

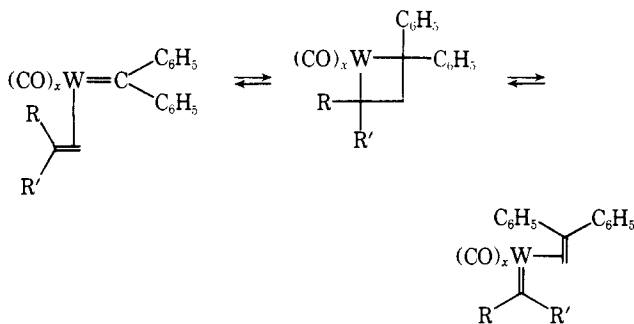
- (33) The assignment is based on our observation that a mixture of *Z*- and *E*-4,5-dimethyloct-4-ene shows its vinyl methyl resonances at 18.03 and 18.32 ppm.
- (34) The ratio in the most accurately measured spectrum (see footnote 25b) was 0.19.
- (35) In an uncatalyzed reaction the half-life of 1-methylcyclobutene at 50° is 1.7×10^8 h (H. M. Frey, *Trans. Faraday Soc.*, **58**, 957 (1962)).
- (36) Say for hydroboration: G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

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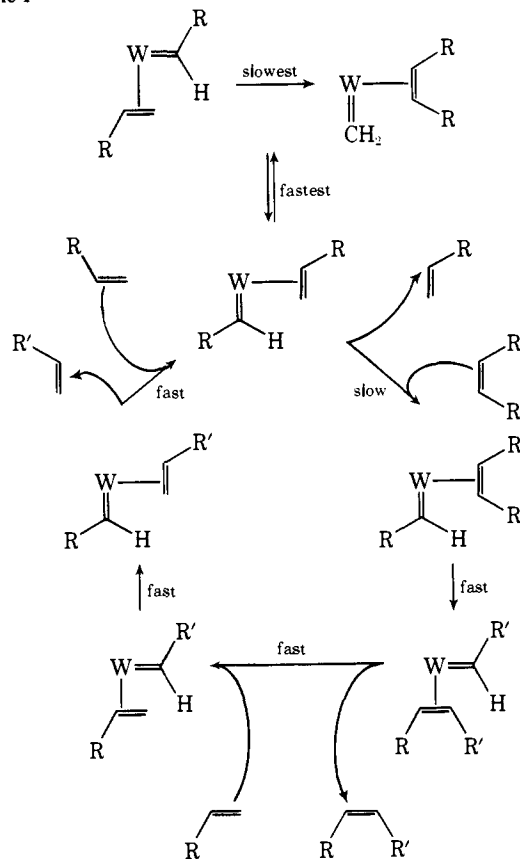
Reactions of $(\text{CO})_5\text{WC}(\text{Tol})_2$ with Alkenes. A Model for Structural Selectivity in the Olefin Metathesis Reaction

Sir:

The olefin metathesis reaction¹ is a fascinating transition metal catalyzed reaction which involves the intermolecular exchange of alkylidene units between alkenes. Recently we discovered that $(\text{CO})_5\text{WC}(\text{C}_6\text{H}_5)_2$ 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 metathesis³ that differs from all previous mechanisms¹ 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-

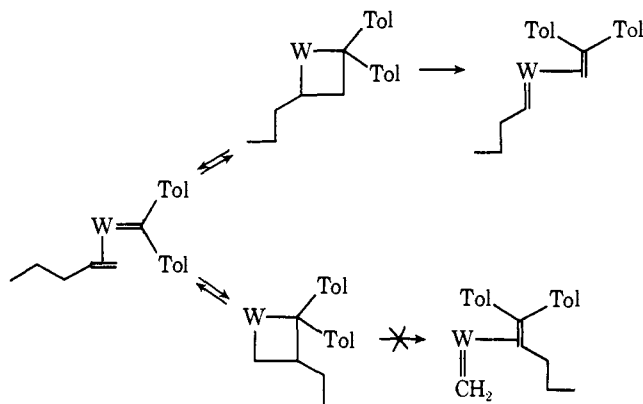
Table I. Reactions of Alkenes with $(\text{CO})_5\text{WC}(\text{Tol})_2$ ^a

Alkene	$(\text{CO})_5\text{WC}(\text{Tol})_2$	Products ^{b,d}
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_3$	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$ 35.9 ± 0.3%	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}_3$ 0.06 ± 0.02%
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$ 73.2 ± 0.2%	$(\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{CH}_3)_2$ <0.06%
$\text{CH}_2=\text{CHC}_6\text{H}_5$ ^e	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$ 61.0 ± 1.8%	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHC}_6\text{H}_5$ <0.2%
$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}_3$	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}_3$ <0.9%	$(\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{CH}_3)_2$ <0.5%
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$ ^f	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCH}_3$ 27.0 ± 0.3%	

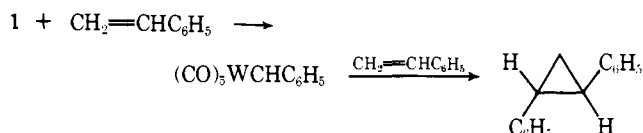
^a A solution of 25–35 mg of $(\text{CO})_5\text{WC}(\text{Tol})_2$ in 1–2 ml of alkene in sealed tubes was heated to $70 \pm 2^\circ\text{C}$ for 3.25 h. ^b Products were identified by comparison of GC retention times on two different columns with the retention times of independently prepared authentic 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 $(\text{CO})_5\text{WC}(\text{Tol})_2$. 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 $(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$ were found.

nal alkenes > (4) metathesis of terminal alkenes to give ethylene and internal alkenes. To understand this reactivity pattern in terms of the metallocyclobutane mechanism for olefin metathesis, we have studied the reaction of $(\text{CO})_5\text{WC}(\text{Tol})_2$, **1**, with a series of unsymmetrical alkenes to determine which alkylidene fragment of an alkene is preferentially transferred to the carbene ligand to form a new alkene. In addition, we have studied the relative reactivity of a series of alkenes towards **1**. Here we report (1) that the least substituted alkylidene unit of an alkene is transferred to the initial carbene ligand and (2) that less substituted alkenes are more reactive towards **1**. These two observations allow an explanation of the observed relative reactivities of alkenes in the olefin metathesis reaction.

Table I lists the products containing the $\text{C}(\text{Tol})_2$ moiety which were found in the reactions of $(\text{CO})_5\text{WC}(\text{Tol})_2$ with alkenes. In all cases, a strong preference for the formation of the least substituted 1,1-diaryllkene was found. For 1-pentene, the ratio of $\text{CH}_2=\text{C}(\text{Tol})_2$ to $\text{CH}_3(\text{CH}_2)_2\text{C}=\text{C}(\text{Tol})_2$ was 600; for isobutylene, the ratio of $\text{CH}_2=\text{C}(\text{Tol})_2$ to $(\text{CH}_3)_2\text{C}=\text{C}(\text{Tol})_2$ was >600. Transfer of a substituted alkylidene unit is not precluded since 27% $\text{CH}_3\text{CH}=\text{C}(\text{Tol})_2$ was formed in the reaction with *cis*-2-butene. The trisubstituted alkene, 2-methyl-2-hexene, did not react with $(\text{CO})_5\text{WC}(\text{Tol})_2$ to give significant amounts of 1,1-diaryllkenes. The observation that the least substituted alkylidene unit of an alkene is transferred to the diarylcarbene ligand is probably related to the concurrent formation of the more substituted metal-carbene complex.

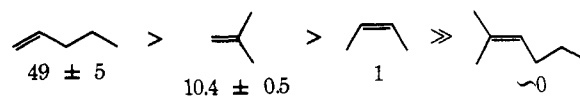


Formation of cyclopropanes from the presumed metallocyclobutane intermediate was observed as a side reaction in most cases and was greatest for the reaction of 1-pentene, the least substituted alkene. In the case of styrene, the formation of 9% *cis*- and 37% *trans*-1,2-diphenylcyclopropane was observed. Presumably, these products are derived from reaction of styrene with $(\text{CO})_5\text{WCHC}_6\text{H}_5$, formed in situ from reaction of **1** with styrene.



The relative reactivity of alkenes towards **1** was determined by competition techniques using approximately equal volumes of *cis*-2-butene and a second alkene. In a competition between 1-pentene and *cis*-2-butene (0.86 mole ratio), the ratio of $\text{CH}_2=\text{C}(\text{Tol})_2$ derived from 1-pentene to $\text{CH}_3\text{CH}=\text{C}(\text{Tol})_2$ derived from *cis*-2-butene was found to be 42 ± 5 . In a competition between isobutylene and *cis*-2-butene (0.95 mole ratio), the ratio of $\text{CH}_2=\text{C}(\text{Tol})_2$ derived from isobutylene to $\text{CH}_3\text{CH}=\text{C}(\text{Tol})_2$ derived from *cis*-2-butene was found to be 9.9 ± 0.5 . In a competition be-

tween 2-methyl-2-hexene and *cis*-2-butene, only $\text{CH}_3\text{CH}=\text{C}(\text{Tol})_2$ derived from *cis*-2-butene was observed. The relative reactivity of this series of alkenes towards transfer of an alkylidene unit to the diarylcarbene unit, corrected for the mole ratio of reactants, is shown below:



This reactivity series roughly parallels the thermodynamic stability of olefin-metal complexes.¹²

The observation that the selectivity for transfer of the least substituted alkylidene unit of an alkene to the carbene ligand is much greater than the selectivity for reaction of the carbene complex with the least substituted alkene is significant since it explains why mixtures of terminal and internal alkenes undergo predominant cross metathesis^{3,8,9} (Scheme I). The degenerate metathesis of the terminal alkene is the fastest reaction occurring in a mixture of terminal and internal alkenes under metathesis conditions. Occasionally, an internal alkene enters the reaction cycle to produce a new alkyl-substituted carbene complex and a new internal alkene (one of the cross metathesis products). The new carbene complex then undergoes rapid reaction with a terminal alkene to produce a new terminal alkene (the other cross metathesis product).^{13,14}

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References and Notes

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- (2) (a) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974). (b) Previously, Lappert has observed related exchange reactions of tetraaminoethylenes and bisnitrogen substituted carbene-metal complexes: D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 927 (1972).
- (3) A similar mechanism had previously been proposed by Chauvin, J. L. Herrisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970); J. P. Soufflet, D. Commereuc, and Y. Chauvin, *C.R. Acad. Sci., Ser. C.*, **276**, 169 (1973).
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- (8) E. A. Zeuch, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Am. Chem. Soc.*, **92**, 528 (1970).
- (9) J. Lai and R. R. Smith, *J. Org. Chem.*, **40**, 775 (1975).
- (10) $(\text{CO})_5\text{WC}(\text{Tol})_2$ [Tol $\equiv p$ -tolyl] was prepared in 49% yield by a procedure similar to that used for $(\text{CO})_5\text{WC}(\text{C}_6\text{H}_5)_2$.¹¹ NMR (C_6D_6): δ 7.06 (d, $J = 8.0$ Hz, 4 H), 6.76 (d, $J = 8.0$ Hz, 4 H), 1.88 (s, 6 H); ir (CS_2) 2142 w, 2063 s, 1954 vs cm^{-1} ; m/e for M - CO (calcd for $\text{C}_{19}\text{H}_{14}\text{O}_4\text{W}$, 490.0401) 490.0381; mp dec $\sim 120^\circ$.
- (11) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973).
- (12) F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973).
- (13) If the selectivity for terminal vs. internal alkenes had been much greater than the selectivity for transfer of the least substituted alkylidene unit, then the major reaction would simply have been metathesis of the terminal alkene to give ethylene and an internal alkene.
- (14) A priori, the cross metathesis reaction and the degenerate reactions of terminal alkenes might have explained by selective transfer of the most substituted alkylidene unit and by reactions favoring the least substituted carbene complexes. However, the data presented here make this alternate mechanism highly unlikely.
- (15) N.S.F. undergraduate research participant, summer 1975.

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