Figure 3. Cyclic voltammograms of melt background (A), 1.5×10^{-3} M ferrocene (B), and 1.5×10^{-3} M hexamethylbenzene, (C), in the 2:1 aluminum chloride:ethylpyridinium bromide melt, at 25°. Scan rate = 0.2 V/sec.

the corresponding diffusion coefficients of these complexes in 11 M H_2SO_4. However, the viscosity of the melt is ca. three times greater than that for 11 M H_2SO_4. An estimate of the solvodynamic mean radii for these complexes in the molten salt yields values very close to the structural mean radii. This indicates that in the melt solvation of the complex species is not of major importance. In point of fact, the potential solvating species would be the ethylpyridinium ion or aluminum chloride both of which have larger structural mean radii than simple water molecules or hydronium ions.

Cyclic voltammograms of the melt background, ferrocene, and hexamethylbenzene at a vitreous carbon electrode are shown in Figure 3. Ferrocene was found to undergo a reversible one-electron transfer ($E_{1/2} = 0.25$ V) over sweep rates ranging from 0.1 to 100 V/sec. The anodic to cathodic peak separation was found to be 60 ± 5 mV and the ratio of peak currents equaled one. A computer simulation of the data yielded voltammograms which were superimposable with the experimental curves.

At slow sweep rates hexamethylbenzene was observed to undergo an irreversible two-electron transfer ($E_p = 1.4$ V). A cathodic wave, $E_p = 0.15$ V, appeared only after cycling into or through the anodic wave. This was taken to be the reduction of proton to hydrogen by analogy with previous work.[10]

When hexamethylbenzene was subjected to sweep rates exceeding 10 V/sec a coupled cathodic wave ($\Delta E_p \sim 80$ mV) appeared and increased in height with faster sweep rates. To our knowledge, this is the first report of the hexamethylbenzene cation radical being electrochemically detected at room temperature.[15] This reinforces previous results[11,12] which propose that aluminum chloride based molten salts stabilize cation radicals. A comprehensive study of this phenomenon as well as preparative electrooxidations of hexamethylbenzene in this fused salt will be reported on shortly.[13]

It is clear from the data presented here that room temperature,[14] strong Lewis acid, molten salt systems offer a new choice of media in which to study the chemical and electrochemical properties of a variety of compounds. Such solvents can easily be maintained free of proton, water, and oxygen.

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## Consideration of the Mechanism of the Olefin Metathesis Reaction

Sir:

One of the most intriguing problems in organometallic chemistry has been the determination of the mechanism of the olefin metathesis reaction.[1] Two classes of mechanism have received the most attention. The earliest suggestions involved a concerted switching of carbons through a "quasi-cyclobutane" transition state. This suggestion received much theoretical consideration.[2,3] A later suggestion involved the rearrangement of a diolefin complex through a five-membered metallocycle.[4,5]

metallocycle
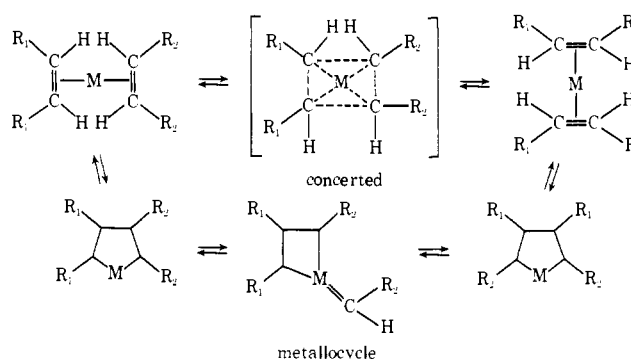
This mechanism was supported by a number of studies of model systems.[5-8] Both of these mechanisms require the pair-wise interchange of carbon atoms.

Recently, carbene-metal complexes have been demonstrated to be rather stable and relatively easy to generate in the early transition metal series.[9] Schrock[10] has demon-

strated that tantalum–alkyl carbenes can be prepared from tantalum alkyls and Casey[11] has demonstrated that a tungsten carbene will undergo exchange with an olefin. In the light of these studies, the following mechanism[12] becomes a reasonable alternative.
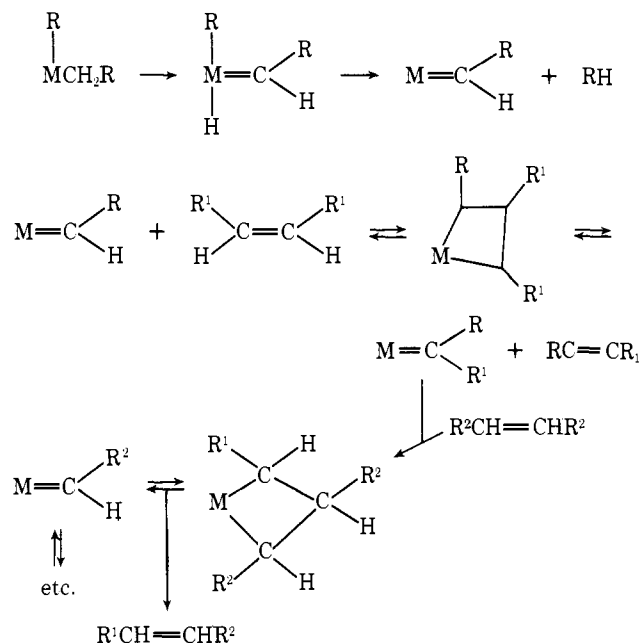
The difference between this third alternative and the earlier considered mechanisms is that this reaction involves a chain transfer of methylene groups instead of a "pair-wise" interchange.

In order to distinguish between these classes of mechanisms, the metathesis of mixtures of 1,7-octadiene-$1,1,8,8$-d_4[13] (I) and 1,-7-octadiene (II) was carried out. The major products of the metathesis of 1,7-octadiene are cyclohexene and ethylene.[14]

An examination of the possible "pair-wise" interchange mechanisms provide a prediction of the ethylene ratios for this mixture.
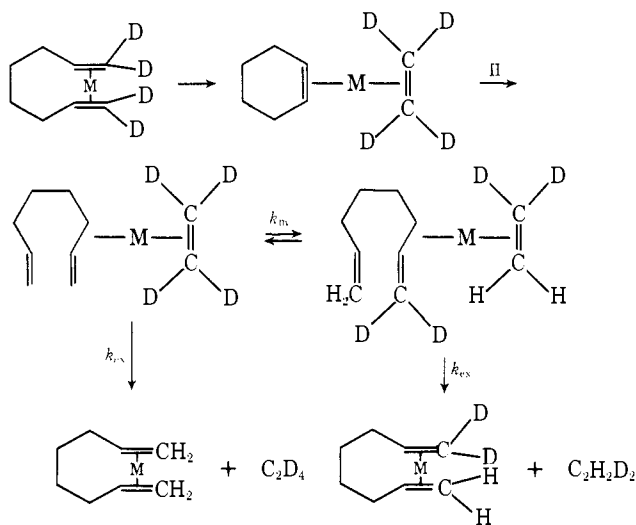
If $k_{ex} \gg k_m$ then a $d_4{:}d_2{:}d_0$ ratio of 1:0:1 would be produced under nonequilibrating conditions. The other extreme, $k_m \gg k_{ex}$,[1] provides a route for the formation of ethylene-d_2. A calculation of the $d_4{:}d_2{:}d_0$ ratio based on this mechanism predicts[15] a maximum ratio of $d_4{:}d_2{:}d_0$ of 1: 1.6:1 (corrected 1:1.76:1.16).

The carbene mechanism requires the production of a statistical distribution (1:2:1) of ethylene $d_4{:}d_2{:}d_0$.

A 1:1.1 mixture of 1,7-octadiene-d_4/-d_0(I:II) was allowed to react with the heterogeneous catalyst prepared from tungsten hexachloride and butyllithium in benzene.[16] After 28 min (2% conversion)[17] at room temperature, the gas over the reaction was removed with a syringe; the ethylene was separated by GPC and analyzed by mass spectroscopy (15 eV ionization voltage). The ratio of ethylene d_4: $d_2{:}d_0$ was 1:3.6 ± 0.2:3.2 ± 0.1 (calcd equilibrium mixture = 1:3.6:3.1).[18] The reaction was repeated with 2 ml of ethylene-d_0 added to the starting reaction mixture. If the ethylene-d_2 resulted from the equilibration of the initially formed ethylene-d_4 and $-d_0$, then a new equilibrium ratio would result. The ratio after 36 min was 1:3.7 ± 0.2:16.0. This result indicates the ethylene-d_2 was not produced by subsequent equilibration of the ethylene. Significant amounts of ethylene-d_3 and $-d_1$ were produced. These must result from a monohydride exchange scheme and complicate the analysis. The $d_4{:}d_2{:}d_0$ ratio of 1,7-octadiene recovered at the end of the reaction had not changed.[17] These results, although obscured by the monohydride equilibration, do, however, support the "carbene" scheme.

The above reaction sequence was repeated with a new metathesis catalyst, PhWCl$_3$–AlCl$_3$,[19,20] which is homogeneous.[19] More importantly, this reagent does not require an alkyl lithium, tin, or aluminum as an activator. Consequently, the initiation step as outlined above is not possible. A 1:1.1 mixture of 1,7-octadiene-$1,1,8,8$-d_4 and 1,7-octadiene was added to a chlorobenzene solution of the catalyst, and samples were taken during the first approximately 10% of the reaction.[17] Each ethylene sample collected during this period showed a ratio of ethylene-$d_4{:}d_2{:}d_0$ of 1:2.3 ± 0.13:1.4 (equilibrium 1:2.3:1.4). There was less than 5% 1,7-octadiene-d_2 produced during this reaction period (m/e 112/114 = 0.24 ± 0.02 before, m/e 112/114 = 0.25 ± 0.01 after reaction). The reaction was repeated with ethylene-d_0 present in the starting reaction mixture. The ethylene-$d_4{:}d_2{:}d_0$ ratio was 1:2.3 ± 0.1:5. These data are most consistent with the carbene mechanism and provide much cleaner evidence than the first experiment.

The earlier work on the reactions of tetramethylene metallocycles suggests that they may be the source of the carbenes[4,5] in at least some of these catalyst systems which do not require an alkyl activating reagent.[21]

The results from the studies with two different catalysts, one heterogeneous and alkyl activated the other homogeneous and nonalkyl activated, suggest that the olefin metathesis reaction proceeds through a non "pair-wise" interchange of carbons between two olefins. The carbene mechanism outlined above is most consistent with these results.[23]

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(15) Calculated by an iterative procedure using the following equations:

$E0, \; E2, \; E4$ = ethylene ratios produced

$R0, \; R2, \; R4$ = metal–ethylene complex ratios at start

$Z0, \; Z2, \; Z4$ = metal–ethylene complex ratios produced

$A0, \; A4$ = 1,7-octadiene ratio

$E0 = R0(A0 + BA4) + R2A0B$

$E2 = B \cdot R0 \cdot A4 + D \cdot R2(A0 + A4) + B \cdot R4 \cdot A0$

$E4 = C \cdot R2 \cdot A4 + R4(A4 + B \cdot A0)$

$Z0 = A0(R0 + D \cdot R2 + B \cdot R4)$

$Z2 = A0(C \cdot R2 + B \cdot R4) + A4(B \cdot R0 + C \cdot RZ)$

$Z4 = A4(B \cdot R0 + D \cdot R2 + R4)$

The *B*, *C*, and *D* factors represent the probabilities of the combination of the *A* and *R* factor producing the desired *E* or *Z* under consideration. The *Z* values became the *R* factors for the next iteration. After approximately 20–30 iterations the calculated ratios become constant and are independent of the assumed starting ratios. Very large isotope effects have a small effect on the calculated values. Only those equilibration steps indicated in the scheme were allowed.
(16) Isolated by centrifugation of the reaction mixture, washed twice with benzene, and used as a suspension in benzene.
(17) The ratio of the *m/e* peaks of 114, 112, and 110 for the starting mixture and the recovered reaction mixture of I and II were compared on spectra determined under identical conditions. The per cent reaction was determined by comparing the ratio of cyclohexene and 1,7-octadiene in the reaction mixture.
(18) The equilibration ratio was calculated from the equation (1 + *A*)² which yields the ratio, *d*₄:2*Ad*₂:*A²d*₀. Without monohydride equilibration *A* = II/I. With some equilibration *A* = ½ the ratio of (ethylene-*d*₄:ethylene-*d*₂).
(19) Prepared from equal molar quantities of PhWCl₃ and AlCl₃ in chlorobenzene, the suspension was centrifuged and the supernatant, homogeneous by light scattering, was used.
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Abnormal Regioselectivity in the Photochemical Cycloaddition of Singlet *trans*-Stilbene with Conjugated Dienes

Sir:

The regioselectivity of 1,2-cycloaddition to conjugated dienes has been investigated for a number of electrophilic species. Such diverse reactions as radical,[1] ionic,[1b] concerted [$_\pi 2_s + _\pi 2_a$],[2] 1,3-dipolar,[3] and carbene[3b,4] additions display similar regioselectivities. Addition to *cis*- or *trans*-1,3-pentadiene occurs selectively at the monosubstituted double bond (>90%), whereas addition to 2-methyl-1,3-pentadiene occurs selectively at the disubstituted double bond (70–80%).[5] The observed regioselectivities have been attributed to one or more of the following: (a) formation of the more stable bifunctional intermediate, (b) preferential addition to the sterically less hindered terminus, and (c) addition to the terminus of highest electron density. In spite of the fact that concerted photochemical [$_\pi 2_s + _\pi 2_s$] cycloaddition is a symmetry-allowed reaction, there are few examples of concerted 1,2-cycloaddition to conjugated dienes.[8,9] We wish to report that 2 + 2 cycloaddition of the singlet excited state of *trans*-stilbene to conjugated dienes occurs preferentially at the *more* substituted double bond. Application of frontier orbital theory[10] for a concerted 2 + 2 cycloaddition correctly predicts the observed regioselectivities.

Irradiation of *trans*-stilbene in the presence of dienes results in the efficient formation of mixtures of 2 + 2 cycloadducts.[11] Direct irradiation of *cis*-stilbene or triplet sensitized irradiation of either *cis*- or *trans*-stilbene in the presence of dienes results in stilbene cis–trans isomerization, but no cycloaddition. Addition of singlet *trans*-stilbene to the disubstituted double bond of the isomeric 1,3-pentadienes occurs with complete retention of diene and stilbene stereochemistry (eq 1), as is the case for addition of *trans*-

(1)
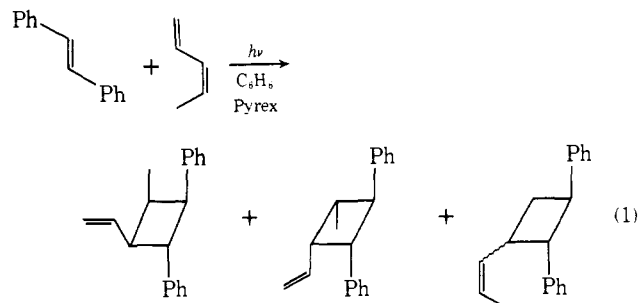
stilbene to the isomeric 2-butenes.[12c,13] The regioselectivity of cycloaddition of *trans*-stilbene with several conjugated dienes is given in Table I. Addition to the more substituted double bond predominates in all cases and attains a maximum value of 80% for *cis*-1,3-pentadiene. Since the quantum yields for cycloaddition are high,[11] the regioselectivities reflect relative rates of addition rather than selective partitioning of a 1,4-biradical intermediate. A biradical mechanism[1a,b] appears unlikely in view of the high stereospecificity and abnormal regioselectivity of cycloaddition. It is possible that the stereochemical outcome of the cycloaddition process is determined by the formation of an excited state π-donor–acceptor complex (exciplex) prior to bond formation. The rate of addition of singlet *trans*-stilbene to alkenes displays a negative temperature dependence,[12b] in-

Table I. Regioselectivity of Cycloaddition and Diene Frontier Orbital Coefficients

Diene	Regioselectivity			Orbital coefficients			
	1, 2%	3, 4%		C_1	C_2	C_3	C_4
4-Methyl-1,3-pentadiene	34	66	HO	0.495	0.294	0.510	0.492
			LU	0.501	0.351	0.441	0.554
trans-1,3-Pentadiene	46	54	HO	0.525	0.337	0.469	0.521
			LU	0.528	0.382	0.437	0.562
cis-1,3-Pentadiene	20	80	HO	0.522	0.339	0.473	0.526
			LU	0.528	0.384	0.437	0.564
2-Methyl-1,3-pentadiene	70	30	HO	0.621	0.429	0.337	0.500
			LU	0.566	0.428	0.407	0.544