$$
\begin{array}{ccc}
n\text{-}C_5H_{11} & n\text{-}C_3H_7 & C_6H_5 \\
\quad\,\,\diagdown C{=}CD_2 & \quad\,\,\diagdown C{=}CH_2 & \quad\,\,\diagdown C{=}W(CO)_5 \\
CH_3\diagup & CH_3\diagup & C_6H_5\diagup \\
IV & V & VI
\end{array}
$$

analysis we assumed that the rates of reactions 2a and 2b were unchanged when R and R' are interchanged, that reaction is effected by those metal–carbenes, RCH=M, in which R = alkyl to the exclusion of those in which R = H,[11] and that the concentration of RCH=M is proportional to the amount of RCH= residue present as olefin.[13]

The observation is that with these catalysts 26–155 methylene interchanges, undetectable except for the isotopic labels, occur for every conventional metathesis. The selectivity is lowest for the molybdenum catalyst most effective for the conventional metathesis of terminal olefins and higher for the less effective tungsten catalysts. Thus the data are in accord with proposal 1 above.

As might reasonably be expected, substituting ethylene twice at the 1-position magnifies the selectivity induced by substituting it only once. To demonstrate this it was impossible to use some of the catalyst mixtures containing WCl_6 or aluminum halides because these acids oligomerize olefins IV and V. However, the isolable metal–carbene VI, which Casey and Burkhardt had cleverly synthesized[15] and found to react stoichiometrically with olefins according to equations similar to 2a,[16] is an effective initiator for metatheses of IV and V as well as of other olefins.[17] Its effectiveness shows that Lewis acid cocatalysts are not essential components of the active catalysts,[5b,18] and that such metal–carbene complexes can be useful in bringing about metathesis of olefins that are very sensitive to acid. An example is in the accompanying paper in which the metathesis selectivity is measured for a trisubstituted olefin.[19]

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(2) (a) See numerous examples in the review by W. B. Hughes, *Organomet. Chem. Synth.*, **1**, 341 (1972), on p 346; (b) J. L. Hérisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970); (c) V. I. Mar'in, A. D. Shebaldova, T. A. Bol'shinskova, M. L. Khidekel', and I. V. Kalechits, *Kinet. Catal. (USSR)*, **14**, 528 (1973).

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(5) (a) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975); (b) E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975).

(6) W. J. Kelly and N. Calderon, *J. Macromol. Sci. Chem.*, **9**, 911 (1975), found scrambling between 1-pentene and 1-pentene-d_{10}.

(7) There are heterogeneous catalysts: (a) A. M. Popov et al., *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **22**, 1397 (1973); (b) R. L. Banks and R. B. Regier, *Ind. Eng. Chem., Prod. Res. Dev.*, **10**, 46 (1971); (c) L. F. Heckelsberg, Belgium Patent, 713 184 (1967); (d) H. Knoche, German Patent, 2 024 835 (1970); *Chem. Abstr.*, **74**, P44118 (1971); (e) for the reverse reaction: D. L. Crain, *J. Catal.*, **13**, 110 (1969).

(8) *n*-Heptane for experiments 3 and 6–11, *n*-nonane for experiments 4 and 5, and *n*-hexadecane for experiments 1 and 2.

(9) 10 ft × 1/8 in. 20% Apiezon L on Chromosorb W Regular.

(10) Same as 9, but Apiezon J and 1/4 in.

(11) The experiments by Casey, Tuinstra, and Saemen in the accompanying manuscript support this assumption and measure in a different way selectivities similar to those recorded here.[12]

(12) C. P. Casey, H. E. Tuinstra, and M. Saemen, *J. Am. Chem. Soc.*, **98**, 608 (1976).

(13) With HEX, OCT, and OCTO representing the number of protons at positions 1 in hexene, octene, and "octene-d_2", R the molar ratio of hexene and octene, and MET the molar ratio (IIIa + IIIb + IIIc)/(I + II),

$$\frac{k}{k'} = (-1/\mathrm{MET})\ln\left[1 - \left(\frac{2-\mathrm{HEX}}{2-\mathrm{OCTO}}\right)(1+R)\right]$$

or

$$(1/\mathrm{MET})\ln\left[\frac{1-[\mathrm{OCTO}(1+R)/(2R+\mathrm{OCTO})]}{1-[\mathrm{OCT}(1+R)/(2R+\mathrm{OCTO})]}\right]$$

(14) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974).

(15) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973).

(16) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).

(17) 2-Hexene for example.

(18) H. Höcker and F. R. Jones, *Makromol. Chem.*, **161**, 251 (1972).

(19) T. J. Katz, J. McGinnis, and C. Altus, *J. Am. Chem. Soc.*, **98**, 606 (1976).

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Metathesis of a Cyclic Trisubstituted Alkene. Preparation of Polyisoprene from 1-Methylcyclobutene

Sir:

When metal–carbene complexes combine in the olefin metathesis reaction[1] with olefins that are unsymmetrically substituted, the two reactions indicated in eq 1 take place at

(1)
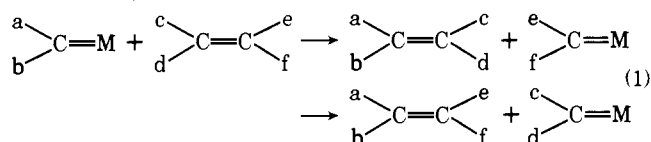
different rates.[2,4] This accounts for the selective formation of oligomers whose structures may be represented as $RCH{=}$ᴠᴠᴠᴠ$={=}CH_2$ in reactions of cycloolefins with terminal acyclic olefins[2] and for the selective formation of starting olefins in reactions of terminal olefins with themselves.[4a]

If this selectivity also applied to trisubstituted olefins, a predicted consequence (eq 2) would be that cycloalkenes

(2)
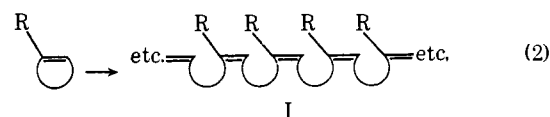
unsymmetrically substituted on the double bond would yield polymers that, except possibly for geometrical isomerism, are translationally invariant. Such polymers are said to be "perfectly alternating".[5] To test this prediction a way must be found to effect metatheses of olefins that are trisubstituted. We report below a solution to the problem, the preparation by metathesis of a polymer from a cyclic trisubstituted alkene, and an analysis of the metathesis selectivity.

A number of years ago Dall'Asta and Manetti tried to polymerize 1-methylcyclobutene with WCl_6 and either triethylaluminum or ethylaluminum dichloride, but the polymers produced were largely saturated.[6] With similar catalyst mixtures trimethylethylene gives olefin oligomers,[7] although 2-methyl-2-pentene is said to give the expected metathesis products.[8]

Other metathesis catalysts are also ineffective. The combination of $MoCl_2(NO)_2[(C_6H_5)_3P]_2$ and $(CH_3)_3Al_2Cl_3$ in chlorobenzene at room temperature[9] with both 1-methylcyclobutene[10] for 18 h[11] and 1-methylcyclopentene for 2 h gives products shown by their proton NMR spectra to be too saturated to contain structures like I in quantity.[12] WCl_6 and $(C_6H_5)_3SnC_2H_5$ in chlorobenzene at room temperature[4a] for 3 h[13] with 1-methylcyclobutene gives some-

what better material.[14] The combination W(CO)$_6$, CCl$_4$, 1-methylcyclobutene, and 3500 Å light[15] effects neither acid-catalyzed oligomerization nor olefin metathesis, but adds CCl$_4$ to the double bond.[16]

One fairly effective catalyst mixture is WCl$_6$ (86 μmol) and n-butyllithium (171 μmol) in benzene (2 ml),[17] which with 1-methylcyclobutene (4790 μmol) and n-heptane (423 mg, reference standard for GLC) after 18 h at room temperature consumed 83% of the olefin[18] and gave a polymer whose ^{1}H and ^{13}C NMR spectra were similar to those of polyisoprene,[19,20] although there were resonances in the aromatic region attributable to reactions of the solvent, and some at high field indicating that about 8% of the sample's mass was aromatic impurities and about 17% saturated impurities.

The best way discovered to effect metathesis of 1-methylcyclobutene was to warm it (7.71 mmol)[21] with (diphenylcarbene)pentacarbonyltungsten (0.21 mmol)[22] and 512 mg of n-heptane (GLC reference standard) at 50 °C for 18 h. This consumed 91% of the 1-methylcyclobutene[18] giving[23] a 101% yield of polymer (plus hydrocarbon residue from the carbene catalyst), which gel permeation chromatographic analysis in tetrahydrofuran showed to have a broad molecular weight distribution, with M_w = 11 400 and M_n = 1400.[24]

The proton NMR spectrum of the polymer shows olefin, methylene, and methyl resonances in the required ratio, 0.94:4.03:3.03, and these resonances account for about 94% of the spectrum discounting the benzenoid resonances, whose intensities are those expected for the quantity of diphenylcarbene moiety used. This spectrum and the ^{13}C NMR spectrum[20] are largely those of polyisoprene that is 84–87% Z ("cis") and 13–16% E ("trans"),[25] but the following characteristics indicate that for every 10.1 ± 1.2 2-methyl-2-butene units there is one 2-butene and one 2,3-dimethyl-2-butene unit, due to imperfect alternation: in the proton NMR (CCl$_4$) of this sample as well as of one prepared during an 8-h incubation, there is a well-resolved absorption at δ 5.33 (cf. polybutadiene[19d,28]) 0.20 ± 0.03 as intense as that at δ 5.07 (cf. polyisoprene[19b,c,28a]) and poorly resolved absorption at δ 1.62[29] about 0.15 times as intense as the absorptions of polyisoprene methyls at δ 1.66 and 1.59;[25] in the ^{13}C NMR (CDCl$_3$) there are resonances at 18.14 and 18.43 ppm from tetramethylsilane (assigned to 2,3-dimethyl-2-butene units)[33] that are 0.18 ± 0.01 times as intense as the polyisoprene methyl resonances[20] at 15.98 and 23.43 ppm.[25b,34]

The translational invariance in the polymer formed using WCl$_6$ and n-butyllithium catalyst seems even less perfect. The sample's impurity confuses the analysis, but both the olefin proton and methyl ^{13}C NMR's imply that 2-butene and 2,3-dimethyl-2-butene units occur once for every 4.3–4.6 2-methyl-2-butenes. The latter units, however, seem to be 17% E and 83% Z, much as in the other samples.

It is unlikely that the mechanism by which the polymers form involves 1-methylcyclobutene first yielding isoprene,[35] as isoprene (204 mg) after reaction with (diphenylcarbene)pentacarbonyltungsten (60.5 mg) and n-heptane (254 mg) for 40 h at 50° is 98% unchanged, as the C$_5$H$_8$ recovered from one polymerization reaction of 1-methylcyclobutene was the starting material and not isoprene, and as the spectroscopic characteristics attributed to imperfect alternation would not be accounted for.

Accordingly the reactions described show for the first time how metatheses of trisubstituted olefins may be effected. They provide the first materials in which the preference for alternating sequences of monomeric units can be measured and in which the stereochemistry of trisubstituted olefin metathesis can be determined. The selectivity is small

compared to that for other additions[36] or for metatheses of terminal olefins.[4] The stereochemistry can be interpreted as that for 1,2-disubstituted olefins.[2]

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(11) After 1 h 10% was consumed; after 18 h 67%.
(12) The ratio of olefinic to saturated proton resonances in the product from 1-methylcyclobutene showed no more than 20% polyisoprene. The ratio in the distillable (oligomeric ?) product from 1-methylcyclopentene was 1:49.
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(17) J.-L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968). We combined the butyllithium with WCl$_8$ in benzene before adding the olefin.
(18) GLC at 67 °C on 20% Apiezon L on 100/120 Chromosorb W Regular.
(19) (a) H. Y. Chen, *Anal. Chem.*, **34**, 1793 (1962); (b) M. A. Golub, S. A. Fuqua, and N. S. Bhacca, *J. Am. Chem. Soc.*, **84**, 4981 (1962); (c) J. P. Kistler, G. Friedman, and B. Kaempf, *Bull. Soc. Chim. Fr.*, 4759 (1967); (d) Y. Tanaka, Y. Takeuchi, M. Kobayashi, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **9**, 43 (1971).
(20) M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).
(21) 98.2% pure; GLC at 38 °C on 10 ft × ⅛ in. 60/80 Chromosorb W Regular coated with half its weight of 17% AgNO$_3$ in ethylene glycol (cf. J. Shabtai, J. Herling, and E. Gil-Av, *J. Chrometogr.*, **11**, 32 (1963)).
(22) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973); **96**, 7808 (1974). See the acccmpanying manuscript, ref 4, for the use of this material as a catalyst for olefin metathesis.
(23) After dissolving in benzene, adding decolorizing charcoal, centrifuging, filtering through Celite, and evaporating solvent.
(24) An effective Q of 25.5 was assumed (cf. J. V. Dawkins, *Eur. Polym. J.*, **6**, 831 (1970) and J. V. Dawkins, R. Denyer, and J. W. Maddock, *Polymer*, **10**, 154 (1969)).
(25) (a) The proton resonances in CCl$_4$ at δ 1.66 for the Z isomer and at 1.59 for the E indicated 16% E. These resonances and that at 1.62 overlapped. (b) The percent E measured by Fourier transform ^{13}C NMR spectroscopy using 58° pulses repeated at 5.1-s intervals with proton noise decoupling applied only while the spectrum was being acquired[26] was 13%. The methyl resonances were at 15.98 (E) and 23.43 ppm (Z). The percentage measured three times on two samples using a computer program of questionable accuracy was 12.9 ± 0.3% and seemed to vary little whether pulsing was repeated at 1.9-, 5.2-, or 10-s intervals or whether proton decoupling was applied continuously[27] or only during spectrum acquisition.[26]
(26) G. C. Levy and U. Edlund, *J. Am. Chem. Soc.*, **97**, 4482 (1975), and references therein.
(27) The NOE defined as C_z/C_0 is 14% more for the trans isomer than the cis *in the solid* (J. Schaefer, *Macromolecules*, **5**, 427 (1972)).
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(29) Schué et al. reported E-poly-2,3-dimethylbutadiene to absorb in CCl$_4$ at δ 1.63, but the Z isomer at 1.76. Our samples do show peaks at 1.62 and not at 1.76, but since they show ^{13}C NMR resonances of similar intensity attributable to both isomers, we suppose both methyl proton resonances are at δ 1.66 or higher fields. Others also found the chemical shifts of the two isomers to be similar.[31] Poly-1,2-dimethylocta-1,5-dienamer in CCl$_4$ absorbs at 1.62.[32]
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(33) The assignment is based on our observation that a mixture of Z- and E-4,5-dimethyloct-4-ene shows its vinyl methyl resonances at 18.03 and 18.32 ppm.

(34) The ratio in the most accurately measured spectrum (see footnote 25b) was 0.19.

(35) In an uncatalyzed reaction the half-life of 1-methylcyclobutene at 50° is 1.7 × 10⁶ h (H. M. Frey, Trans. Faraday Soc., **58**, 957 (1962)).

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Reactions of (CO)₅WC(Tol)₂ with Alkenes. A Model for Structural Selectivity in the Olefin Metathesis Reaction

Sir:

The olefin metathesis reaction[1] is a fascinating transition metal catalyzed reaction which involves the intermolecular exchange of alkylidene units between alkenes. Recently we discovered that $(CO)_5WC(C_6H_5)_2$ reacts with alkenes to give diphenylethylenes and cyclopropanes.[2] The diphenylethylenes were suggested to be formed through interconversion of complexes bearing both an alkene and a carbene ligand via a metallocyclobutane intermediate. This process also provides a sufficient mechanism for olefin metathesis[3] that differs from all previous mechanisms[1] in that it alone
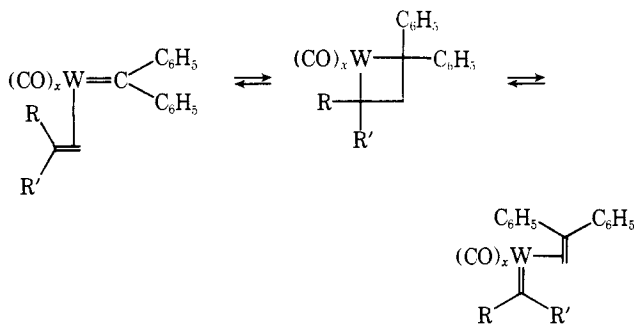
Scheme I
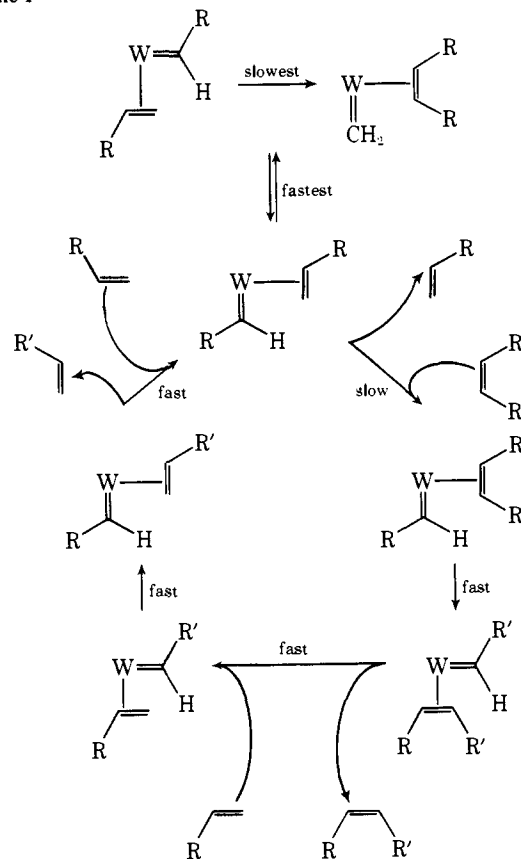
requires a nonpairwise exchange of alkylidene units between alkenes. Such nonpairwise exchange has recently been reported in several elegant studies by Chauvin,[3] Katz,[4] and Grubbs.[5]

The olefin metathesis reaction shows a pronounced structural selectivity.[1] The relative rates of metathesis decrease in the order: (1) the degenerate exchange of methylene units between terminal alkenes[6,7] > (2) cross metathesis of terminal and internal alkenes[3,8,9] > (3) metathesis of inter-

Table I. Reactions of Alkenes with $(CO)_5WC(Tol)_2$[a]

Alkene	Products[b,d]		
$CH_2=CH(CH_2)_2CH_3$	$(Tol)_2C=CH_2$ 35.9 ± 0.3%	$(Tol)_2C=CH(CH_2)_2CH_3$ 0.06 ± 0.02%	 26.9 ± 0.2%
$CH_2=C(CH_3)_2$	$(Tol)_2C=CH_2$ 73.2 ± 0.2%	$(Tol)_2C=C(CH_3)_2$ <0.06%	 5.2 ± 0.2%
$CH_2=CHC_6H_5$[e]	$(Tol)_2C=CH_2$ 61.0 ± 1.8%	$(Tol)_2C=CHC_6H_5$ <0.2%	 8.4 ± 0.4%
$(CH_3)_2C=CH(CH_2)_2CH_3$	$(Tol)_2C=CH(CH_2)_2CH_3$ <0.9%	$(Tol)_2C=C(CH_3)_2$ <0.5%	
cis-$CH_3CH=CHCH_3$[f]	$(Tol)_2C=CHCH_3$ 27.0 ± 0.3%		 2 ± 1%

[a] A solution of 25–35 mg of $(CO)_5WC(Tol)_2$ in 1–2 ml of alkene in sealed tubes was heated to 70 ± 2°C for 3.25 h. [b] Products were identified by comparison of GC retention times on two different columns with the retention times of independently prepared authentic samples. [c] At least two independent runs of each reaction using internal standards and at least five repeated GC analyses of each run were performed. [d] Yields are based on $(CO)_5WC(Tol)_2$. The average yield ± standard deviation of the mean is presented. [e] Secondary products were cis- and trans-1,2-diphenylcyclopropane. [f] In addition, variable amounts (5–10%) of $(Tol)_2C=CH_2$ were found.