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Cumulene-Derived Metallacyclic Complexes. 3. Stereo- and Regiochemical Selectivity in the Formation of Asymmetric Exo-Unsaturated Metallacyclopentanes from Methylallene

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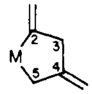
The reaction of methylallene with $[(C_5Me_5)_2ZrN_2]_2N_2$ to form exo-unsaturated metallacyclopentanes has been found to demonstrate geometric selectivity, regioselectivity, and stereoselectivity. Reaction at -45 °C produces two isomers which account for >95% of the products. They have been identified by ^1H and ^{13}C NMR data, with use of comparisons to two other exo-unsaturated metallacyclopentanes which have been prepared and reported earlier. The mechanistic implications of the selectivity displayed in this reaction are discussed.

Introduction

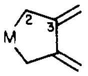
We have investigated the formation of exo-unsaturated metallacyclopentanes from a variety of allenes, with an eye toward the elucidation of the mechanism of this oxidative coupling mechanism as well as toward the synthesis of compounds whose chemistry is of interest in its own right. In other reports[1,2] we have described metallacyclic products that have been obtained from allene and from 1,3-dimethylallene. In this paper are presented the results of the reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$[3] with methylallene. It is important to realize that while study of the 1,3-dimethylallene reaction provided information as to the stereochemical selectivity of the coupling reaction, with methylallene, the product distribution may reveal both regio- and stereochemical trends. The combination of the two may, it is hoped, advance our knowledge of the mechanisms involved.

Reaction of allenes with metal complexes has been found[1,2,4] to yield products of the geometrical forms A–C. The forces that drive the reaction toward a particular form are unknown, but it is likely that both electronic and steric criteria come into play. Any hypothesis purporting to rationalize the kinetic selectivity between isomer types A, B, and C must also be consistent with more refined observations on substituted systems. Our other papers point out that the reaction of allene with the pentamethylzirconocene system results in the formation of a metallacycle of type A, whereas 1,3-dimethyl substitution on the constituent allene shifts the observed product from type A to type B. It is also found that this latter reaction produces only one stereoisomer, where others are possible and have been found to be even more stable (they are prepared by thermal rearrangment of the product from the 1,3-dimethylallene reaction).



A

B



C

In this paper we will show that the analogous reaction with methylallene produces two main products, which are found to be the *only* detectable products when the reaction is carried out at -45 °C. The selectivity of this reaction is notable when it is realized that there are 48 geometric and regio- and stereochemical isomers possible. To some extent this selectivity may be attributed to steric requirements for product stability, but where substitution patterns are known to be feasible by the identification of sterically similar species from related reactions, conclusions may be drawn regarding the structure of the transition state.

Experimental Section

$[Zr(C_5Me_5)_2N_2]_2N_2$ was prepared as reported in the literature[3] with modifications indicated by Bercaw. All reactions were carried out by using ~200 mg of the dinitrogen complex with an excess over 2 mol of methylallene/mol of zirconium. The reactions were done in ~5 mL of toluene, and the temperature was controlled by use of a Neslab CC-80F cryocooling unit with a temperature controller. Color change from deep violet to orange is seen after ~1-2 h at -45 °C and instantaneously (as soon as warm) at room temperature. After the color is constant, the toluene is evaporated, leaving a red-orange oil which is dissolved in butane and filtered at ~-60 °C. Very little solid is left behind if the starting material is pure—the product is virtually entirely soluble in butane. Spectroscopic measurements were carried out on the red-orange oil obtained by evaporation of the butane. The description of the workup of this reaction is identical with those carried out at room temperature.

The materials produced in this reaction were characterized with use of infrared spectroscopy of the neat oil (Perkin-Elmer 283) and ^1H (Nicolet 360) and ^{13}C NMR spectra (Bruker WM-250) of toluene-d_8 solutions.

Proton NMR data will be listed for each isomer separately, the major isomer labeled I and the minor isomer, II. The furthest upfield aromatic absorption for toluene-d_7 was used to calibrate the chemical shifts. Each datum will be identified with the appropriate assignment according to the standard ring numbering. For I: $C(2){=}CHCH_3$, 1.66 ppm (d of t, $J_d = 6.3$ Hz, $J_t = 1.2$ Hz); $C(2){=}CHCH_3$, 4.24 ppm (q of t, $J_q = 6.3$ Hz, $J_t = 2.3$ Hz); $CH_2(3)$, 3.04 ppm (b m); $C(4){=}CHCH_3$, 5.05 ppm (q of p $J_q = 6.6$ Hz, $J_p = 1.5$ Hz); $C(4){=}CHCH_3$, obscured by C_5Me_5 absorption, ~1.87 ppm; $CH_2(5)$, 1.18 ppm, combined with absorption from minor isomer; C_5Me_5, 1.81 ppm. For II: $C(2){=}CHCH_3$, 1.11 ppm (d of t, $J_d = 6.6$ Hz, $J_t = 1.7$ Hz); $C(2){=}CHCH_3$, 6.08 ppm (q of t, $J_q = 6.6$ Hz, $J_t = 2.0$ Hz); $CH_2(3)$, 2.94 ppm (b m); $C(4){=}CHCH_3$, obscured by C_5Me_5 absorption, ~1.82 ppm; $C(4){=}CHCH_3$, 5.03 ppm (q of p, $J_q = 6.6$ Hz, $J_p = 1.5$ Hz); $CH_2(5)$, 1.18 ppm, combined with absorption from major isomer; C_5Me_5, 1.86 ppm. Approximate location of obscured methyl resonances was confirmed by decoupling experiments.

Integrations were carried out on various regions of the proton spectrum by using computer integration of the NTC-360 or the cut-and-weigh technique, whichever was appropriate. The following results were obtained: $CH_2(3)(I){:}CH_2(3)(II) = 2.54{:}1$ (corresponds to 28% minor isomer, II); $(R(I) + R(II) + C(4){=}CHCH_3(I) + C(4){=}CHCH_3(II)){:}(CH_2(5)(I) + CH_2(5)(II)) = 33{:}2.0$ (confirms 1:2 Zr:methylallene stoichiometry in each isomer) (R denotes C_5Me_5 ring absorptions); $C(2){=}CHCH_3(I){:}C(2){=}CHCH_3(II) = 2.49{:}1$ (corresponds to 29% II); $(C(2){=}CHCH_3(I) + C(2){=}CHCH_3(II)){:}(CH_2(5)(I) + CH_2(5)(II)) = 3{:}1.98$ (confirming peak (5,5′) to be due to absorption by *both* isomers); $(C(2){=}CHCH_3(I) + C(2){=}CHCH_3(II)){:}(C(4){=}CHCH_3(I) + C(4){=}CHCH_3(II)) = 1.94{:}2.00$ (confirming, within 5%, that the 5 ppm absorption is an overlap of two signals, as can be seen from Figure 2).

Carbon-13 NMR data were recorded relative to Me_4Si, with the furthest downfield toluene-d_8 absorption being used to calibrate. The

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[1] J. R. Schmidt and D. M. Duggan, *Inorg. Chem.*, **20**, 318 (1981).
[2] J. R. Schmidt and D. M. Duggan, submitted for publication.
[3] J. M. Manriquez and J. E. Bercaw, *J. Am. Chem. Soc.*, **96**, 6229 (1974).
[4] P. Diversi, G. Ingrosso, A. Immirzi, and M. Zocchi, *J. Organomet. Chem.*, **104**, C1 (1976); G. Ingrosso, L. Porri, G. Pantini, and P. Racanelli, *ibid.*, **84**, 75 (1975); G. Ingrosso, A. Immirzi, and L. Porri, *ibid.*, **1973**, **60**, C35 (1973); P. W. Jolly, C. Krüger, R. Salzand, and J. C. Sekutowski, *ibid.*, **165**, C39 (1979).

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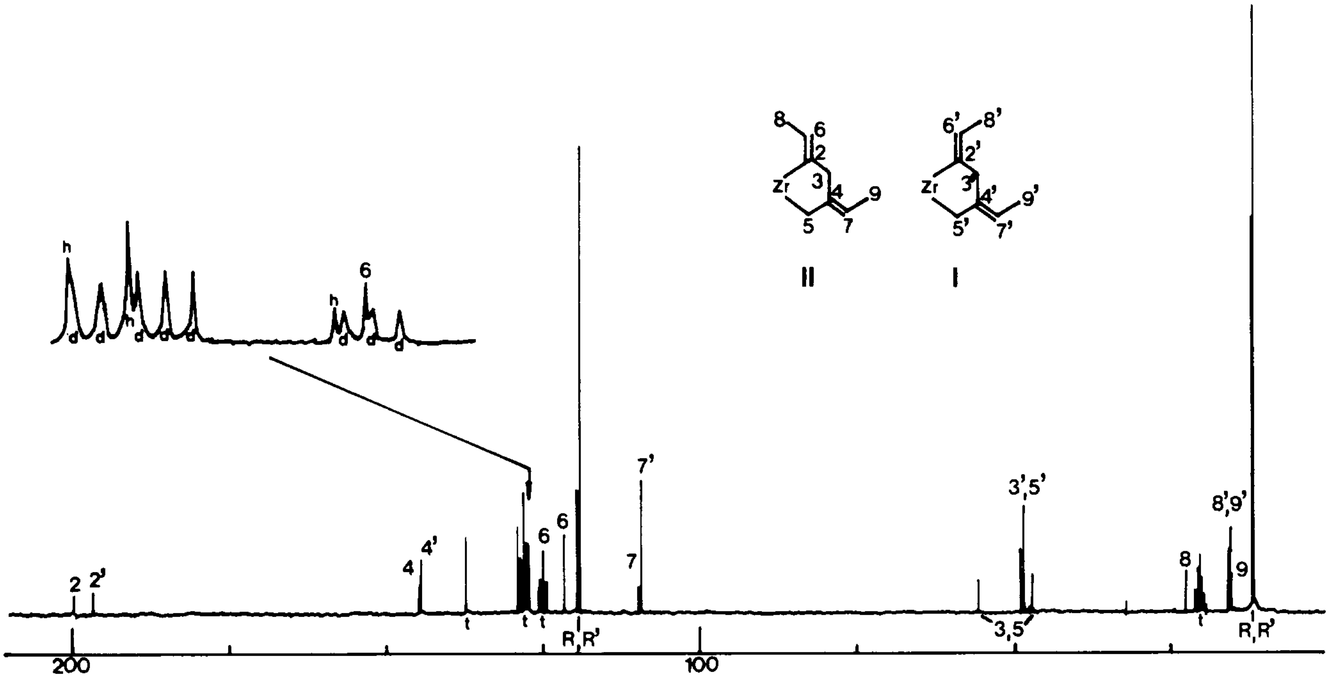


Figure 1. ^{13}C NMR spectrum of the subject compound mixture resulting from reaction at −25 °C (chemical shifts in ppm downfield from Me_4Si) taken in toluene-d_8 with a Bruker WM-250 instrument. The toluene absorptions are indicated by "t" and the peak assignments for the metallacyclic complexes are as indicated in the inset diagrams. The C_5Me_5 methyl absorptions are labeled "R", the downfield pair corresponding to the carbons of the C_5 ring. The expanded region shows a detailed view of the absorption region due to toluene-d_8 and some residual toluene-h_8. These are marked d and h, respectively.

data are listed below with the appropriate assignments. For I: C(2), 196.8 ppm; $C(2){=}\mathit{C}HCH_3$, 120.0 ppm; $C(2){=}CH\mathit{C}H_3$ and $C(4){=}CH\mathit{C}H_3$, 15.62 and 15.46 ppm; C(3) and C(5), 48.5 and 49.1 ppm; C(4), 144.6 ppm; $C(4){=}\mathit{C}HCH_3$, 109.5 ppm; C_5Me_5, 119.3 ppm; $C_5\mathit{Me}_5$, 11.7 ppm. For II: C(2), 199.8 ppm; $C(2){=}\mathit{C}HCH_3$, 125.2 ppm; $C(2){=}CH\mathit{C}H_3$, 22.6 ppm; C(3) and C(5), 47.3 and 55.8 ppm; C(4), 144.8 ppm; $C(4){=}\mathit{C}HCH_3$, 109.9 ppm; $C(4){=}CH\mathit{C}H_3$, 15.35 ppm; C_5Me_5, 119.9 ppm (confirmed by off-resonance decoupling); $C_5\mathit{Me}_5$, 11.9 ppm. No observed peaks are unaccounted for and all absorptions expected of the proposed structures have been confirmed.

The infrared spectra recorded for the reaction products are not well understood. From the peaks observed in the regions around ~1600 and ~800 cm^{-1}, all is clear that mixtures of isomers are being produced. It is apparent from the NMR spectra that for the 25 °C reaction, other isomers besides I and II are formed with a total abundance of <25%, but the infrared absorptions are apparently more intense for these compounds than for I and II, for some peaks cannot be accounted for in mixtures that by NMR seem to be nothing more than I and II. Of course <5% of another isomer would be difficult to detect by NMR. It is notable that two strong peaks at ~1000 cm^{-1} are seen (1023 and 1000 cm^{-1}) that have about the same relative intenstiy as the ratio of major to minor isomers, respectively. These are probably the "ring-breathing" modes of the C_5Me_5 rings. Metallacycle vibrations are detected at 1585, 1637, 791, 758, 726, and 629 cm^{-1}. These can be identified since the absorptions due to the C_5Me_5 ligands are so few in number. No assignment to individual isomers will be attempted.

Results

The reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with methylallene in toluene at temperatures of −25 °C or below produces a mixture of two products which can be identified by NMR studies. A description of the data gathered is included in the Experimental Section and in Figures 1 and 2. In this section we shall analyze these data in terms of the probable structures of the products. Chemical shift and coupling constant data will both be useful in this endeavor particularly in view of the observations made for related compounds, reported in a previous paper.[1]

It is best to begin by consideration of the ^{13}C spectra shown in Figure 1. The spectrum shown is for a product mixture obtained from methylallene reaction carried out at −25 °C. Note first the twin peaks at ~119 ppm (peaks R and R′). These fall in the region common for the inner carbons of the C_5Me_5 ligands and have been confirmed as such by off-resonance decoupled spectra where they are not found to be coupled to any adjacent hydrogen nuclei. Apparently two isomers are present, and the relative abundance as calculated from these peaks is 70:30. The C_5Me_5 methyl groups at ~11 ppm show less splitting, but the relative intensities are about the same. An overall view of the ^{13}C spectrum suggests that there are other pairs of peaks of similarly disparate intensities. Consistent with their assignments, these are marked *n*,*n*′.

In order to determine the structures of these isomers, we first note that each isomer has a peak in the 200-ppm region, characteristic of an sp^2 carbon bound to zirconium.[1] The number of peaks that are assignable to metallacyclic carbons for each isomer suggests that the geometric form of these isomers is that of a type A metallacycle. The ^{13}C chemical shifts found for the type A structure derived from allene are 209.9, 153.3, 114.3, 101.3, 57.0, and 55.2 ppm.[1] It seems obvious that the methylallene reaction has produced very similar compounds, the minor differences in chemical shifts being due mainly to substituent effects. The most reasonable assignments for the peaks are indicated in Figure 1. The high sample concentration and field strength (62.9 Hz) used for this spectrum allow unambiguous identification of all peaks due to the metallacyclic system. There are no peaks for which we have been unable to account. The consideration of the proton spectrum will confirm the above analysis and provide regio- and stereochemical information.

The full proton NMR spectrum of the methylallene reaction products is shown in Figure 2. The chemical shifts are similar enough for the two isomers that, to resolve several regions of the spectrum, the use of a 360-MHz instrument was required. The largest absorptions in the spectrum are labeled R,R′ and these correspond to the C_5Me_5 methyl groups. Note that *two* peaks are observed, and their relative intensities (70:30) again confirm the notion of two isomers being present. The next most important region to notice is that at 3 ppm. For the type A allene-derived metallacycle,[1] it was noticed that the doubly

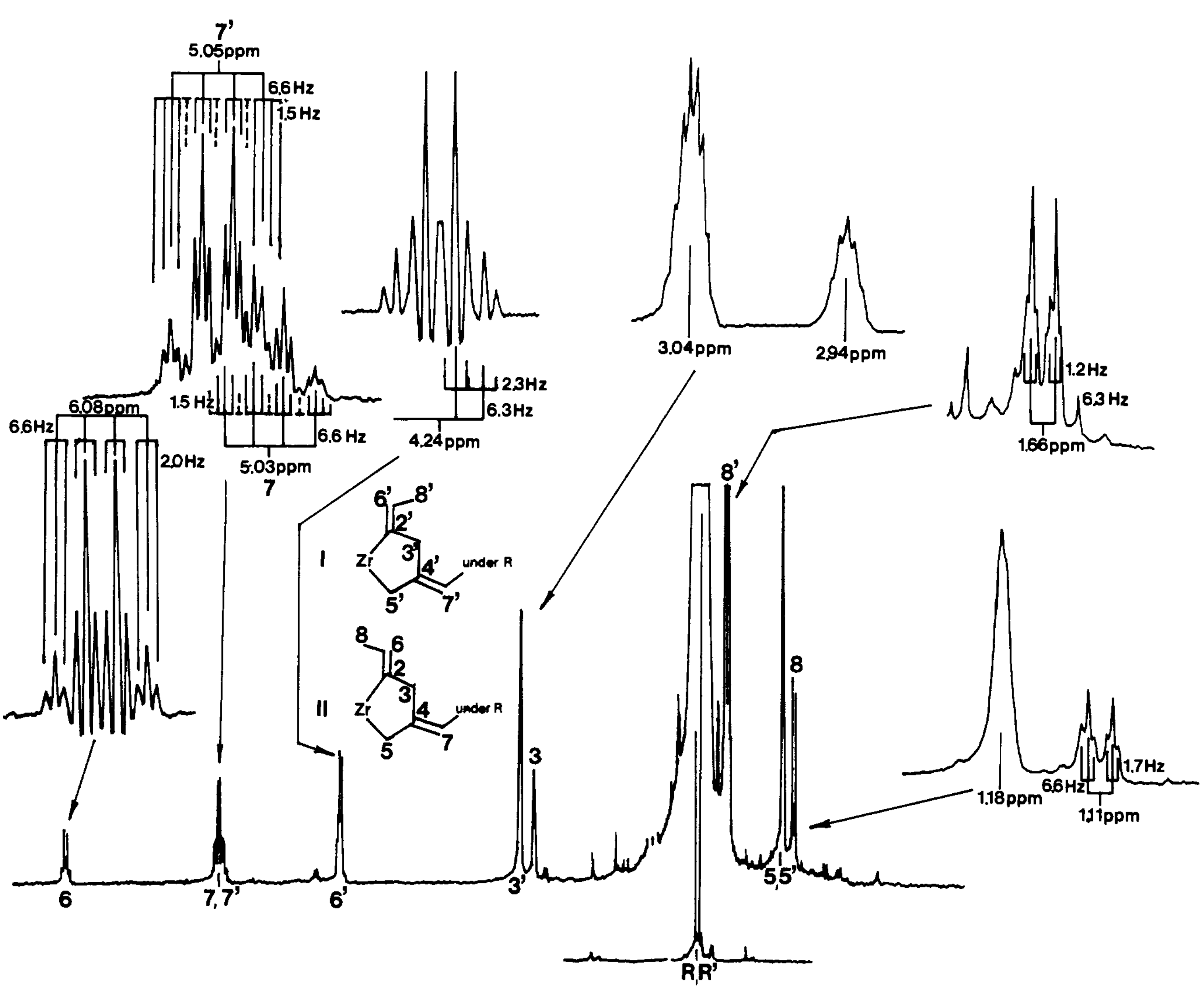


Figure 2. ${}^1H$ NMR spectrum of the mixture of isomers obtained from the reaction of $[(C_5Me_5)_2ZrN_2]N_2$ with methylallene at −25 °C. The absorptions due to the C_5Me_5 ring methyl groups are labeled with an "R". A toluene-d_7 impurity peak at high field has been removed for clarity and the space is marked with a "t". The spectrum was acquired with a Nicolet 360-MHz instrument. The expanded details at 5.08, 5.04, 5.24, and 3.0 ppm were produced with use of resolution-enhancement software. Peak assignments are made according to the inset diagrams for the two isomers.

allylic hydrogens absorbed at 3.05 ppm. For the methylallene reaction, the two peaks at 3.04 and 2.94 ppm in the 70:30 ratio provide strong evidence for type A systems *and* for their being no methyl substitution on the doubly allylic (C(3)) carbons. Note that peaks 3 and 3′ in the spectrum are broad, symmetric peaks, only showing structure under "enhanced resolution" conditions. Were a methyl substituent to be present on C(3) for either isomer, a quartet splitting of ~6 Hz would be the most obvious feature of these peaks.[1] As it is, no coupling constant larger than 2–3 Hz is possible within the bandwidth—the pattern is complex due to two allylic and two homoallylic couplings being possible for each isomer. For the metallacyclic complex isolated from the reaction with 1,3-dimethylallene,[1] we saw methyl substitution upon an allylic sp^3 carbon. The adjacent proton gave a broadened NMR absorption peak upon which the methyl quartet structure was plainly visible.

In the upfield region the peak labeled 5,5′ stands out due to its broadness and lack of structure. All methyl group absorptions in this region appear with a 6-Hz doublet splitting due to the geminal proton. The peak at 1.18 ppm must therefore be assigned to the C(5) methylene group, α to the metal. The absorption due to the α-methylene in the allene-derived compound was found[1] at 1.35 ppm. Both isomers absorb at 1.18 ppm (±0.005 ppm), and this was confirmed by the integrations described in the Experimental Section.

Note that no methyl substitution upon the α-methylene carbons is observed for either isomer. It can therefore be concluded that the methyl substitution in isomers I and II from the methylallene reaction is found upon the sp^2 carbons only. This settles the questions of geometric and regio isomerism. There remain only four possible isomers not yet ruled out by the NMR analysis; they differ only in the stereochemistry at the exocyclic-sp^2 carbons (6 and 7 or 6′ and 7′).

To define the stereochemistry of these compounds, we need to look at the vinylic hydrogen NMR absorptions. Peaks 6,6′ and 7,7′ in Figure 2 tell the tale. The easiest region to deal with shall be described first, i.e., the α-ethylidene moiety, $C(2){=}CHCH_3$. We have established in other papers[1,2] that for external-ring unsaturation α to the zirconium, the exo hydrogen has a chemical shift much further downfield than the endo hydrogen. This was identified for the allene-derived type A complex as well as for all three isomers of the 1,3-dimethylallene type B products. For the methylallene system we note that peaks 6 and 6′ are in an intensity ratio of 30:70 and are in the regions expected for exo and endo α-ethylidene hydrogens, respectively. The allylic coupling constants for these multiplets are 2.0 and 2.3 Hz, respectively. This is also consistent with our observations for exo and endo hydrogens of this type; for the allene-derived complex, the exo and endo allylic couplings (cisoid and transoid) were found to be 1.8 and 2.4 Hz, respectively.[1]

We may confidently identify the α-ethylidene stereochemistry for the major and minor isomers of the methylallene-derived products as exo and endo, respectively (methyl group orientation).

Further confirmation of the above assignment can be obtained from consideration of the homoallylic couplings of the α-ethylidene methyl groups. The methyl coupling to the doubly allylic hydrogens should be larger for the transoid orientation than for the cisoid orientation.[5] The α-ethylidene methyl resonances, $C(2)H{=}CHCH_3$, for the major and minor isomers have been found at 1.66 and 1.11 ppm, respectively (identification was confirmed by decoupling experiments). These relative shifts are again consistent with the assigned stereochemistry—an upfield shift for α-ethylidene methyl groups cis to the metal has been identified for type B isomers.[2] The ratio of intensities for peaks 8 and 8′ is the expected 70:30, and the homoallylic coupling constants are 1.2 and 1.7 Hz, respectively. The minor isomer II has the largest homoallylic coupling, again consistent with the endo assignment for α-ethylidene stereochemistry.

The orientation of the methyl group on the α double bond has therefore been established by four distinct observations for the two isomers: the chemical shifts for the methyl group and the geminal proton and the couplings of each of these to the doubly allylic hydrogens. These four criteria have each been evolved from previous studies on related complexes that were structurally characterized by X-ray methods. All four observations support the stereochemistry indicated in Figure 2.

Now we must consider the stereochemistry of the 4-ethylidene group. This turns out to be a very important consideration because it is at this group that the highest degree of stereoselectivity is observed.

It has been established that a difference between isomers I and II lies in the orientation of the 2-ethylidene methyl (vide supra). If the 4-ethylidene methyl were *also* to orient in either direction, then is is most probable that *four* isomers would be observed rather than two. This suggests that the orientation is similar for I and II.

It turns our to be very difficult to *prove* the assertion made above by determination of the actual stereochemistry. The analysis of chemical shift data is uncertain because the molecule with which these can best be compared, $Zr(C_5Me_5)_2(C_2H_4)_2$, has no methyl substituent and displays very similar shifts for the two 4-vinylidene hydrogens. Allylic coupling constants cannot be used because the cisoid and transoid values are very similar and the region where any effect could be seen (5.03 ppm) is very complex. Decoupling experiments show that the 4-ethylidene hydrogen is coupled to both the C(3) and C(5) methylenes, and we cannot distinguish between their respective coupling constants due to the resolution required. Homoallylic coupling constants tend to have better defined ranges of values for cisoid and transoid couplings. It may, therefore, be possible to distinguish the 4-ethylidene stereochemistry by means of decoupling experiments involving the $CH_2(3)$ and $CH_2(5)$ methylenes and the 4-ethylidene methyl. Unfortunately these methyl groups lie *very* close (within 0.01 ppm) to the C_5Me_5 absorptions, and in any case the homoallylic couplings are small compared to other coupling interactions to the same nuclei. We have been unable to obtain unambiguous stereochemical evidence from this approach.

A fourth approach to the determination of the 4-ethylidene stereochemistry is also of limited applicability. In theory one can irradiate the 4-ethylidene methyl group at the frequency of its proton NMR absorption and monitor the enhancement of NMR intensity of the $CH_2(3)$ and $CH_2(5)$ positions incumbent upon altering their relaxation rate via the nuclear Overhauser effect. Since the "observing" nuclei are geminal pairs, one would not expect the enhancement to be no more than a few percent. We have been unable to detect enhancement in either the $CH_2(3)$ or $CH_2(5)$ directions.

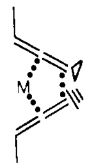
While the actual stereochemistry at the 4-ethylidene group has not been established for the two isomers, it is nonetheless apparent from an argument made earlier that they have the *same* stereochemistry. It will be found that this observation fits well into the mechanistic suggestion to be made in the next section. Also, it should be noted that the 4-ethylidene methyl orientation chosen for Figures 1 and 2 is purely arbitrary.

A word should be said regarding the distribution of products when this reaction is carried out at room temperature. ^{13}C spectra show that when the reaction is carried out at higher temperatures, products other than I and II are produced, but still in low (<20%) yields. We have not detected new absorptions at ~200 ppm, so it seems that the most abundant of these new products probably do not have α unsaturation. The proton NMR spectrum shows especially interesting peaks in the ~2-ppm region. There are two new sharp singlets and several minor peaks that are very sharp and separated by chemical shift differences, i.e., there is no significant (>1 Hz) coupling to these protons. It is possible that the spectroscopic observations are consistent with the formation of type C isomers with various substitution patterns on the exocyclic methylenes, but we have been unable to assign more than a couple of absorptions for any one possible isomer. We will not atempt to define the nature nor to rationalize the formation of these minor products. The specificity observed for the formation of I or II is, on the other hand, worthy of comment and such is included in the following section.

Discussion

Some effort will now be made to rationalize the geometric and regio- and stereochemical selectivities observed for allene and substituted-allene oxidative coupling. The first question to answer is whether the oxidative coupling proceeds through a symmetrical intermediate (i.e., whether the overall reaction may be concerted).

Evidence has been obtained for the stepwise nature of the coupling from a consideration of the methylallene studies reported here. Recall that neither I nor II has a methyl-bearing doubly allylic carbon (C(3)). If the oxidative coupling, wherein the C(3)–C(4) bond is formed, were to arise from a symmetrical transition state, it is very likely that some *C(3)*-methyl substitution would be observed. It can be said that if both 1,3-dimethylallene and methylallene coupling were concerted, then *C(3)*-methyl substitution could be found for the latter case as well as the former. Considering the transition-state possibilities D and E it is clear that there is not significant difference in the steric demands of either structure.



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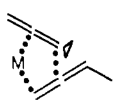

E

The arguments above do not, of course, *prove* that a stepwise process must be in effect for either system, but they show that with our level of sophistication a concerted mechanism cannot be shown to account for the lack of observation of an isomer that might be derived from diadduct E. It will be shown below that most major features of our observed regio- and stereo-

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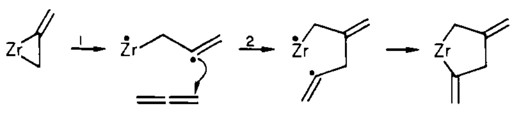
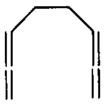
(5) G. P. Newsoroff and S. Sternhell, *Tetrahedron Lett.*, **58**, 6117 (1968). See also discussion in ref 1.

Scheme I



chemical selectivity *can* be accounted for easily by using a stepwise scheme for which ample precedent is found in the organic chemistry of allenes. As such it is a stepwise coupling scheme which we are currently drawn to favor.

Let us look as what is known of allene coupling reactions and of electrophile attack on allenes in non-metal-containing systems. Roth and Erker[6] have shown that the thermolysis of the dimethylene-bridged diallene (a) leads to the same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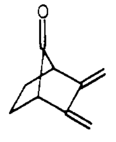
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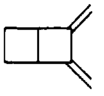
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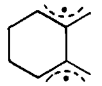
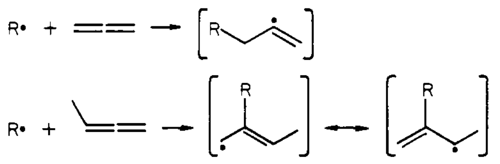
distribution of products as observed for thermolysis of b and c. This suggests a common intermediate, which must be the *diradical*



Radical coupling mechanisms are also suggested by the analyses of the dimerization products of substituted allenes,[7] where substitution is dominantly found on the exocyclic methylene groups, not on the ring (similar to our observations reported here).

It is known that whereas radical attack on allene occurs predominantly at the terminal carbon, center carbon attack becomes favored for substituted allenes.[8]



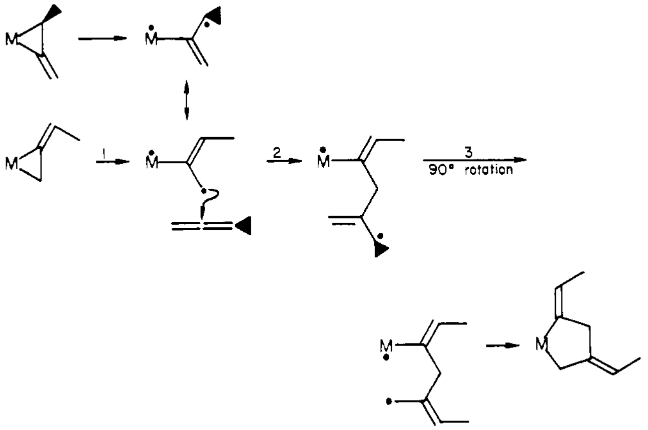
Note that the second example is shown to have achieved a planar π-allyl transition state prior to further reaction. Rapid 90° rotation for the initially formed nonplanar radical has been proven in one case.[9]

It will be shown below that the concept of diradical intermediates for zirconocene-mediated allene coupling is consistent with our observations for allene and methylallene. It is *necessary* to assume different sites for radical attack for these two systems—consistent with the radical hypothesis by analogy to the organic observations stated above.

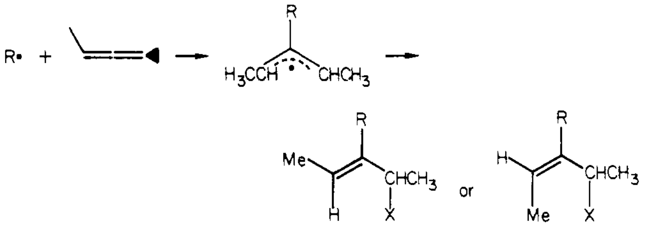
For metal-mediated allene coupling, Scheme I is suggested. This scheme demonstrates the greater stability of the vinyl radical at both stages 1 and 2. We have required the C–C radical attack in step 2 to go terminal in light of results for $H_3C\cdot$ attack on allene.[10]

For methylallene, a mechanism can be drawn (see Scheme II) that is just the opposite of that shown above, i.e., the ring

Scheme II



Scheme III



closure takes place in the "other direction". Only the exo *C*(*2*)-ethylidene case is illustrated. Both steps 1 and 2 in Scheme II are shown to involve central carbon attack. Step 2 demonstrates attack on the entering allene from the unsubstituted and more reactive end of the methylallyl radical; this selects against *C*(*3*)-methyl substitution in the final product.

An important facet of the suggested methylallene coupling mechanism is the selectivity implied at step 3. Caserio has found for tosyl iodide[11] and *tert*-butyl hypochlorite[9] additions to methyl-substituted allenes that cis,trans stereoselectivity is observed in the products (see Scheme III). For *tert*-butyl hypochlorite there is a 6:1 selectivity for the cis isomer, whereas for tosyl iodide only the trans isomer is detected. The reasons for this stereoselectivity are not explained, but it is only important for us to note that it *is* empirically *observed* for these radical processes. We see only one stereochemical configuration of the *C*(*4*)-ethylidene for the methylallene-derived metallacyclopentanes, and this parallels the selectivity observed for the free-radical chemistry.

Further definition of the mechanism of metal-induced allene coupling will possibly arise from our studies with di-, tri-, and tetramethylene-bridged diallenes, where the orientation of the "second" allene moiety is restricted relative to that bound to the metal.

Conclusion

One of our original questions in the field of cumulene-derived metallacycles pertains to the metal dependence of coupling geometry. Why do we isolate asymmetric type A metallacycles for allene and methylallene reactions with "zirconocene" whereas for rhodium(I) and iridium(I) complexes, symmetric metallacycles[4] are found? On the basis of our suggestion of the stepwise, one-electron pathway for the zirconocene-mediated coupling, an electronically distinct symmetric transition state for the group 8 systems would be consistent with a systematic difference in the kinetically preferred products. What this boils down to is the hypothesis that for group 8 systems there is a low-energy path involving

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(6) W. R. Roth and G. Erker, *Angew. Chem., Int. Ed. Engl.* **12**, 503, 505 (1973).

(7) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

(8) M. C. Caserio, "Selective Organic Transformations", Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, 1970, p 239.

(9) L. R. Byrd and M. C. Caserio, *J. Am. Chem. Soc.*, **92**, 5422 (1970).

(10) H. G. Meunier and P. J. Abell, *J. Chem. Phys.*, **71**, 1430 (1967).

(11) L. R. Byrd and M. C. Caserio, *J. Org. Chem.*, **37**, 3881 (1972).

coordination of both allenes *prior* to carbon–carbon bond formation. We are now studying the coupling of substituted allenes by a rhodium(I) system[12] in an attempt to evaluate the merit of this hypothesis. In the next paper of this series we shall report evidence that for the zirconocene systems, bis(allene) adducts only exist as very high-energy species.

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Registry No. I, 76068-71-8; II, 76123-95-0; $[Zr(C_5Me_2)_2N_2]_2N_2$, 54387-50-7; methylallene, 590-19-2.

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[12] D. M. Duggan, Z. Mester, S. R. Keenan, and J. Jacobson, work in progress.

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Homo- and Heterometal Triple-Decker Complexes of *cyclo*-Triphosphorus with Mixed Triphosphine Ligands. Crystal Structure of $[[MeC(CH_2PPh_2)_3]Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe[MeC(CH_2PEt_2)_3]](PF_6)_2\cdot CH_2Cl_2$

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By use of the tripodal triphosphine ligands $CH_3C(CH_2PPh_2)_3$, triphos, and $CH_3C(CH_2PEt_2)_3$, etriphos, a new series of mixed-ligand dinuclear complexes of *cyclo*-triphosphorus has been obtained. The complexes have the general formula $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]M(etriphos)]Y_2$, where M = Fe, Co, Ni and Y = PF_6, BPh_4. In contrast to the phenyl-substituted triphosphine triphos, the ethyl-substituted etriphos has been found to coordinate the iron(II) cation, thus allowing dinuclear complexes of $c\text{-}P_3$ with 30 valence electrons to be obtained for the first time. The compound $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)](PF_6)_2\cdot CH_2Cl_2$ has been characterized by an X-ray diffraction study. Crystal data: orthorhombic, $P2_1nb$, $Z = 4$, $a = 24.108$ (5) Å, $b = 21.346$ (7) Å, $c = 14.348$ (3) Å; $R = 0.074$ for 3187 reflections.

Introduction

Several dinuclear triple-decker sandwich metal complexes containing the *cyclo*-triphosphorus or the *cyclo*-triarsenic unit as the internal layer have been prepared in this laboratory.[1–3] Some of these represent the first examples of paramagnetic triple-decker sandwich metal complexes.[1] The external ligand in these complexes is the tripodal tris(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, triphos. To these complexes have been attributed a number of valence electrons (NVE) equal to 31, 32, 33 or 34, depending on the nature of the metal atoms (cobalt, nickel, and their analogues of the higher transition series) and on the charge of the cation.

For the complexes with 30 valence electrons to be obtained, the corresponding iron derivatives had to be synthesized, but all attempts to prepare complexes of this type were unsuccessful due to the inability of the ligand triphos to coordinate strongly the iron(II) cation.

Iron derivatives have now been obtained by using the ligand 1,1,1-tris(diethylphosphinomethyl)ethane, $CH_3C(CH_2PEt_2)_3$, etriphos, which differs from triphos in the nature of the substituent groups on the phosphorus atoms. Complexes with formula $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]M(etriphos)]Y_2$, where M = Fe, Co, Ni and Y = PF_6, BPh_4, have been prepared by reaction of the ancillary complex $[(triphos)Co(\eta^3\text{-}P_3)]$ (**1**) with etriphos and iron(II), cobalt(II), or nickel(II) aquo cations. These complexes have been characterized by means of magnetic, spectrophotometric, and conductivity measurements. A complete X-ray structural investigation has been carried out on the compound $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)](PF_6)_2\cdot CH_2Cl_2$.

Experimental Section

Reagents. Iron(II), cobalt(II), and nickel(II) tetrafluoroborates, sodium tetraphenylborate, tetrabutylammonium hexafluorophosphate, ethanol, methylene chloride, and petroleum ether were of reagent grade and were used without further purification. Complex **1** and the ligand etriphos were prepared as previously described.[1a,4]

Preparation of the Complexes. All operations were performed under dry nitrogen and with oxygen-free solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen.

$[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)](PF_6)_2\cdot CH_2Cl_2$ (2). A solution of **1** (0.5 mmol) in 40 mL of CH_2Cl_2 was added, at room temperature, to a mixture of $[Fe(H_2O)_6](BF_4)_2$ (0.5 mmol) in ethanol (35 mL) and etriphos (0.5 mmol) in CH_2Cl_2 (10 mL). On addition of $(NBu_4)PF_6$ (1 mmol) in CH_2Cl_2 (10 mL) and slow evaporation of the solvent, dark blue crystals were formed which were separated by filtration and washed with ethanol and petroleum ether. They were recrystallized from CH_2Cl_2/ethanol.

$[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]M(etriphos)](BPh_4)_2$ (M = Co (3), Ni (4)). Complex **1** (0.5 mmol) in 40 mL of CH_2Cl_2 was added, at room temperature, to a solution obtained by mixing etriphos (0.5 mmol) in CH_2Cl_2 (10 mL) and $[Co(H_2O)_6](BF_4)_2$ (or $[Ni(H_2O)_6](BF_4)_2$) (0.5 mmol) in ethanol (40 mL). Solid $NaBPh_4$ (1 mmol) was then added to the resultant solution. Upon concentration red-brown (dark violet) crystals precipitated and were washed as above. They were recrystallized from CH_2Cl_2/ethanol.

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recording of the UV–visible spectra have been described previously.[5] The analytical, magnetic, and conductivity data for the complexes are given in Table I. The electronic spectral data are listed in Table II.

X-ray Data Collection and Reduction. The needle-shaped crystals of compound **2** belong to the orthorhombic system. Lattice constants, obtained by least-squares refinement of the setting angles of 24

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[1] (a) Di Vaira, M.; Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1978**, *100*, 2550. (b) Di Vaira, M.; Midollini, S.; Sacconi, L.; Zanobini, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 676.

[2] Di Vaira, M.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1979**, *101*, 1757.

[3] Bianchini, C.; Di Vaira, M.; Meli, A.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 405.

[4] Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

[5] Sacconi, L.; Morassi, R. *J. Chem. Soc. A* **1968**, 2997; Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* **1968**, *7*, 1417.

0020-1669/81/1320-1169$01.25/0