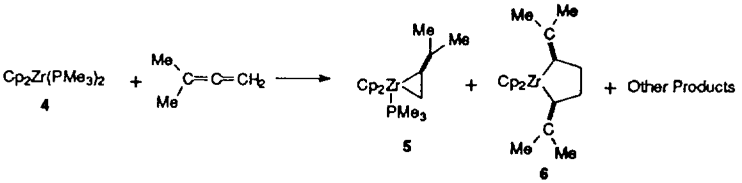
At this time, we report the use of β-hydrogen elimination to prepare zirconocene complexes of 1,1-dimethylallene, 1-methyl-1,2-cycloheptadiene, 1-methyl-1,2-cyclohexadiene and 1-phenyl-1,2,3-cyclohexatriene.[7]

RESULTS AND DISCUSSION

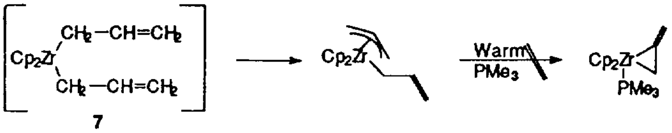
Synthesis of Allene and Cumulene Complexes

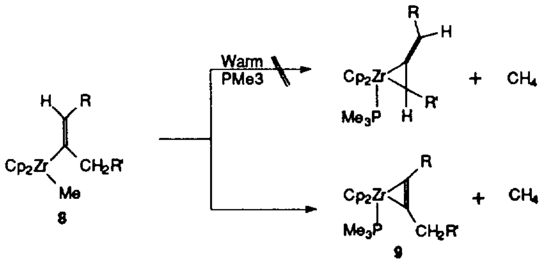
In principle, it should be possible to prepare zirconocene complexes of stable allenes by simple ligand displacement. However, Duggan's[9] finding that reaction of **3** (Cp* = C_5Me_5) with allene, 1,2-butadiene or 2,3-pentadiene (albeit with an excess of the allenes) gave only metallacyclopentanes suggested the likelihood that facile competitive coupling might make it difficult to prepare pure zirconocene complexes of allenes by this method. Indeed, we found that, regardless of the ratio of starting materials and despite carrying out the reaction in the presence of excess PMe_3 (which should stabilize the allene complex and retard coupling),[10] reaction of **4** with 3-methyl-1,2-butadiene[13] gave complex, inseparable mixtures of products. These products showed spectra consistent with, among other materials, both the allene adduct **5** and the metallacyclopentane **6**.[14] Confirmation of the presence of both of these products is discussed below. In an attempt to retard coupling, **4** was warmed with the more sterically encumbered allene, 2,4-dimethyl-2,3-pentadiene (tetramethylallene). However, in this case, no allene containing product was observed; only the known zirconocene[15] dimer was formed. On the other hand, Binger[8a] found that reaction of 1,1-diphenylallene with (η^2-1-butene)(trimethylphosphine)zirconocene gave 31% of the allene complex corresponding to **5**. Thus, for synthetic purposes, it appears that ligand displacement will have only limited use as a method to prepare allene-zirconocene π-complexes although it appears to be general for allene complexes of titanocene.



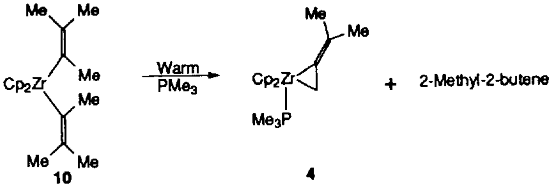


In principle, it should be possible to prepare allene and higher cumulene complexes of zirconocene by β-hydrogen elimination. For example, either **7** or **8** could give an allene complex. However, it was found that attempts to prepare **7** gave only the π-allyl complex (which was stable to PMe_3) while warming **8** with PMe_3 has been reported to give only alkyne complexes **9**.[16] The former result was expected since π-allyl formation is the norm for allyl ligands sigma bonded to sixteen electron transition metals and the latter, although originally surprising[12a] appears to be general and is believed to be due to the more favorable distance and orientation between the zirconium and the β-hydrogen.[12a] It occurred to us that complexes such as **10** in which neither π-allyl nor alkyne formation (no cis-vinyl hydrogen) is possible might undergo β-hydrogen elimination

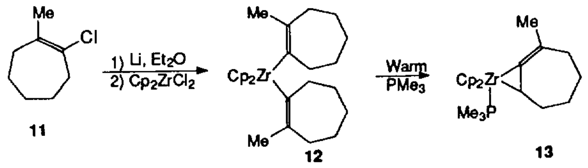




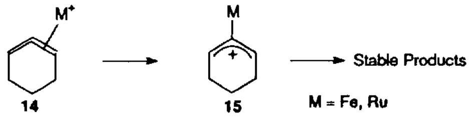
despite unfavorable distance and orientation. Indeed, warming **10** in the presence of PMe_3 gave the allene complex **5** in 52% isolated yield.



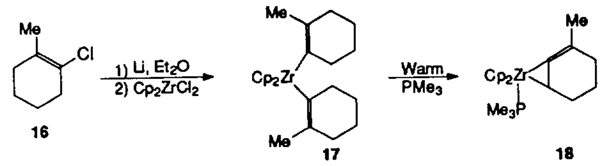
As a method to prepare allene complexes of zirconocene, β-hydrogen elimination will probably be limited to vinyl sigma complexes that have no cis-β-hydrogen. Despite this limitation, the facility of allene formation from **10** suggested this as a potential method to prepare zirconocene complexes of appropriately substituted strained, cyclic allenes. To this end, 1-chloro-2-methylcycloheptene **11** was prepared and converted to the zirconocene complex **12**. Warming **12** for 12 hr at 30 °C in the presence of PMe_3 led to clean extrusion of 1-methylcycloheptene and concomitant formation of the 1-methyl-1,2-cycloheptadiene complex **13** (60% isolated yield).[7]



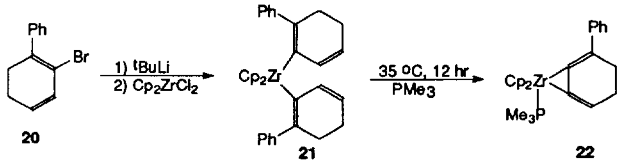
To date, the most highly strained allenes for which transition metal complexes have been successfully prepared are 1,2-cycloheptadiene[1,2] and 1,2,4,6-cycloheptatetraene;[1] attempts to prepare complexes (iron,[17] ruthenium[18] or platinum[2]) of smaller ring allenes have invariably failed. For iron and ruthenium complexes, this failure is believed to be due to rearrangement of the highly strained allene complex **14** to the essentially strain-free allyl cation **15**. However, the zirconocene complex of 1,2-cyclohexadiene should be less likely to relieve its strain in the same way as iron for two reasons: first, the zirconocene complex should be less strained than its Fp^+ counterpart due to greater metallacyclopropane character; the C1-C2 bond lengths for 1,2-cycloheptadiene complexes of iron and zirconium are 1.385(6) Å[1c] and 1.442(9) Å,[7] respectively, and their bend-back angles are 41.9(3)°and 48.2(4)°. Second, in the zirconocene complex, conversion to the allyl cation would place a negative charge on the electropositive zirconium.

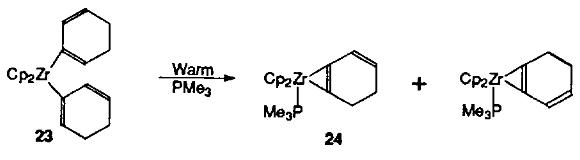


1-Chloro-2-methylcyclohexene **16** was therefore converted to the zirconocene sigma complex **17** which, in turn, was warmed (53 °C for 8 hr) in the presence of Me_3P. To our delight, this led to clean elimination of 1-methylcyclohexene with concomitant formation (71% isolated yield) of the 1-methyl-1,2-cyclohexadiene complex **18**. At this time it is not known whether the more robust conditions required for the six membered ring (53 °C vs 30 °C for the seven membered ring) are due to ring strain in the product or a less accessible β-hydrogen in the starting material (or a combination of the two). Whatever the reason, in our hands the six membered ring has been the limit for the preparation of zirconocene complexes of 1-methyl-1,2-cycloalkadienes since heating the five membered analogue of **17** at 120 °C for 12 hr gave no detectable reaction.



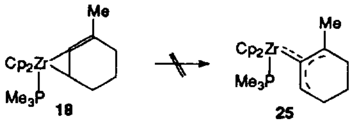
To our knowledge the only reported complex of a cyclic 1,2,3-butatriene is a rhodium complex of 1,2,3-cyclononatriene.[5] However, it occurred to us that although molecular mechanics calculations predict small ring trienes to be far more strained than their allene counterparts (e.g. 82.3 kcal/mol vs. 35.8 kcal/mole for 1,2,3-cyclohexatriene and 1,2-cyclohexadiene, respectively),[19] comparison of their zirconocene precursors suggested the possibility that preparation of a zirconocene complex of a 1,2,3-cyclohexatriene might still be possible due to a shorter distance and more favorable dihedral angle between zirconium and the hydrogen undergoing β-elimination. The phenyl substituted bromocyclohexadiene was therefore prepared (attempts to prepare 1-methyl-2-bromo-1,3-cyclohexadiene failed) and converted to the zirconocene sigma complex **21**. To our surprise, this required warming to only 35 °C for 12 hr (or RT for three days) in the presence of PMe$_3$ for clean conversion to the cyclohexatriene complex **22** (72% isolated yield). The mild conditions required for formation of the triene are truly remarkable and emphasize the importance of hydrogen proximity[12b] since, as mentioned above, more severe conditions (53 °C, 8 hr) were required to produce the zirconocene complex of the less highly strained 1,2-cyclohexadiene complex. As expected, in the absence of the blocking phenyl ring, **23** gave only the complex of the cycloalkenyne (**24**).





Properties of Zirconocene-Allene Complexes

All four of the cumulene complexes of zirconocene are light yellow, air sensitive (both in the solid state and in solution) solids that decompose in halogentated solvents but, in the absence of air, are stable in hydrocarbon solvents. From X-ray crystal structures[7,20] of **13**, **18** and **22** the bond lengths of the double bonds complexed to the metal are significantly longer than the corresponding allene bonds in comparable late transition metal (iron and platinum) allene complexes.[10a,10b,11] This is consistent with zirconocene complexes of acyclic alkenes[9a,9b,10] and suggests significant metallacyclopropane character (*vide supra)* in the allene complexes. From its ^{1}H and ^{13}C NMR spectra, the dimethylallene complex is formed as a single material which shows no tendency to rearrange to any of its more sterically hindered isomers. In both the cyclohexadiene and cycloheptadiene complexes, the ^{1}H NMR spectra show sharp, non-equivalent Cp resonances. The six membered ring complex (the most strained of the allene complexes) was warmed to 55 °C but showed no evidence of coalescence. This places a minimum energy for ring opening of the metallamethylene-cyclopropane to the metal equivalent of a trimethylenemethane at about 17 kcal/mole.

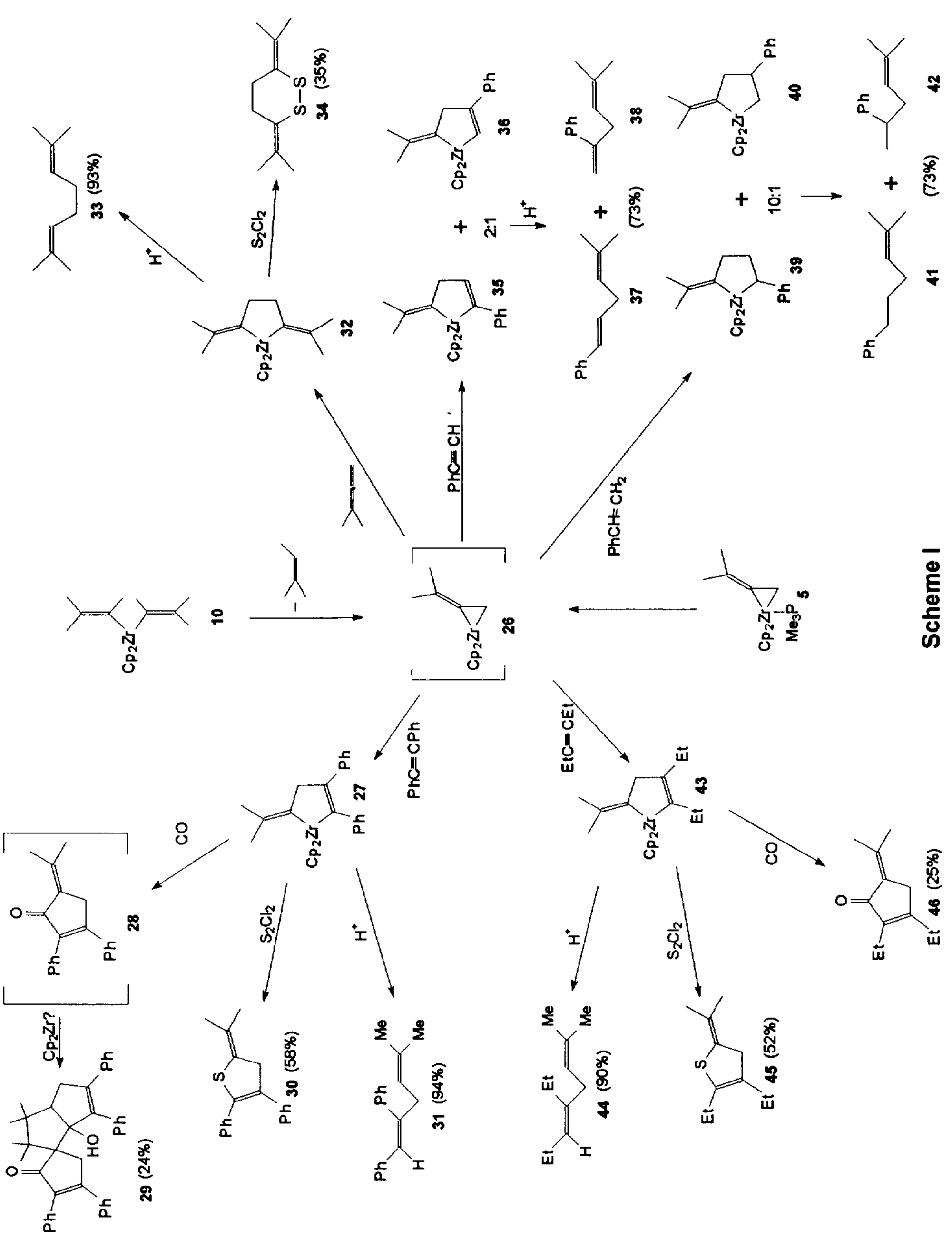


Some coupling reactions of the dimethylallene complex are recorded in Scheme I. In general, these reactions parallel those of alkyne and alkene complexes of zirconocene as do the reactions of their adducts with the indicated reagents[8a,10,13,21] although one significant difference (see below) was noted. No significant difference was observed when the sixteen electron allene intermediate **26** was generated *in situ* from **4** or **10**. All coupling reactions were completely regiospecific with respect to the complexed allene with the alkene, the alkyne or the second allene bonding exclusively to the terminal carbon of the complexed double bond. This regiospecificity greatly reduced the complexity of these reactions which makes them of more potential use in organic synthesis although some yields were not particularly high. Alkynes showed no tendency to displace the allene as has been seen in some alkene complexes. This may be due to a somewhat stronger bond in the allene complex due to the sp hybridization on the central carbon. Stilbene does displace the allene.

Consistent with Binger's[8a] results, coupling of the 3-methyl-1,2-butadiene complex with a second mole of the allene gave a single regioisomer. On the other hand, the unsymmetrical alkyne (phenylacetylene) and alkene (styrene) gave mixtures of regioisomeric coupling products. In all three cases, the bulky substituent prefers the position adjacent to the zirconium. The origin of this preference is not obvious. Benzylic and/or agostic stabilization has been suggested[21] as a possible reason for preferential formation of α-aryl substituted zirconocyclopentanes from coupling of styrene with alkene complexes. Such an effect may apply to some of the cases at hand although it is not obvious how this could play a significant role in all of them.

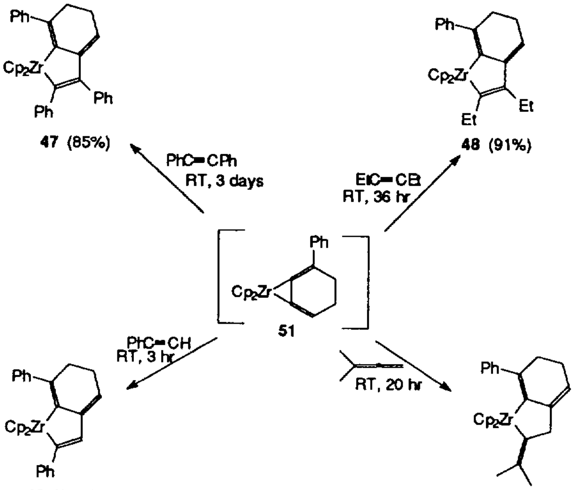
To begin to explore the synthetic potential of allene coupling products, the metallacycles were treated with some of the reagents that have been found to react with other five-membered zirconocycles.[10,22] Although yields were not high in some cases, in general the allene adducts appear to behave pretty much like other zirconocycles. One interesting deviation was observed in the reactionof the bis-allene adduct **32** with S_2Cl_2 in that the product clearly has two sulfur atoms (rather than the expected one). This product is tentatively assigned structure **34**. Another curious product resulted from treatment of the diphenylacetylene adduct **27** with CO. Instead of the expected methylenecyclopentenenone **28**, a reduced formal dimer **29** was formed. We have no evidence for the mechanism of this dimerization although the reduction suggests involvement of zirconium. Regardless of mechanism, the structure is secure, having been confirmed by X-ray.[23] Finally, it should be noted that products similar to those resulting from coupling with dimethylallene have been produced by reactions of the zirconocene complex of isoprene[24] but the allene complex is more convenient to prepare and the products from isoprene are not formed stereospecifically.

To date, examination of the chemistry of the cyclic cumulene complexes of zirconocene has focused primarily on the complex of 4-phenyl-1,2,3-cyclohexatriene. Successful coupling reactions are summarized


Cp2Zr
10
26
Cp2Zr
Me3P
5
PhC≡CH
PhCH=CH2
H+
33 (93%)
S2Cl2
34 (35%)
S–S
32
35
36
2:1
H+
37
38
(73%)
39
40
10:1
41
42
(73%)
Ph
PhC≡CPh
27
CO
28
Cp2Zr?
29 (24%)
HO
S2Cl2
30 (58%)
H+
31 (94%)
Me
H
EtC≡CEt
43
Et
H+
44 (90%)
S2Cl2
45 (52%)
CO
46 (25%)
O
S

Scheme I

in Scheme 2. Attempts to effect coupling with dimethylacetylenedicarboxylate, 1,4-dichloro-2-butyne, cyclopentene, stilbene, acetonitrile or acetone failed, all giving complex mixtures. Coupling with the unsymmetrical allene and phenylacetylene is completely regiospecific and is consistent with Buchwald's rule[25] that substituents will avoid C3 and C4 if these carbons are both sp^2 hybridized. Coupling reactions of the cyclic allene complexes **18** and **13** have yet to be studied beyond reactions with diphenylacetylene which was successful in both cases and stilbene which coupled with the six membered ring but gave only the displacement product (the stilbene complex) with the seven membered ring.[7] As mentioned above, displacement was also the result of treating the acyclic allene complex with stilbene. Selective coupling to the more highly strained six membered ring is intuitively reasonable; relief of strain should accelerate coupling while the greater strain in the allene ligand should retard displacement.



Scheme II

EXPERIMENTAL SECTION[26]

General

All experiments involving organometallic compounds were carried out in a dry atmosphere of nitrogen in a dry box or by standard Schlenk line techniques. Hexane, diethylether and toluene were distilled from CaH$_2$ and benzophenone ketyl. 2-Bromo-3-methyl-2-butene,[27] was prepared by literature procedures. Cp$_2$ZrCl$_2$, ^{t}BuLi, 3-hexyne, KO^{t}Bu, PMe$_3$, 3-methyl-1,2-butadiene, and tetramethylallene were purchased from Aldrich chemical company. NMR spectra were taken on a Varian XL-300 spectrometer with TMS or solvent peaks as reference for ^{1}H and ^{13}C NMR. IR spectra were recorded on a Perkin-Elmer 1600 FTIR. MS spectra were obtained on a Finnigan Mat 95Q spectrometer. Elemental analyses were done in the microanalysis lab of the Chemistry Department of the University of Florida. Melting points were obtained in sealed capillaries and are not corrected.

Cp$_2$Zr(PMe$_3$)(3-Methyl,2-butadiene) (5) To a solution of 0.63 g (4.23 mmol) of 2-bromo-3-methyl-2-butene in 30 ml of diethylether was added dropwise a solution of 5 ml (1.7 N, 8.5 mmol) of ^{t}BuLi in pentane at -60 °C over 10 min. The mixture was stirred at this temperature for 0.5 h and was then warmed to 0 °C over one hour. The resulting yellow solution was cooled to -60 °C and 0.40 g (1.37 mmol) of Cp$_2$ZrCl$_2$ was added. The resulting mixture was stirred at this temperature for one h. and 0.3 ml of PMe$_3$ was added to the resulting red-orange solution. The mixture was stirred overnight allowing it to warm from -60 °C to r.t.. The mixture was cooled to -20 °C for 30 min and the filtered solution was concentrated to 10 ml and kept in dry ice overnight to give greyish crystals which were washed with 5 ml of hexane at -10 °C and dried under vacuum, yield 0.26 g (52 %). ^{1}H NMR (C_6D_6): δ 5.14 (d, 10H, $^3J_{PH}$=1.7 Hz), 2.53(t, 3H, $^5J_{HH}$=2.0Hz), 2.19(t,3H, $^5J_{HH}$=2.4Hz)), 0.80(d,9H, $^2J_{PH}$=5.6Hz), 0.11(m, 2H). ^{13}C NMR(C_6D_6): δ 167.68 (d, $^2J_{PC}$=6.2Hz), 125.96(d, $^3J_{PC}$=3.7Hz), 29.19, 26.44, 16.89(d, $^2J_{PC}$=16.5Hz), 1.80(d, $^2J_{PC}$=16.4Hz). ^{31}P NMR(C_6D_6) d 1.691. Anal. calcd. for $C_{18}H_{27}PZr$: C, 59.14; H, 7.44. Found: C, 58.79; H, 7.20.

2,7-Dimethyl-2,6-octadiene (33) and 32 The following procedure, with the indicated modifications was used for the preparation of **29, 30, 31, 34, 41, 44** and **45.** To a solution of 0.70 g (4.7 mmol) of 2-bromo-3-methyl-2-butene in 30 ml of diethyl ether was added a solution of 9.4 mmol of n-BuLi in pentane at -60 °C. The reaction mixture was stirred 0.5 h at this temperature and warmed to 0 °C over one hour to give a yellow solution. The solution was cooled to -60 °C and 0.44 g (1.5 mmol) of Cp_2ZrCl_2 was added and the mixture was stirred 1 h at this temperature. To the resulting red solution was added 0.20 g (2.9 mmol) of 3-methyl-1,2-butadiene. The mixture was stirred overnight allowing it to warm from -60 °C to r.t. and treated with 3N HCl solution. The organic layer was separated and the aqueous solution was extracted with ether. The combined ether extracts were washed with water and dried over $CaCl_2$. The solution was filtered through a short silica gel column and the solvent was evaporated to give 0.19 g (93%, based on Cp_2ZrCl_2) colorless liquid. The ^{1}H NMR is identical to the reported spectrum.[28] ^{13}C NMR ($CDCl_3$) δ 131.55, 124.45, 29.74, 28.40, 25.75.

The head-to-head coupling as the only coupling mode of two allene molecules has been comfirmed by the NMR of the zirconocyclopentane derivative **32**, the precursor of compound **33**, which was prepared by the reaction of complex **5** with 3-methyl-1,2-butadiene. To a solution of 60 mg (0.16 mmol) of $Cp_2Zr(PMe_3)$(3-methyl-1,2,-butadiene) in 2 ml of C_6D_6 was added 20 ul of 3-methyl-1,2-butadiene. The mixture was kept at r.t. for 4 h to give a single coupling product (87 % by NMR) which showed spectra identical to those reportedfor this material by Binger.[8a] When the solution of **32** was treated as described above, **33** was obtained in 85 % yield.

Reaction of $Cp_2Zr(PMe_3)_2$ with 3-Methyl-1,2-butadiene To a solution of 38 mg (0.1 mmol) of $Cp_2Zr(PMe_3)_2$ in 0.5 ml of C_6D_6 was added a solution of 10 ul (0.10 mmol) of 3-methyl-1,2-butadiene in 1.5 ml of C_6D_6. The mixture was kept at r.t. for 30 min.. The ^{1}H NMR showed substantial starting material (ca 30 %) and three other products identified as **5**, **32** and ziconocene dimer[15] in a ratio of 6 : 2 : 0.8.

Reaction of $Cp_2Zr(PMe_3)_2$ with Tetramethylallene. To a solution of 32 mg (0.09 mmol) of $Cp_2Zr(PMe_3)_2$ in 0.5 ml of C_6D_6 was added a solution of 12 ul (0.09 mmol) of tetramethylallene. The solution was kept at r.t. for 12 h and the ^{1}H NMR showed zirconocene dimer as the only product.

5-Methyl-1,2-diphenyl-1(Z),4-hexadiene (31) and 27 See preparation of **33.** 3-Methyl-1,2-butadiene was replaced with 0.20 g (1.11 mmol) of diphenylacetylene. Filtration of the final solution through a short silica gel column gave 0.26 g (94% based on diphenylacetylene) of yellowish oil. ^{1}H NMR($CDCl_3$) δ 6.8-7.2(m, 10H), 6.33(s, 1H), 5.17(t, 1H, $^3J_{HH}$=7.2 Hz), 3.07(d, 2H, $^3J_{HH}$=7.2 Hz), 1.66(s,3H), 1.52(s, 3H). ^{13}C NMR($CDCl_3$) δ 142.23, 141.82, 137.57, 133.67, 128.99, 128.48, 128.41, 127.78, 126.77, 126.04, 125.98, 121.28, 39.03, 25.79, 17.78. HRMS: calcd. for $C_{19}H_{20}$ (M) 248.1549, found 248.1545.

The coupling reaction of complex **5** with diphenylacetylene can be monitored by NMR. 61 mg (0.17 mmol) of **5** and 30 mg (0.17 mmol) of diphenylacetylene was dissolved in 2 ml of C_6D_6. The solution was kept at r.t. for 2 h to insure complete reaction. The zirconocyclopentene **27** was formed quantitatively. ^{1}H NMR(C_6D_6) δ 6.7-7.2(m, 10H), 6.03(s,10H), 3.30(s, 2H), 1.62(s,3H), 1.10(s, 3H). ^{13}C NMR($CDCl_3$) δ

185.70, 177.38, 149.80, 145.55, 138.25, 133.95, 131.92, 129.05, 128.59, 127.09, 125.65, 122.97, 112.19, 41.31, 26.50, 20.32.

Carbonylation of Zirconocyclopentene from 26 and Diphenylacetylene: Preparation of 29. See preparation of **33**. To the red solution was added 0.20 g (1.12 mmol) of diphenylacetylene and stirred under CO (1.2 atm.) for 3 h at 0 °C. Workup and chromatography on silica gel with hexane / ether (5/1, v/v) and recrystallization from hexane gave 75 mg (24 %, based on diphenylacetylene) **29** as colorless needles, m.p. 171-172 °C. ^{1}H NMR ($CDCl_3$) δ 6.8-7.3 (m, 10 H), 6.73 (s, 1H, OH), 3.10 (s, 1H), 2.92(m, 1H), 2.80 (m,1H), 1.36 (S, 3H), 1.11 (s, 3H), 1.06 (s, 3H), 0.87 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 168.84, 141-102 (phenyl and vinyl peaks), 61.69, 54.74, 45.52, 42.29, 34.98, 27.21, 24.27, 22.18, 19.63. IR (KBr) 3342, 1666, 1631, 1595, 1480, 1443, 1390, 1364, 1296, 1161, 1025, 890, 755, 696, 532. Anal. calcd. for $C_{40}H_{38}O_2$: C, 87.29; H, 6.96. Found: C, 87.14; H, 7.02.

2,3-Diphenyl-4-(dimethylmethylene)thiocyclopentene-2 (30) See preparation of **33**. 3-Methyl-1,2-butadiene was replaced with 0.18 g (1.0 mmol) diphenyl acetylene. Dropwise addition of 0.20 g (1.5 mmol) S_2Cl_2 followed by workup and chromatography on alumina with pentane / ether (20/1, v/v) gave 0.16 g (58 %, based on diphenylacetylene) **30** as a yellow oil. ^{1}H NMR($CDCl_3$) δ 6.95-7.25(m, 10H), 3.60(s, 2H), 1.80(s,3H), 1.71(s,3H). ^{13}C NMR($CDCl_3$) δ 142.39, 141.75, 138.24, 131.95, 130.09, 128.93, 128.06, 127.93, 127.50, 126.69, 126.03, 40.187, 23.56, 21.48. HRMS calcd. for $C_{19}H_{18}S$ (M) 278.1129, found 278.1105.

2,5-Bis(dimethylmethylene)dithiocyclopentane (34) See preparation of **33**. After warming from -60° to r.t., 0.33 g (2.4 mmol) of S_2Cl_2 was added dropwise over 5 min. Workup and chromatography on alumina with hexane /ether (20/1, v/v) followed by recrystallization from pentane at -50 °C gave 95 mg (35 %, based on Cp_2ZrCl_2) **34** as yellowish needles, m.p.88-89 °C. ^{1}H NMR ($CDCl_3$) δ 2.71(s, 4H), 1.86(s, 6H), 1.77 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 129.32, 126.44, 29.35, 22.09, 20.79. HRMS calcd for $C_{10}H_{16}S$ (M) 168.0972, found 168.0972. Anal. (triplicate; all virtually identical) calcd. for $C_{10}H_{16}S_2$: C, 59.94; H, 8.05. Found: C, 59.88; H, 8.08

5-Methyl-1-phenyl-1(E),4-hexadiene (37) and 5-Methyl-2-phenyl-1,4-hexadiene (38) See preparation of **38**. 3-Methyl-1,2-butadiene was replaced by 0.14 g (1.4 mmol) phenylacetylene to give 0.17 g (72 %) of a mixture of **37** and **38** (**37**:**38** = 2:1) as a yellowish liquid. No effort was made to separate these two compounds. ^{1}H NMR($CDCl_3$) for **37** δ 6.20 (d, 1H, $^3J_{HH}$=15.9Hz), 6.10 (dt, 1H, $^3J_{HH}$=15.9hz, $^3J_{HH}$=6.4Hz), 5.22 (t, 1H, $^3J_{HH}$=7.5Hz), 2.83 (dd, 2H, $^3J_{HH}$=7.5Hz, $^3J_{HH}$=6.4Hz), 1.67 (s, 3H), 1.59 (s, 3H). ^{1}H NMR ($CDCl_3$) for **38** δ 5.32(s, 1H), 5.06 (s, 1H), 5.22 (t, 1H, $^3J_{HH}$=7.5Hz), 3.10 (d, 2H, J=7.5Hz), 1.64 (s,3H) 1.59 (s, 3H). The assignments of chemical shifts listed above for these two compounds have been comfirmed by decoupling experiments. HRMS calcd. for $C_{13}H_{16}$ (M) 172.1252, found 172.1241.

2-Methyl-6-phenyl-2-hexene (42) and 2-Methyl-6-phenyl-2-hexene (41) See preparation of **33**. 3-Methyl-1,2-butadiene was replaced by 0.16 g (1.53 mmol) styrene. Workup and chromatography on silica gel gave 0.20 g (75% based on styrene) of a mixture of **41** (^{1}H NMR chemical shifts identical to reported[29] and **42** in a ratio ca 10:1 as a colorless liquid. ^{1}H NMR ($CDCl_3$) for **41**: δ 7.1-7.3 (m, 5H, Ph), 5.17 (m, 1H, vinyl proton), 2.62 (t, 2H, $PhCH_2$, $^3J_{HH}$=7.8Hz), 2.02 (m, 2H, $Ph(CH_2)_2CH_2$, 1.70 (m, 2H, $CH_2CH_2CH_2$), 1.72 (s, 3H, CH_3), 1.60 (s, 3H, CH_3). **42**: 7.10-7.30 (m, 5H), 5.05 (t, 1H), 2.70 (m, 2H), 1.80 (m, 2H), 1.22 (d, 3H). The assignment was confirmed by decoupling experiments. HRMS calcd for $C_{13}H_{18}$ (M) 174.1408, found 174.1317.

5-Ethyl-2-methyl-2,5(E)-octadiene (44) See preparation of **33**. 3-Methyl-1,2-butadiene was replaced by 0.3 ml of 3-hexyne to give 0.16 g (90 %, based on Cp_2ZrCl_2) **44** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.06 (m, 1H), 5.01 (t, 1H, $^3J_{HH}$=7.1Hz), 2.60 (d, 2H, $^3J_{HH}$=7.1Hz), 1.92 m, 4H), 1.64 (s, 3H), 1.55 (s, 3H), 0.88 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 139.82, 132.12, 125.96, 122.92, 35.20, 25.81, 23.24, 20.88, 17.63, 14.75, 13.27. HRMS calcd. for $C_{11}H_{20}$ (M) 152.1565, found 151.1606.

2,3-Diethyl-5-dimethylmethylene-thiocyclopentene-2 (45) See preparation of **33**. 3-Methyl-1,2-butadiene was replaced by 0.3 ml of 3-hexyne and HCl was replaced by 0.27 g (2.0 mmol) of S_2Cl_2 (added dropwise). Workup as described above gave 0.13 g (52 % based on Cp_2ZrCl_2) **45** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 3.13 (s, 3H), 2.36 (q, 2H, $^3J_{HH}$=7.5Hz), 2.22(q, 2H, $^3J_{HH}$=7.6Hz), 1.81 (s, 3H), 1.76 (s, 3H), 1.11 (t, 3H, $^3J_{HH}$=7.5Hz), 1.01 (t, 3H, J=7.6Hz), ^{13}C NMR ($CDCl_3$) δ 143.75, 138.07, 133.24, 122.62, 37.21, 27.32, 26.75, 23.46, 21.23, 13.56. HRMS calcd. for $C_{11}H_{18}S$ (M) 178.1357, found 178.1366.

2,3-Diethyl-5-dimethylmethylene-cyclopenten-2-one (46) A reaction mixture from 0.52 g (3.5 mmol) of 2-bromo-3-methyl-2butene, 1 equiv ^{t}BuLi, 0.33 g (1.1 mmol) of Cp_2ZrCl_2 and 0.3 ml of 3-hexyne was evacuated at -20 °C to 20 mm Hg and recharged with CO. This process was repeated twice and the mixture was stirred under 1.2 atm of CO for 3 h at r.t. The reaction mixture was treated with 3 N HCl and extracted with ether. The ether solution was washed with water. The solvent was evaporated and the residue was chromatographed on an Alumina column with pentane / ether (20/1, v/v) as eluent to give 0.050 g (25 % based on Cp_2ZrCl_2) yellowish liquid which is contaminated with ca 5% uncharacterized inpurity (this inpurity has a doublet at 3.83 ppm and a multiple at 3.2 ppm). ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 2H), 2.38 (q, 2H, $^3J_{HH}$=7.6Hz), 2.24 (s, 3H), 2.15 (q, 2H, J=7.5 Hz), 1.80 (s, 3H), 1.06 (t, 3H, J=7.6Hz), 0.92 (t, 3H, J=7.5Hz). ^{13}C NMR ($CDCl_3$) δ 163.95, 144.17, 143.82, 128.97, 34.33, 24.03, 23.18, 16.42, 13.36, 12.37. IR (film) 2934, 2967, 2886, 1684, 1654, 1632, 1462, 1359, 1070, 1008, 935, 815. HRMS calcd. for $C_{12}H_{18}O$ (M) 178.1357, found 178.1366.

Coupling Reaction of Cyclohexatriene Zirconocene Complex 51 with Diphenylacetylene (47) Zirconocyclopentene **47** was generated by the reaction of **22** as described previously[7], or more conveniently from **21**. Both reactions presumably proceed through the same intermediate in essentially quantitative yield. For example 70 mg (0.13 mmol) of **21** and 23 mg (0.13 mmol) of diphenylacetylene were dissolved in 2 ml of C_6D_6. The solution was kept at r.t. for 60 h to insure complete reaction. ^{1}H NMR (C_6D_6) δ 6.7-7.3 (m, 15H), 5.94 (s, 10H), 5.57(t, 1H, $^3J_{HH}$=5.2 Hz), 2.42 (t, 2H, $^3J_{HH}$=9.2 Hz)), 2.10 (dt, 2H, $^3J_{HH}$=5.2Hz, $^3J_{HH}$=9.2Hz), 2H). ^{13}C NMR (C_6D_6) δ 194.11, 182.58, 149.48, 148.87, 147.27, 146.39, 145.45, 142.48, 130.89, 128.59, 128.40, 127.39, 126.64, 126.25, 125.92, 125.59, 123.02, 119.07, 10.76, 20.53.

Coupling Reaction of 51 with 3-Hexyne Similar to the preparation of **47**, 70 mg of **21** and 30 ul of 3-hexyne were dissolved in 2 ml of C_6D_6. The reaction went to completion in 36 h to form coupling product **48** (91 % by NMR). ^{1}H NMR (C_6D_6) δ 7.0-7.2 (m, 5H), 5.89 (s,10H), 5.70 (t, 1H, $^3J_{HH}$=5.2 Hz), 2.35 (m, 2H), 2.20 (m, 2H), 1.9-2.1 (m, 5H), 1.70 (q, 2H), 1.20(t,3H). ^{13}C NMR (C_6D_6) δ 195.07, 184.18, 145-125 (phenyl and vinyl carbon), 111.67, 27.22, 25.50, 23.39, 21.87, 14.73.

Coupling Reaction of 51 with Phenylacetylene As in the preparation of **47**, 70 mg **21** and 40 ul phenylacetylene were dissolved in 2 ml of C_6D_6. The reaction was complete in 36 h at r.t. to give coupling product **49** (86 % by NMR). Only one coupling product was observed. An attached proton test experiment in the ^{13}C NMR showed that the terminal carbon of phenylacetylene is bonded to the cyclohexatriene unit. ^{1}H NMR (C_6D_6) δ 7.1-7.4 (m, 10H), 5.84 (s, 11H), 5.60 (t, 1H, $^3J_{HH}$=5.0 Hz), 2.45 (m, 2H), 2.25 (m, 2H). ^{13}C NMR (C_6D_6) δ 192.53, 179.27, 148-120 (phenyl and vinyl peaks), 112.11, 25.47, 23.38.

Coupling Reaction of 51 with 3-Methyl-1,2-butadiene (50) As in the preparation of **47**, 60 mg of **21** and 30 μl of 3-methyl-1,2-butadiene were dissolved in 2 ml C_6D_6. The reaction was complete in 24 hr at rt to form coupling product **50** (81% by NMR). ^{1}H NMR (C_6D_6) δ 6.9-7.3 (m, 5H), 5.90 (s, 10 H), 5.70 (t, 1H, $^3J_{HH}$=5.0 Hz), 3.20 (s, 2H), 2.30 (m, 2H), 2.05 (m, 2H), 1.60 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (C_6D_6), two sp^2 carbons bonded to Zr and Cp signals at 181.00, 176.02 and 111.36 ppm.

Acknowledgment

Support of this research by the National Science Foundation, The Univesity of Florida Division of Sponsored Research, and the Chevron Research and Technology Company is gratefully acknowledged.

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(*Received* 29 *August* 1994)