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Intramolecular Cyclopropanation and Olefin Metathesis Reactions of $(CO)_5W{=}C(OCH_2CH_2CH{=}CHOCH_3)C_6H_4\text{-}p\text{-}CH_3$

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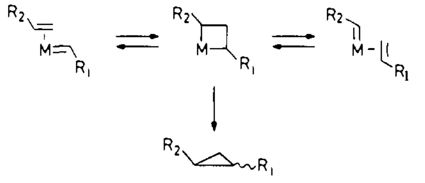
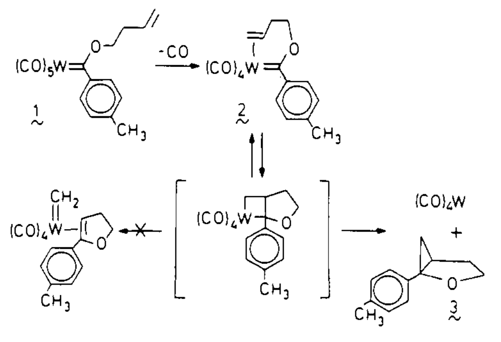
Abstract: In CH_3CN and other coordinating solvents, the tungsten–carbene complexes $(CO)_5W{=}C(OCH_2CH_2CH{=}CHOCH_3)C_6H_4\text{-}p\text{-}CH_3$ (*trans-* and *cis-***5**) are stereospecifically converted to the cyclopropanes 1-(4-methylphenyl)-2-oxa-6-methoxybicyclo[3.1.0]hexane (*exo-* and *endo-***8**) in >95% yield. This cyclopropanation follows clean first-order kinetics in CH_3CN ($k = (2.64 \pm 0.08) \times 10^{-4}\ s^{-1}$ at 42 °C for *trans-***5**). This reaction is proposed to proceed via concerted formation of an 18-electron, 7-coordinate metallacyclobutane that then reductively eliminates cyclopropane. In C_6D_6 and other non-coordinating solvents, decomposition of either *trans-* or *cis-***5** leads to the nonstereospecific formation of cyclopropanes *exo-***8** (8%) and *endo-***8** (14–31%) and to the generation of the olefin metathesis product 5-(4-methylphenyl)-2,3-dihydrofuran, **10** (35–44%). Kinetic studies of the decomposition of **5** in C_6D_6 revealed an initial induction period followed by a rapid autocatalytic decomposition. The chelated tungsten–carbene–alkene complexes $(CO)_4\overline{W{=}C(OCH_2CH_2CH{=}}CHOCH_3)C_6H_4\text{-}p\text{-}CH_3$ (*trans-* and *cis-***6**) were generated by photolysis of **5** in CD_2Cl_2 at −78 °C and were characterized spectroscopically at low temperature. Decomposition of *trans-***6** occurred with a half-life of 1.3 h at 5 °C and led to the formation of cyclopropane *endo-***8** (22%) and dihydrofuran **10** (46%), while decomposition of *cis-***6** occurred with a half-life of 2.7 h at 22 °C and produced *endo-***8** (18%) and **10** (49%). In C_6D_6, the decomposition of **5** is proposed to proceed via the tungsten–carbene–alkene complex **6** which is suggested to cyclize to a 16-electron, 6-coordinate metallacyclobutane that subsequently fragments either to cyclopropane or to a new tungsten–carbene–alkene complex in which dihydrofuran **10** is coordinated to the heteroatom-stabilized carbene unit $W{=}CHOCH_3$. Thus, the partitioning of a metallacycle between cyclopropane formation and olefin metathesis is controlled by both the coordination number of the metallacycle and the stability of the tungsten–carbene complex produced upon olefin metathesis.

The mechanisms most commonly proposed both for the metal-catalyzed cyclopropanation of alkenes[1] and for the olefin metathesis[2] reaction involve the interconversion of metal–carbene–alkene complexes and metallacyclobutanes. Several W(0)-carbene–alkene complexes have been shown to be cyclopropane precursors.[3-5] W(VI) and Ti(IV) metallacyclobutanes have been isolated and shown to be involved in olefin metathesis reactions.[6,7]

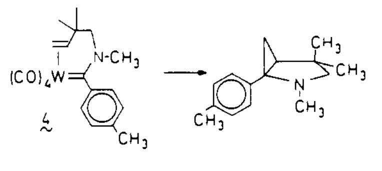


We are interested in the factors which control whether the reactions of alkenes with metal carbene complexes lead to cyclopropane formation or to olefin metathesis. We have generated several chelated tungsten(0)–carbene–alkene complexes and have shown that they are intermediates in intramolecular cyclopropanation reactions. For example, (butenyloxy)carbene complex **1** decomposed thermally to cyclopropane **3**.[3] The tungsten–carbene–alkene complex **2** was observed as an intermediate by ^1H NMR. Kinetic investigations showed an initial induction period, during which decomposition of **1** was slow, followed by a rapid autocatalytic decomposition. The induction period was proposed to involve slow dissociation of CO from **1** leading to tungsten–carbene–alkene complex **2**. Autocatalysis was explained by decomposition of **2** to cyclopropane and an unsaturated "$(CO)_4W$" fragment which then reacted sequentially with two molecules of **1** to generate two molecules of tungsten–carbene–alkene complex **2** for each molecule of **2** converted to cyclopropane.



No olefin metathesis products were seen in the decomposition of **1**. Fragmentation of the metallacycle to a second metal–carbene–alkene complex would have produced a $W{=}CH_2$ unit which is expected to be unfavorable since the carbene carbon is not stabilized by an electron-donating group.

A more stable tungsten–aminocarbene–alkene complex, **4**, was isolated and characterized by X-ray crystallography.[4] Upon thermolysis, **4** decomposed by first-order kinetics to a cyclopropane. No olefin metathesis product was observed, presumably because of the instability of the required $W{=}CH_2$ coproduct.



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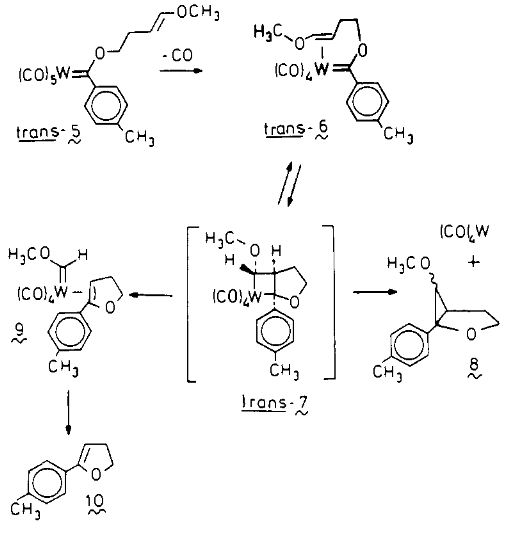
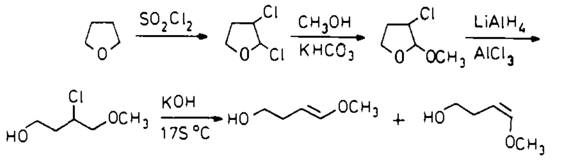
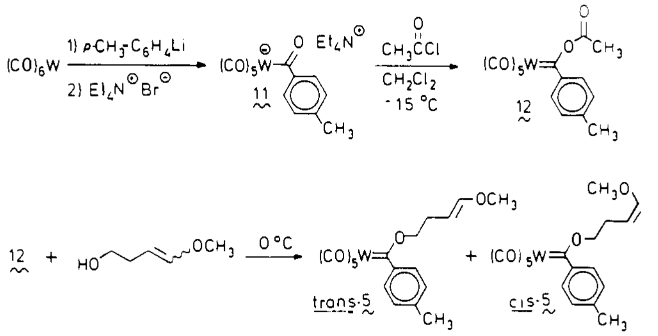
Scheme I



Scheme II



Scheme III



In an effort to favor decomposition of an intermediate metallacyclobutane to olefin metathesis products, we designed the precursor carbene complex *trans*-**5** which possesses a trans vinyl ether side chain. We reasoned that a metallacycle formed from *trans*-**5** would be more likely to fragment to an alkene and the heteroatom-stabilized carbene fragment $W{=}CH(OCH_3)$. We felt that methoxy substitution would be sufficient to favor an olefin metathesis-like fragmentation because Fischer had reported that enol ethers react with tungsten(0) carbene complexes to give both cyclopropanes and olefin metathesis products.[8] Thus, the methoxy-substituted metallacyclobutane intermediate **7** in Scheme I might fragment to dihydrofuran **10** and a $W{=}CH(OCH_3)$ complex or undergo reductive elimination of cyclopropane **8**.

Here we report that complex *trans*-**5** undergoes thermal decomposition both to cyclopropane **8** and to the olefin metathesis product dihydrofuran **10** and that the product distribution and the reaction kinetics are highly dependent on the coordination number of the intermediate metallacycle. In coordinating solvents, the decomposition of *trans*-**5** is suggested to proceed via a *7-coordinate* metallacycle that decomposes selectively to cyclopropane **8**. In noncoordinating solvents, decomposition is proposed to proceed via a *6-coordinate* metallacycle that partitions between an olefin metathesis-like fragmentation and cyclopropane formation.

Results

Synthesis of $(CO)_5W{=}C(OCH_2CH_2CH{=}CHOCH_3)C_6H_4\text{-}p\text{-}CH_3)$ (5). The vinyl ether side chain of **5** was constructed from 4-methoxy-3-buten-1-ol which was obtained as an 85:15 mixture of trans:cis isomers in four steps from THF as shown in Scheme II.[9-12]

In earlier syntheses of alkoxycarbene complexes such as **1** from $(CO)_5W{=}C(OCH_3)C_6H_4\text{-}p\text{-}CH_3$ and commercially available alcohols, we had relied on base-catalyzed alkoxide exchange reactions using a 20–30-fold excess of the alcohols to obtain the carbene complexes in 50–75% yields.[3] Due to the more valuable nature of 4-methoxy-3-buten-1-ol, we instead employed Semmelhack's procedure which uses a more reactive acetoxycarbene complex, $(CO)_5M{=}C(OAc)Ar$, in an exchange reaction with 1.3 equiv of an alcohol.[13] Reaction of $W(CO)_6$ with *p*-tolyllithium followed by workup with $NEt_4^+Br^-$ led to the isolation of $NEt_4^+[(CO)_5WCOC_6H_4\text{-}p\text{-}CH_3]^-$ (**11**) in 74% yield. Acetoxycarbene complex **12**, generated by treatment of acyl tungsten anion **11** with acetyl chloride in CH_2Cl_2 at -15 °C, was reacted directly with 1.3 equiv of an 85:15 mixture of *trans*-:*cis*-4-methoxy-3-buten-1-ol at 0 °C. Evaporation of solvent and recrystallization from hexane at −78 °C led to the isolation of carbene complex *trans*-**5** as a red powder in 47% yield. ^1H NMR analysis showed that the material contained about 5% of the carbene complex *cis*-**5**, which has a cis vinyl ether side chain.

cis-**5** was isolated as a red oil by preparative thin-layer chromatography of the mother liquors from the recrystallization of *trans*-**5**. The two isomers were barely separable by TLC, and samples of *cis*-**5** were obtained containing 7–20% *trans*-**5**.

Carbene complexes *trans*-**5** and *cis*-**5** were characterized by ^1H and ^{13}C NMR and by IR spectroscopy. In the ^1H NMR spectrum of *trans*-**5**, the protons of the methylene group α to oxygen appear at δ 4.63; this substantial downfield shift relative to the corresponding alcohol (δ 3.33) is characteristic of alkoxycarbene complexes. The vinyl resonances of *trans*-**5** at δ 6.27 (d, J = 12.6 Hz) and 4.50 (dt, J = 12.6, 7.4 Hz) are shifted only slightly from those of the alcohol (δ 6.29, 4.53) and retain similar coupling constants. The infrared spectrum shows four carbonyl absorptions at 2064 (m), 1985 (m), 1957 (vs), and 1946 (vs) cm^{-1}, characteristic of a $(CO)_5W$ fragment.

Both *trans*-**5** and *cis*-**5** are air-stable when pure but are thermally unstable. They could be handled for short periods of time at room temperature but were stored at −20 °C.

Cyclopropane Formation from 5 in Coordinating Solvents. Stereospecific formation of cyclopropane from vinyl ether carbene complex **5** was observed in coordinating solvents such as CH_3CN and THF. The thermal decomposition of a 0.07 M red solution of carbene complex *trans*-**5** (*trans*/*cis* = 95:5) in CD_3CN was monitored at 42 °C. After 4.9 h, ^1H NMR analysis of the resulting light orange solution showed the complete disappearance of **5** and the formation of cyclopropanes *exo*-**8** and *endo*-**8** in 83% and 12% yields, respectively. In a similar experiment, a 0.07 M solution of predominantly *cis*-**5** (*cis*/*trans* = 93:7) in CD_3CN gave cyclopropanes *endo*-**8** and *exo*-**8** in 84% and 16% yields, respectively.

Pure samples of cyclopropanes *exo*-**8** and *endo*-**8** were isolated by preparative thin-layer chromatography followed by Kugelrohr distillation. Their structures were assigned by correlation of their ^1H NMR spectra in C_6D_6 with that of the related cyclopropane **3**.[3] For *exo*-**8**, the resonance of the cyclopropyl proton α to the methoxy group appears as a doublet at δ 3.20 coupled to the other cyclopropyl proton at δ 1.85 with a small J_{trans} of 2.6 Hz. For

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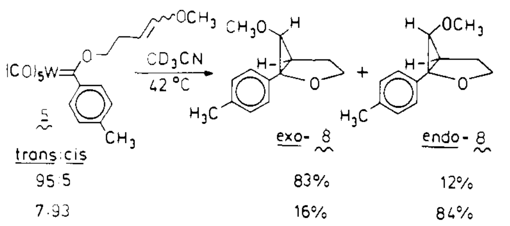
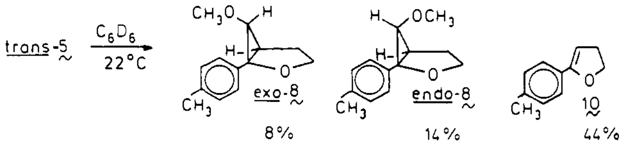


endo-**8**, the related resonance for the cyclopropyl proton α to the methoxy group appears as a doublet at δ 3.35 with a large J_{cis} of 7.5 Hz. In **3**, the cyclopropyl protons show a J_{trans} of 9 Hz and a J_{cis} of 6 Hz. Since electronegative groups decrease coupling constants to adjacent protons,[15] the relative stereochemistry of *exo*-**8** and *endo*-**8** is assigned with confidence.

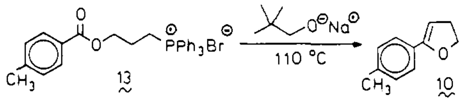
The infrared spectrum of the thermolysis reaction mixtures showed absorptions at 2068 (w), 1947 (vs), and 1931 (w) cm^{-1} due to $(CO)_5W(CD_3CN)$,[16] at 1986 (vs) cm^{-1} due to $W(CO)_6$, and an additional weak absorption at 2058 cm^{-1}. Absorptions attributable to $(CO)_4W(CD_3CN)_2$ were not observed.

Kinetic studies of the conversion of carbene complexes *trans*-**5** and *cis*-**5** to cyclopropanes were performed by ^{1}H NMR at 42 °C in CD_3CN. Clean first-order kinetics were observed for the disappearance of starting material. Both *trans*-**5** and *cis*-**5** decomposed at essentially the same rate: for *trans*-**5**, $k_{\text{obsd}} = (2.64 \pm 0.08) \times 10^{-4}$ s^{-1}; for *cis*-**5**, $k_{\text{obsd}} = (2.55 \pm 0.16) \times 10^{-4}$ s^{-1}. Added carbon monoxide (0.75 atm) did not inhibit the decomposition of *trans*-**5**: $k_{\text{obsd}} = (2.95 \pm 0.12) \times 10^{-4}$ s^{-1} at 41 °C. Dihydrofuran **10**, a major product in noncoordinating solvents (see below), was never detected (<5%) in the product mixture. Tungsten-carbene-alkene complex **6**, which can be generated photochemically in noncoordinating solvents (see below), was not observed at any time during the decomposition of **5** in CD_3CN.

Intramolecular Olefin Metathesis of 5 in Noncoordinating Solvents. Dramatic changes in the kinetics and products of the decomposition of **5** were observed in noncoordinating solvents. In particular, the kinetic behavior of **5** in C_6D_6 is characterized by an induction period followed by a rapid autocatalytic decomposition. Dihydrofuran **10**, formed by an intramolecular olefin metathesis reaction, is the major product. After 3 h at 22 °C, a 0.07 M solution of *trans*-**5** (trans:cis = 95:5) in C_6D_6 had almost completely decomposed (6% of *trans*-**5** remaining). The ^{1}H NMR spectrum of the reaction mixture showed the presence of cyclopropane *exo*-**8** (8%) and cyclopropane *endo*-**8** (12%). In contrast to the observed stereospecific cyclopropanation in CD_3CN, the major cyclopropane formed in C_6D_6 has the inverted stereochemistry of *endo*-**8**. The major decomposition product observed by ^{1}H NMR was dihydrofuran **10** which was formed in 44% yield.



Dihydrofuran **10** was identified in the product mixture by ^{1}H NMR and by GC-MS. The vinyl proton of **10** clearly appears as a triplet at δ 5.15 (J = 2.8 Hz) in the ^{1}H NMR spectrum. A triplet at δ 4.16 (J = 9.4 Hz) for the methylene protons adjacent to oxygen and a triplet of doublets at δ 2.40 (J = 9.4, 2.8 Hz) for the allylic methylene of **10** are also present in the spectrum. GC-MS of the reaction mixture showed two major peaks: the faster moving peak had a molecular ion for dihydrofuran **10** (calcd for $C_{11}H_{12}O$ 160.0888, found 160.0890); the slower moving peak was due to cyclopropanes **8** (M^+, 204). Dihydrofuran **10** was isolated from the reaction mixture by preparative gas chromatography. Although the ^{1}H NMR spectrum of this material was fully consistent with that of dihydrofuran **10**, additional broad resonances in the spectrum showed that some decomposition had occurred during gas chromatography.

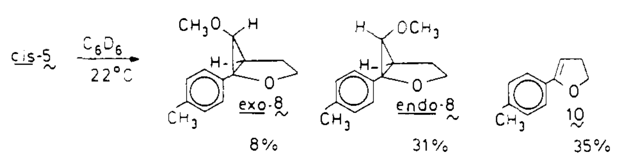


For comparison, an authentic sample of **10** was synthesized. An intramolecular Wittig condensation[17] of phosphonium salt **13** produced **10** as a waxy white solid (mp 28–34 °C) in 58% yield after column chromatography. The ^{1}H NMR and mass spectra of this authentic sample were identical with those of the material produced in the thermal decomposition of carbene complex *trans*-**5**.

The kinetics of the decomposition of *trans*-**5** were much more complex in C_6D_6 and CD_2Cl_2 than in CD_3CN and resembled the kinetics previously discussed for the decomposition of carbene complex **1**, $(CO)_5W{=}C(OCH_2CH_2CH{=}CH_2)C_6H_4\text{-}p\text{-}CH_3$.[3] The rate of decomposition was slow during an initial induction period: after 75 min at 22 °C in C_6D_6, 88% of *trans*-**5** remained in solution. However, after 135 min, the amount of *trans*-**5** had dropped to 47% and after 195 min to 17%.

The product ratios observed during the induction period were substantially different from those observed during the autocatalytic period of the reaction. During the induction period (first 75 min), the reaction was similar to decomposition in CD_3CN: only cyclopropane *exo*-**8** (5% yield) was observed; neither *endo*-**8** nor dihydrofuran **10** were observed at early times. Only during the autocatalytic portion of the reaction (after 75 min) did dihydrofuran **10** (44%) appear as *trans*-**5** rapidly disappeared. In addition, cyclopropane *endo*-**8** (12%) also appeared only during the autocatalytic period and was formed at a faster rate than *exo*-**8** (which increased from 5% to 8%). Isomerization of *trans*-**5** to *cis*-**5** prior to decomposition cannot account for the preferential formation of *endo*-**8** since buildup of the kinetically more stable *cis*-**5** (see below) was not observed.

Evidence for a tungsten-carbene-alkene complex as an intermediate in the decomposition of *trans*-**5** in C_6D_6 was obtained by ^{1}H NMR spectroscopy. In addition to resonances for cyclopropanes **8** and dihydrofuran **10**, many other signals appeared in the spectrum during the course of the reaction. The complexity of the reaction mixture made interpretation of these signals difficult. However, as described below, carbene-alkene complex *trans*-**6** can be cleanly generated from *trans*-**5** by photolysis at low temperature. Comparison of the ^{1}H NMR spectrum of this material to the intermediate spectra obtained during the thermal decomposition of *trans*-**5** showed some resonances attributable to alkene-carbene complex *trans*-**6** rise and fall over the course of the reaction. In particular, one aromatic doublet at δ 7.96 (d, J = 8.3 Hz), built up to 8% after 135 min and gradually disappeared over the following 180 min. An olefinic doublet at δ 5.69 (J = 10.7 Hz) also appeared after the induction period and disappeared by the end of the reaction.



The decomposition of *cis*-**5** in C_6D_6 also led to the formation of a substantial amount of the intramolecular olefin metathesis product, dihydrofuran **10**. After 36 h at 22 °C, a sample of *cis*-**5** (90:10 cis:trans) had completely decomposed to cyclopropanes *endo*-**8** (31%) and *exo*-**8** (8%) and dihydrofuran **10** (35%). The rate of disappearance of *cis*-**5** is slower than that of *trans*-**5**. At 22 °C, 50% decomposition of *trans*-**5** occurred in 2 h and complete decomposition occurred in 4 h. In contrast, 50% decomposition of *cis*-**5** required 12 h and complete decomposition required 36 h. An intermediate, which we believe to be the tungsten-carb-

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ene–alkene complex *cis*-**6**, built up to a concentration of 20% after 18 h and then disappeared after 36 h. The ^1H NMR spectrum of the reaction mixture had an aromatic AB quartet at δ 8.11 and 7.22, an olefinic doublet at δ 6.10 (J = 5.0 Hz), and a multiplet at δ 4.65 (1 H). A downfield shift of the α-proton of vinyl ethers upon complexation has also been seen in $[Cp(CO)_2Fe\text{–vinyl ether}]^+$ complexes.[18] In the present case, the resonance of the proton of the vinyl ether shifts from δ 5.62 downfield to δ 6.10 upon coordination. The tungsten–carbene–alkene complex *cis*-**6** was generated cleanly by photolysis of *cis*-**5** at low temperature (see below). Comparison of the ^1H NMR spectrum of this material to that of the intermediate in the thermal reaction confirms the above assignment of *cis*-**6**.

Decomposition of *trans*-5 in Benzene with Added Trapping Ligands. In principal, the dramatic difference in the kinetics and products of the thermal decomposition of *trans*-**5** in benzene compared with acetonitrile could be attributable either to specific coordinating ability of the solvents or to more general polarity differences between the two solvents. To distinguish between these possibilities, the decomposition of *trans*-**5** was studied in benzene containing low concentrations of added CH_3CN and PPh_3 and major changes were observed (Table I). In all cases, the disappearance of *trans*-**5** followed clean first-order kinetics and led exclusively to formation of cyclopropanes *exo*-**8** (85–90%) and *endo*-**8** (5%). The observed rate constant was independent of both the nature and the concentration of the trapping ligand. Neither dihydrofuran **10** nor carbene–alkene complex *trans*-**6** were observed at any time during the course of these reactions.

When the decomposition of *trans*-**5** in C_6D_6 containing CH_3CN was followed by ^1H NMR, the disappearance of resonances due to carbene complex *trans*-**5** was accompanied by a decrease of the CH_3CN resonance at δ 0.67 and by the simultaneous increase of resonances due to cyclopropane *exo*-**8** and of a singlet at δ 0.24 assigned to $(CO)_5W(CH_3CN)$. The IR spectrum of the product mixture from the decomposition of *trans*-**5** (0.07 M) and CH_3CN (0.31 M) in benzene showed absorptions at 2085 (w), 1947 (s), and 1929 (m) cm^{-1} due to $(CO)_5W(CH_3CN)$,[16] at 1985 (vs) cm^{-1} due to $W(CO)_6$, and at 2075 (w) cm^{-1} (unassigned).

The disappearance of *trans*-**5** and the appearance of cyclopropane *exo*-**8** in the presence of PPh_3 were accompanied by the disappearance of the free PPh_3 (δ 7.01 and 7.40) and by the simultaneous appearance of $(CO)_5W(PPh_3)$ (δ 7.05 and 7.45). An IR spectrum of the product mixtures from the phosphine reactions showed only the presence of $(CO)_5W(PPh_3)$[19] [IR ($CHCl_3$) 2070 (m), 1985 (w), 1940 (vs) cm^{-1}]. In a separate experiment, a solution of *trans*-**5** (0.08 M) and PPh_3 (0.08 M) in C_6D_6 was heated at 45 °C for 6 h in a sealed tube and $(CO)_5W(PPh_3)$ was isolated in 79% yield as a yellow solid by preparative TLC. It should be emphasized that $(CO)_4W(PPh_3)_2$ was not formed in detectable amounts in the above reactions since the IR unambiguously rules out its presence in the product mixtures. $(CO)_4W(PPh_3)_2$ is the product expected from decomposition of a tetracarbonyl carbene–alkene complex such as *trans*-**6**. Previously we had observed $(CO)_4W(PPh_3)_2$ as a major product in the thermal decomposition of aminocarbene–alkene complex **4** in the presence of PPh_3.[4]

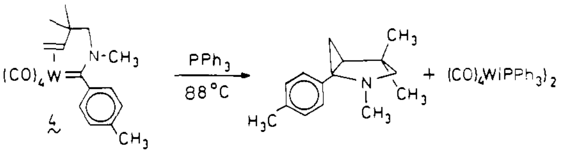


Table I. First-Order Rate Constants for Decomposition of *trans*-**5**[a] at 42 °C in C_6D_6 with Added Ligands

$[trans\text{-}\mathbf{5}]_0$, M	L	$[L]_0$, M	10^4k_{obsd},[b] s^{-1}
0.06	CH_3CN	0.09	1.03 ± 0.03
0.07	CH_3CN	0.31	1.24 ± 0.08
0.07	PPh_3	0.08	0.89 ± 0.03
0.06	PPh_3	0.16	0.85 ± 0.04

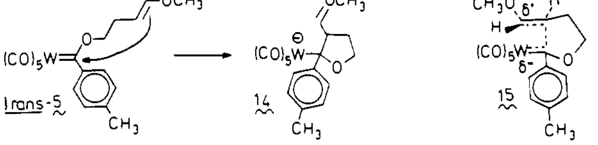
[a] *Trans:cis* = 95:5. [b] Calculated for first five data points (first half-life) only.

Table II. First-Order Rate Constants for the Decomposition of *trans*-**5** and **1** in Coordinating Solvents at 42 °C

	10^4k_{obsd}, s^{-1}		
solv	*trans*-**5**[a,b]	**1**[b]	$k_{trans\text{-}5}:k_1$
C_6D_6/PPh_3	0.89 ± 0.03	0.26 ± 0.02	3.4:1
THF-d_8	1.52 ± 0.08	0.78 ± 0.21	1.9:1
CD_3CN	2.64 ± 0.08	1.71 ± 0.11	1.5:1

[a] *Trans:cis* = 95:5. [b] Calculated for first five data points or first half-life only; initial concentration 0.07 M.

Solvent Dependence of the Rate of Cyclopropanation. Since a plausible mechanism for the conversion of carbene complex *trans*-**5** to cyclopropane *exo*-**8** involves an initial nucleophilic addition of the vinyl ether to the carbene carbon via a zwitterionic transition state such as **14** or metallacycle formation via a polar transition state such as **15**,[20] we decided to investigate the rate of cyclopropanation as a function of solvent polarity. If the reaction involves a polar transition state, the rate would be expected to be faster in polar solvents. In addition, the carbene complex *trans*-**5** with a vinyl ether side chain would be expected to be much more reactive toward cyclopropanation than the carbene complex **1** with a simple alkene side chain. However, only minor solvent rate effects were observed and *trans*-**5** and **1** displayed similar reactivity; polar transition states similar to **13** are apparently not involved in cyclopropane formation.



The first-order rate constant for conversion of *trans*-**5** to cyclopropanes **8** increased by only a factor of 2.9 in changing from benzene (with low concentrations of PPh_3 or CH_3CN) to THF-d_8 to acetonitrile (Table II). In the weakly coordinating solvent THF, *trans*-**5** (95:5 *trans/cis*) was converted mainly to cyclopropanes *exo*-**8** (85%) and *endo*-**8** (13%), although traces of dihydrofuran **10** were also detected by ^1H NMR.

Carbene complex **1** was prepared by treating acyl anion **10** with acetyl chloride and then with 3-buten-1-ol. The thermal decomposition of **1** to cyclopropane **3** was followed by ^1H NMR at 42 °C. First-order kinetics were observed in the coordinating solvents CD_3CN and THF-d_8 and in C_6D_6 with 1 equiv of added PPh_3 (Table II). Cyclopropane **3** was produced in nearly quantitative yield in all cases. As is seen for *trans*-**5**, the rate of decomposition of **1** showed only a small acceleration (6.6) upon changing from benzene to acetonitrile. More importantly, the vinyl ether carbene complex *trans*-**5** reacted only 1.9–3.4 times faster than carbene complex **1** with a simple alkene side chain.

Photochemical Generation of Carbene–Alkene Complexes *trans*-6 and *cis*-6. In an elegant study of the photochemistry of $(CO)_5W{=}C(OCH_3)C_6H_5$ (**16**), Geoffrey reported the low-temperature generation of the tetracarbonyltungsten–carbene–alkyne complex *cis*-$(CO)_4(PhC{\equiv}CPh)W{=}C(OCH_3)C_6H_5$ (**17**).[21] Irradiation into the ligand field transition of **16** led to CO dissociation as the primary photochemical process. The tetracarbonyl intermediate was then trapped by diphenylacetylene in solution to give adduct **17** that was stable below −20 °C.

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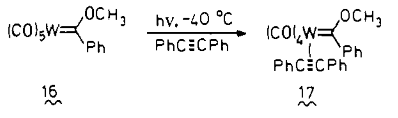
(18) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 81–391.

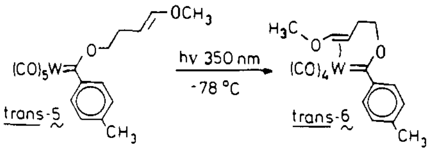
(19) Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200–3203.

(20) (a) Brookhart, M.; Kegley, S. E.; Husk, R. G. *Organometallics* **1984**, *3*, 650–652. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282–7292.

(21) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064–3073.



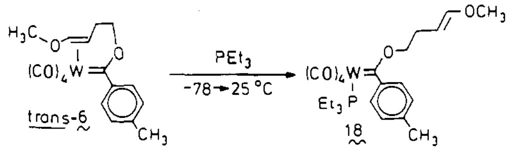
In an effort to cleanly generate tetracarbonyltungsten–carbene–alkene complexes *trans*-**6** and *cis*-**6**, we photolyzed carbene complexes *trans*-**5** and *cis*-**5** in noncoordinating solvents (CD_2Cl_2 and toluene-d_8) at −78 °C. Photolyses were performed in a Rayonet photochemical reactor equipped with bulbs with maximum emission at 350 nm (*trans*-**5** has ϵ = 5592 M^{-1} cm^{-1} at 350 nm). Low-temperature ^1H NMR spectroscopy (−25 °C) showed that a new species, the chelated carbene–alkene complex *trans*-**6**, had been formed cleanly. After photolysis for 26 h, the ratio of *trans*-**6**:*trans*-**5** in solution was 95:5.



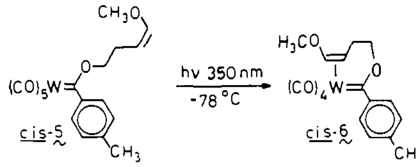
The structure of the chelated metal–carbene–alkene complex **6** was established by ^1H and ^{13}C NMR and IR spectroscopy. In CD_2Cl_2, the vinyl protons of *trans*-**6** appear at δ 6.47 (d, *J* = 10.7 Hz, CH=C*H*OCH$_3$) and 4.88 (multiplet), shifted only slightly from the corresponding signals of *trans*-**5** (δ 6.51 and 4.90). The change in the coupling constant from 12.6 to 10.7 Hz indicates a change in hybridization upon coordination. In toluene-d_8, an upfield shift from δ 6.30 (d, *J* = 12.6 Hz) to 5.56 (d, *J* = 10.5 Hz) for the terminal vinyl proton occurs upon coordination. The resonance for the internal vinyl hydrogen shows essentially no change upon coordination, appearing at δ 4.41 in *trans*-**6** and δ 4.24 in *trans*-**5**. All four protons of the $-CH_2CH_2-$ unit have widely separated chemical shifts, indicative of chelate formation.

The ^{13}C NMR spectrum of *trans*-**6** in CD_2Cl_2 at −40 °C (*trans*-**6**:*trans*-**5** = 4:1) showed four resonances for the inequivalent CO's at δ 210.9, 210.6, 207.9, and 203.5. Two resonances for *trans*-**6** appear at δ 61.0 and 60.2 and were assigned as a CH group (*C*H=CHOCH$_3$) and a CH_3 group (OCH_3), respectively, by two INEPT experiments. A ^1H–^{13}C correlation experiment[22] was required to establish that the ^{13}C resonance at δ 128.2 was due to the overlapping resonances of the terminal vinyl carbon (CH=*C*HOCH$_3$, coupled to the vinyl proton at δ 6.47 in the ^1H NMR) and of an aromatic CH (coupled to an aryl resonance at δ 7.21 in the ^1H NMR). Upon coordination of tungsten, both carbon resonances of the alkene thus show substantial upfield shifts: from δ 148.1 and 95.7 in *trans*-**5** to δ 128.2 and 61.0 in *trans*-**6**.

The IR spectrum of *trans*-**6** obtained at −78 °C showed four carbonyl bands of approximately equal intensity at 2015, 1929, 1909, and 1884 cm^{-1} in CH_2Cl_2 and three bands at 2026 (m), 1945 (m), and 1918 (vs) cm^{-1} in hexane, consistent with the presence of a 6-coordinate *cis*-$M(CO)_4$ fragment with C_1 symmetry.



Tungsten–carbene–alkene complex *trans*-**6** was further characterized by its reaction with PEt_3. Addition of PEt_3 to a solution of *trans*-**6** at −78 °C followed by warming to room temperature led to the formation of phosphine adduct **18** which was isolated by chromatography as a red oil in 71% yield. The cis arrangement of PEt_3 and the carbene ligand in **18** was established by IR spectroscopy; **18** has four CO bands at 2016 (m), 1928 (s), 1921 (s), and 1894 (s) cm^{-1} consistent with local C_{2v} symmetry. This spectrum is similar to that previously reported for *cis*-$(CO)_4(PEt_3)W{=}C(OCH_2CH_2CH{=}CH_2)C_6H_4$-*p*-$CH_3$, the product of carbene–alkene complex **2** and PEt_3.[3] In the ^{13}C NMR, **18** has three carbonyl resonances at δ 212.8, 207.2 (d, J_{P-C} = 17.7 Hz), and 203.7 in a 1:1:2 ratio.



Tungsten–carbene–alkene complex *cis*-**6** was cleanly generated by photolysis of *cis*-**5** (cis:trans = 90:10) in CD_2Cl_2 for 21 h at −78 °C. The mixture of *cis*-**5** and *trans*-**5** was converted to a 80:10 mixture of *cis*-**6**:*trans*-**6** in addition to 10% remaining starting material. In the ^1H NMR of tungsten–carbene–alkene complex *cis*-**6** at −35 °C, coordination shifts the resonance of the vinyl proton α to the methoxy group downfield to δ 6.92 (d, *J* = 5.2 Hz) in *cis*-**6** from δ 6.09 (d, *J* = 5.9 Hz) in the uncomplexed starting material *cis*-**5**. In contrast, coordination shifts the vinyl proton β to the methoxy group upfield to δ 2.90 *cis*-**6** from δ 5.28 in *cis*-**5**. In $[Cp(CO)_2Fe\text{–vinyl ether}]^+$ complexes similar downfield shifts of the α-protons and upfield shifts of the β-protons of the vinyl ethers have been reported.[18] Like carbene–alkene complex *trans*-**6**, *cis*-**6** has four carbonyl resonances in the ^{13}C NMR spectrum at δ 214.0, 209.7, 201.0, and 199.6. The IR spectrum of *cis*-**6** in hexane is similar to that of *trans*-**6**: 2024 (m), 1931 (m), 1916 (vs) cm^{-1}.

Thermal Decomposition of Tungsten–Carbene–Alkene Complexes. Solutions of *trans*-**6** and *cis*-**6** in CD_2Cl_2 were indefinitely stable at −78 °C and showed no signs of decomposition at −25 °C during spectroscopic characterization. Upon warming, both isomers of the carbene–alkene complex decomposed to similar mixtures of dihydrofuran **10** and cyclopropanes **8**. At 5 °C, *trans*-**6** decomposed to dihydrofuran **10** (46%), cyclopropane *endo*-**8** (22%), and a trace of cyclopropane *exo*-**8** (3%). Clean first-order kinetics were observed when the reaction was monitored by ^1H NMR: $k = (1.52 \pm 0.10) \times 10^{-4}$ s^{-1}, $t_{1/2}$ = 1.3 h at 5 °C. *cis*-**6** is more thermally stable than the trans isomer and decomposed at 22 °C to dihydrofuran **10** (49%), cyclopropane *endo*-**8** (18%), and cyclopropane *exo*-**8** (4%). Again, clean first-order kinetics were observed when the reaction was monitored by ^1H NMR: $k = (7.10 \pm 0.23) \times 10^{-5}$ s^{-1}, $t_{1/2}$ = 2.7 h at 22 °C.

The decomposition of *trans*-**6** in the coordinating solvent THF-d_8 was monitored by ^1H NMR at 5 °C. A solution of *trans*-**6** was prepared by photolysis of *trans*-**5** (10 mg) in CH_2Cl_2. Evaporation of CH_2Cl_2 at −15 °C under high vacuum and condensation of THF-d_8 produced a THF-d_8 solution of a 75:25 mixture of *trans*-**6**:*trans*-**5**. After 6.7 h at 5 °C, ^1H NMR analysis showed *trans*-**6** had completely disappeared and cyclopropanes *exo*-**8** (5%) and *endo*-**8** (39%) and dihydrofuran **10** (15%) had been formed.

Discussion

The mechanism of the decomposition of tungsten carbene complexes *trans*-**5** and *cis*-**5** is clearly very different in coordinating solvents such as CD_3CN than it is in noncoordinating solvents such as C_6D_6. In CD_3CN, clean first-order decomposition occurred and cyclopropane **8** was formed in nearly quantitative yield and with high stereospecificity. In contrast, in C_6D_6, a kinetically complex autocatalytic decomposition led both to the formation of olefin metathesis products and to the nonstereospecific generation of cyclopropanes.

The mechanism shown in Scheme IV for the conversion of *trans*-**5** to cyclopropane *exo*-**8** in CD_3CN is consistent with the observed first-order rate law, stereospecificity of cyclopropane formation, lack of CO inhibition, and formation of $(CO)_5W(CH_3CN)$. In the rate-determining step, concerted cycloaddition of the alkene to the metal–carbon double bond of *trans*-**5** leads to formation of metallacycle *trans*-**19** with retention of stereochemistry. Reductive elimination with retention of stereochemistry produces cyclopropane *exo*-**8** and $(CO)_5W$. The $(CO)_5W$ is then

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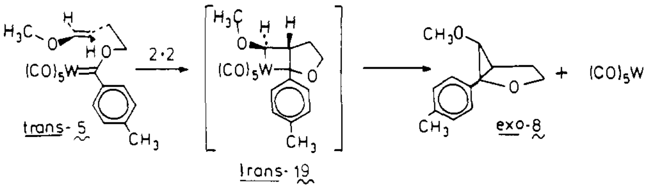
[22] Bax, A. *J. Magn. Reson.* **1983**, *53*, 517–520.

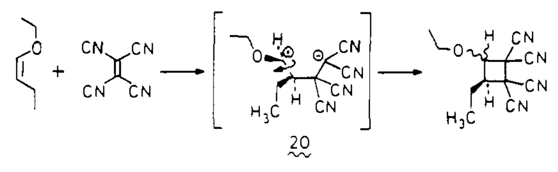
Scheme IV



rapidly trapped by solvent or added ligands to give the observed $(CO)_5W–L$. In principle, olefin metathesis from the 18-electron 7-coordinate metallacycle *trans*-**19** could occur by the microscopic reverse of metallacycle formation, but this is apparently a higher energy process than reductive elimination to give cyclopropane. Similarly, breakdown of the metallacycle to a 20-electron metal–carbene–alkene complex is also a high-energy process.

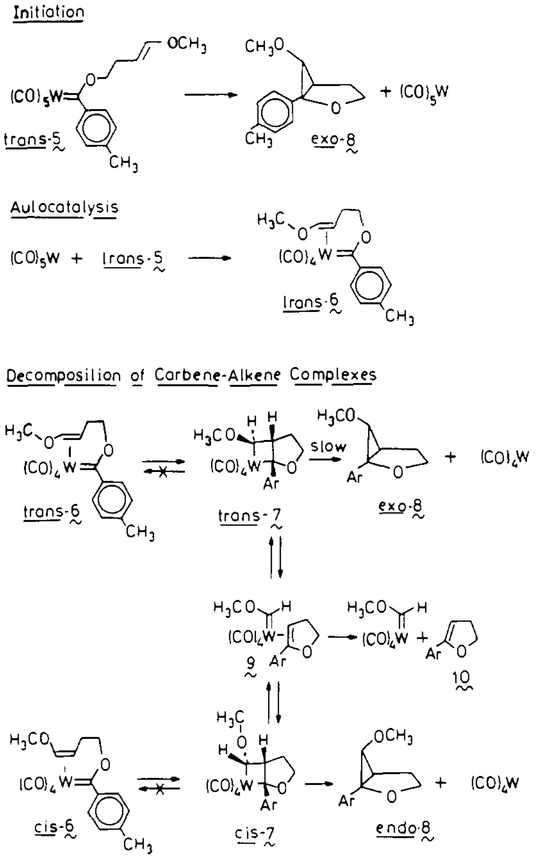
Mechanisms for metallacycle formation involving buildup of substantial positive charge at the terminal carbon of the alkene in the transition state as in **15** or a zwitterionic intermediate such as **14** were also considered, but we concluded that such processes were not important in the dominant reaction–stereospecific formation of cyclopropane. Decomposition of *trans*-**5** was only 2.9 times faster in CD_3CN than in C_6D_6 containing PPh_3, indicating that the transition state leading to metallacycle *trans*-**19** is not much more polar than the starting material. Moreover, if positive charge buildup at the terminal carbon of the alkene were important, then a substantial rate acceleration would have been expected for *trans*-**5**, which has a vinyl ether side chain, compared to **1**, which has a terminal alkene side chain. Since cyclopropane formation is only 2.6 times faster from *trans*-**5** than from **1** in CH_3CN, little positive charge buildup is occurring in the transition state for cyclopropane formation.

The above results can be contrasted with the reactions of enol ethers with the electron-deficient alkene tetracyanoethylene (TCNE) which give cyclobutanes via zwitterionic intermediates such as **20**.[23] Simple alkenes are inert toward TCNE, but enol ethers react rapidly at room temperature to give cyclobutanes. Huge solvent effects were observed: for example, $k(CH_3CN)/k(\text{cyclohexane}) = 10\,800$ for the reaction of butyl vinyl ether with TCNE.[23d] In polar solvents such as CH_3CN and ethyl acetate, some loss of alkene stereochemistry in the reaction of TCNE with *cis*-1-ethoxy-1-butene was observed as the lifetime of the zwitterionic intermediate increased and bond rotation competed more effectively with ring closure.[23b,c]



The 8% loss of stereochemistry seen in the conversion of *trans*-**5** to cyclopropane in CH_3CN is difficult to explain. No isomerization of starting material was seen during decomposition, and no variation in the ratio of cyclopropanes *exo*-**8**:*endo*-**8** was detectable over the course of the decomposition. The cyclopropanes did not interconvert when the CD_3CN reaction mixture was heated at 43 °C for an additional 18 h after complete decomposition of carbene complex *trans*-**5**. Although the above results indicate a concerted, nonpolar mechanism for metallacycle formation as the major reaction pathway, some competition from a polar mechanism in CD_3CN could account for the loss of stereochemistry. Isomerization via rotation of the ring-opened dipolar intermediate **14** could account for the small amount of isomerization. Intermediate **14** might be accessed directly from starting material or via reversible ring opening of the metallacycle in the more polar solvent CD_3CN.

Scheme V



A tetracarbonyl-chelated carbene–alkene complex cannot be involved in the decomposition of *trans*-**5** and *cis*-**5** in coordinating solvents. Loss of carbon monoxide from **5** is expected to be much slower at 42 °C than the observed rate of cyclopropanation. The half-life for CO dissociation from the related complex $(CO)_5W{=}C(OCH_3)C_6H_5$ (**16**) is 7 h at 77 °C.[24] Moreover, decomposition of the chelated tungsten–carbene–alkene complex *trans*-**6** in THF led to nonstereospecific formation of cyclopropanes *exo*-**8** (5%) and *endo*-**8** (39%) and to the formation of olefin metathesis product dihydrofuran **10** (15%).

In noncoordinating solvents such as C_6D_6, the decomposition of *trans*-**5** and *cis*-**5** proceeds by a different mechanism that leads to olefin metathesis products as well as cyclopropanes. The kinetics of the decomposition are characterized by an induction period followed by rapid autocatalytic decomposition. The role of a coordinatively unsaturated intermediate in the autocatalytic decomposition is demonstrated by the dramatic change in products and kinetics when the reaction is carried out in the presence of ligands such as PPh_3 and CH_3CN. Dihydrofuran **10**, the product of intramolecular olefin metathesis, was the major decomposition product of both *trans*-**5** (41%) and *cis*-**5** (35%) in C_6D_6. Cyclopropane *endo*-**8** was formed preferentially from *both* enol ether isomers of the carbene complex. *trans*-**5** (95:5 trans:cis) gave 12% *endo*-**8** and 8% *exo*-**8**, while *cis*-**5** (90:10 cis:trans) gave 31% *endo*-**8** and 8% *exo*-**8**.

To explain these results, we propose the mechanism shown in Scheme V. During the induction period, *trans*-**5** slowly decomposes to cyclopropane *exo*-**8** and $W(CO)_5$ in a reaction analogous to stereospecific cyclopropanation in CH_3CN. However, in the absence of trapping ligands, the unsaturated $(CO)_5W$ fragment is proposed to abstract CO from the starting material to give metal–carbene–alkene complex *trans*-**6**. Cyclization of *trans*-**6** produces the 16-electron *6-coordinate* metallacycle **7** which can either decompose to cyclopropane and $W(CO)_4$ or ring open to form the new metal–carbene–alkene complex **9** from which the

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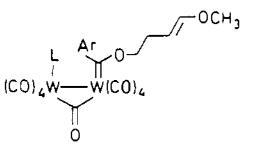
(23) (a) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117–124. (b) Huisgen, R.; Steiner, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 5054–5055. (c) Huisgen, R.; Steiner, G. *Ibid.* **1973**, *95*, 5055–5056. (d) Steiner, G.; Huisgen, R. *Ibid.* **1973**, *95*, 5056–5058.

(24) Casey, C. P.; Cesa, M. *Organometallics* **1982**, *1*, 87–94.

dihydrofuran **10** can be released. Two critical features of this system allow olefin metathesis to occur. The first is that dihydrofuran **10** is stabilized by complexation to tungsten. The second is that cleavage of the metallacycle **7** converts the methoxy-substituted terminal carbon of the vinyl ether into a heteroatom-stabilized carbene unit, W=CHOMe. As discussed previously, the related complex $(CO)_5W{=}C(OCH_2CH_2CH{=}CH_2)C_6H_4$-*p*-$CH_3$ (**1**), which lacks an electron-donating group at the terminal position of the alkene, did not undergo olefin metathesis in noncoordinating solvents since this would have required cogeneration of an unstabilized $W{=}CH_2$ unit.[3]

Decomposition of tungsten-carbene-alkene complex **6** produces the coordinatively unsaturated species $W(CO)_4$ in conjunction with cyclopropane formation and $(CO)_4W{=}CHOMe$ in conjunction with olefin metathesis. These unsaturated species are proposed to abstract CO from starting material **5** to generate additional amounts of metal-carbene-alkene complex **6**. The CO abstraction reaction, an important step in the chain decomposition, is envisioned to proceed via bridged CO complexes such as **21**.



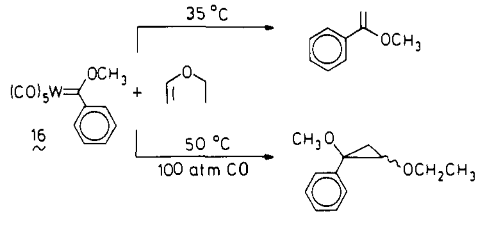
21

The intermediacy of the chelated tungsten-carbene-alkene complexes *trans*-**6** and *cis*-**6** in the autocatalytic portion of the decomposition of *trans*-**5** and *cis*-**5** was established by independent generation of these complexes. *trans*-**6** and *cis*-**6** were cleanly generated by photolysis of *trans*-**5** and *cis*-**5** at −78 °C. Upon warming to +5 °C, *trans*-**6** gave *endo*-**8** (22%) and dihydrofuran **10** (46%) in yields similar to those observed in the thermal reaction of *trans*-**5**. The more stable *cis*-**6** gave *endo*-**8** (18%) and **10** (49%) upon warming to 22 °C.

A mechanism for the decomposition of *trans*-**6** and *cis*-**6** has to explain the preferential formation of *endo*-**8** from both isomers. Isomerization of *trans*-**6** to *cis*-**6** did not occur since buildup of the kinetically more stable *cis*-**6** was never observed during the decomposition of *trans*-**6**. Cyclopropanes *exo*-**8** and *endo*-**8** are configurationally stable under the reaction conditions. A possible explanation for formation of isomerized cyclopropanes involves interconversion of the metallacycles *trans*-**7** and *cis*-**7** via carbene-alkene complex **9** as shown in Scheme V. If this metathesis reaction is reversible, rotation about the tungsten-carbene carbon bond in **9** followed by reclosure to metallacycle would accomplish cis-trans isomerization of the metallacycles. Reductive elimination of cyclopropane *endo*-**8** from *cis*-**7** must then be preferred over elimination of *exo*-**8** from *trans*-**7**. Reversion of the metallacycles to the original carbene-alkene complexes must be slower than the decomposition reactions since isomerization of *trans*-**6** and *cis*-**6** was never observed.

The results obtained here indicate that the competition between olefin metathesis and cyclopropane formation in the reactions of Fischer carbene complexes with alkenes is controlled both by the coordination number of the intermediate metallacycle and by the ability of substituents on the alkene to stabilize the new carbene complex generated in an olefin metathesis reaction. Reactions proceeding through 18-electron 7-coordinate metallacyclobutanes yield only cyclopropanes regardless of alkene substituents. In this case, formation of a cyclopropane and a monounsaturated metal species such as $W(CO)_5$ is greatly favored over formation of a new carbene complex and an uncoordinated alkene. In contrast, reactions proceeding through 16-electron 6-coordinate metallacyclobutanes can lead either to cyclopropanes and doubly unsaturated species such as $W(CO)_4$ or to olefin metathesis products depending on the nature of the alkene substituents. The 16-electron metallacycle can be converted to an 18-electron metal-carbene-alkene complex in which alkene formation is facilitated by coordination to the metal. However, metal complexation of the alkene is insufficient by itself to favor olefin metathesis. In our work, the observation of olefin metathesis has also required stabilization of the metal carbene fragment by an electron-donating methoxy group derived from a vinyl ether.

Early work by Fischer on the reactions of methoxy carbene complex **16** with ethyl vinyl ether[8] can also be explained in this manner. Fischer showed that cyclopropanation and olefin metathesis could be controlled by external CO pressure: with no added CO, metathesis dominated; under 100 atm of CO, cyclopropanation dominated.



Experimental Section

General Data. All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. Tetrahydrofuran, diethyl ether, and C_6D_6 were distilled from purple solutions prepared from sodium and benzophenone. Toluene was distilled from sodium, benzophenone, and tetraglyme. CD_2Cl_2 was distilled from P_2O_5. CH_3CN and CD_3CN were distilled from P_2O_5 and stored over CaH_2, from which they were distilled immediately prior to use.

^1H NMR spectra were obtained on a Bruker WP-270 spectrometer. When quantitative results were required, a 30-s pulse delay was used between scans to minimize the effects of different relaxation times. ^{13}C NMR spectra were obtained on a JEOL FX-200 spectrometer, a Bruker AM-360 spectrometer, or a Bruker AM-500 spectrometer. Infrared spectra were recorded on a Beckman IR-4230 spectrophotometer. Low-temperature infrared spectra were obtained by using a Beckman-RIICC VLT-2 variable-temperature cell. Mass spectra were obtained on a Kratos MS-25 or a MS-80 spectrometer. GC-MS was performed on a Carlo-Erba gas chromatograph equipped with a 30 m × 0.32 mm capillary column coated with 5% phenylmethyl silicone interfaced to a Kratos MS-25 mass spectrometer.

Low-temperature photolyses were carried out in a Rayonet Srinivasan-Griffin photochemical reactor equipped with Sylvania F8T5/BLB bulbs (maximum emission at 350 nm). Samples were placed in an unsilvered Dewar flask (Pyrex glass) containing a CO_2-acetone bath (−78 °C), and the flask was placed inside the Rayonet reactor.

$N(CH_2CH_3)_4^+[(CO)_5WCOC_6H_4$-*p*-$CH_3]^-$ (11). *n*-BuLi (1.66 M, 12 mL, 20 mmol) was added to a stirred solution of *p*-bromotoluene (3.42 g, 20 mmol) in 50 mL of Et_2O at 0 °C. The solution was warmed to room temperature and transferred via cannula to a stirred suspension of $W(CO)_6$ (7.05 g, 20 mmol) in 200 mL of Et_2O at 0 °C. The resulting red-orange solution was stirred 1 h at room temperature. Addition of $NEt_4^+Br^-$ (8.4 g, 40 mmol) in 100 mL of degassed water led to the precipitation of **11** (8.48 g, 74%) as an orange solid which was dried under vacuum: mp 97–98 °C; ^1H NMR (acetone-d_6) δ 7.46 (d, $J = 7.8$ Hz, 2 H, C_6H_4), 7.09 (d, $J = 7.8$ Hz, 2 H, C_6H_4), 3.45 (q, $J = 7.3$ Hz, NCH_2), 2.27 (s, $ArCH_3$), 1.35 (tt, $J = 7.3$, $J_{^{14}N-^1H} = 1.9$ Hz, NCH_2CH_3); ^{13}C NMR (50.1 MHz, CD_3CN, 0.07 M $Cr(acac)_3$) δ 278.1 (W=C), 209.1 (trans CO), 204.8 (cis CO), 156.1, 138.8 (ipso, para), 128.9, 126.6 (ortho, meta), 53.3 (NCH_2), 21.2 ($ArCH_3$), 7.8 (NCH_2CH_3); IR (CH_2Cl_2) 2040 (m), 1940 (m), 1890 (vs), 1870 (sh) cm^{-1}. Anal. Calcd for $C_{21}H_{27}NO_6W$: C, 44.00; H, 4.75; N, 2.44. Found: C, 43.96; H, 4.92; N, 2.31.

$(CO)_5W{=}C(OCH_2CH_2CH{=}CHOCH_3)C_6H_4$-*p*-$CH_3$ (5). Acetyl chloride (0.21 mL, 3.0 mmol) in 10 mL of CH_2Cl_2 was added to a stirred solution of **11** (1.51 g, 2.6 mmol) in 100 mL of CH_2Cl_2 at −15 °C. After 45 min, 4-methoxy-3-buten-1-ol[9-12] (0.30 mL, 2.9 mmol, 85:15 trans:cis) in 10 mL of CH_2Cl_2 was added. After 6 h at 0 °C, the CH_2Cl_2 was evaporated under vacuum and the residue was washed repeatedly with several milliliters of cold hexane until the extracts were no longer red (total volume 50 mL). The hexane extracts were concentrated to 10–15 mL and cooled to −78 °C to precipitate **5**. Cold filtration (−78 °C) gave **5** (0.65 g, 47%) as a red solid which was dried under high vacuum and stored at −20 °C. This material was a 95:5 mixture of trans and cis vinyl ether isomers as shown by ^1H NMR.

A sample enriched in the cis vinyl ether isomer was isolated from the mother liquors obtained from a 7-mmol scale reaction. Preparative TLC (95:5:4 hexane/ether/NEt_3) gave the more rapidly moving *cis*-**5** as a red oil (R_f 0.68, 55 mg, 10% based on the cis isomer of 4-methoxy-3-buten-1-ol, 1.5% of mixture). This material was a 90:10 mixture of cis and trans vinyl ether isomers as shown by ^1H NMR.

For *trans*-**5**: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.61 (d, *J* = 8.2 Hz, 2 H, $\mathrm{C_6H_4}$), 6.81 (d, *J* = 8.1 Hz, 2 H, $\mathrm{C_6H_4}$), 6.27 (d, *J* = 12.6 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{OCH_3}$), 4.63 (t, *J* = 6.4 Hz, $\mathrm{OCH_2}$), 4.50 (dt, *J* = 12.6, 7.4 Hz, $\mathrm{C}\mathit{H}\mathrm{{=}CHOCH_3}$), 3.08 (s, $\mathrm{OCH_3}$), 2.11 (dt, *J* = 7.4, 6.4 Hz, $\mathrm{OCH_2C}\mathit{H}_2$), 1.90 (s, $\mathrm{ArCH_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50.1 MHz, $\mathrm{CD_2Cl_2}$, 0.07 M $\mathrm{Cr(acac)_3}$, −45 °C) δ 313.8 (W=C), 203.4 (trans CO), 196.9 (cis CO), 149.8, 143.5 (ipso, para), 148.1 ($\mathrm{CH{=}}\mathit{C}\mathrm{HOCH_3}$), 128.0 (ortho, meta), 95.7 ($\mathit{C}\mathrm{H{=}CHOCH_3}$), 83.2 ($\mathrm{O}\mathit{C}\mathrm{H_2}$), 27.2 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 20.9 ($\mathrm{ArCH_3}$), not observed $\mathrm{OCH_3}$. In $\mathrm{CD_3CN}$ at −8 °C, the $\mathrm{OCH_3}$ resonance is observed at δ 56.1. A $^{13}\mathrm{C}\{^1\mathrm{H}\}$ INEPT experiment confirmed the assignments of the resonances at δ 148.1, 128.0, and 95.7 as methine carbons. IR (hexane): 2064 (m), 1985 (m), 1957 (vs), 1946 (vs) $\mathrm{cm^{-1}}$. UV–vis: $\lambda_{\max}$ 410 nm (ε 11 000 $\mathrm{M^{-1}\,cm^{-1}}$), 355 (ε 6100). HRMS: calcd for $\mathrm{C_{18}H_{16}O_7{}^{184}W}$ 528.037, found 528.041.

For *cis*-**5**: ^{1}H NMR ($\mathrm{C_6D_6}$) 7.65 (d, *J* = 8.0 Hz, 2 H, $\mathrm{C_6H_4}$), 6.81 (d, *J* = 8.0, 2 H, $\mathrm{C_6H_4}$), 5.62 (dd, *J* = 6.2, 1.0 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{OCH_3}$), 4.76 (t, *J* = 6.6 Hz, $\mathrm{OCH_2}$), 4.25 (q, *J* = 6.7 Hz, $\mathrm{C}\mathit{H}\mathrm{{=}CHOCH_3}$), 3.05 (s, $\mathrm{OCH_3}$), 2.56 (qd, *J* = 6.7, 1.0 Hz, $\mathrm{OCH_2C}\mathit{H}_2$), 1.90 (s, $\mathrm{ArCH_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50.1 MHz, $\mathrm{CD_3CN}$, 0.07 M $\mathrm{Cr(acac)_3}$) δ 317.2 (W=C), 204.7 (trans CO), 198.2 ($J_{^{13}\mathrm{C}-^{184}\mathrm{W}}$ = 127.3 Hz, cis CO), 152.7, 144.5 (ipso, para), 149.5 ($\mathrm{CH{=}}\mathit{C}\mathrm{HOMe}$), 129.5, 128.8 (ortho, meta), 100.7 ($\mathit{C}\mathrm{H{=}CHOMe}$), 84.6 ($\mathrm{OCH_2}$), 60.0 ($\mathrm{OCH_3}$), 24.7 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 21.4 ($\mathrm{ArCH_3}$); IR (hexane) 2066 (m), 1985 (w), 1952 (vs), 1946 (vs) $\mathrm{cm^{-1}}$.

1-(4-Methylphenyl)2-oxa-6-*exo*-methoxybicyclo[3.1.0]hexane (*exo*-8). A solution of **5** (80 mg, 0.15 mmol, 95:5 trans:cis) in 10 mL of $\mathrm{CH_3CN}$ decomposed at ambient temperature within 24 h. $\mathrm{CH_3CN}$ was evaporated under vacuum, the residue was subjected to TLC (9:1 hexane/ether), and the band at R_f 0.36 was eluted with ether to give *exo*- and *endo*-**8** (>95:5). Distillation on a Kugelrohr apparatus gave *exo*-**8** (12 mg, 37%) as a clear oil: bp 80 °C (7 mm); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.66 (d, *J* = 7.4 Hz, 2 H, $\mathrm{C_6H_4}$), 7.09 (d, *J* = 7.4 Hz, 2 H, $\mathrm{C_6H_4}$), 3.76 (td, *J* = 8.3, 5.9 Hz, $\mathrm{OC}\mathit{H}\mathrm{H}$), 3.44 (td, *J* = 8.2, 6.3 Hz, $\mathrm{OCH}\mathit{H}$), 3.20 (d, *J* = 2.6 Hz, CHOMe), 2.89 (s, $\mathrm{ArCH_3}$), 1.85 (ddd, *J* = 6.7, 2.6, 1.4 Hz, bridgehead H), 1.73 (ddt, *J* = 12.0, 8.1, 6.3 Hz, $\mathrm{OCH_2C}\mathit{H}\mathrm{H}$), 1.53 (dddd, *J* = 12.0 7.5, 5.8, 1.4 Hz, $\mathrm{OCH_2CH}\mathit{H}$); ^{1}H NMR ($\mathrm{CD_3CN}$) δ 7.28 (d, *J* = 8.2 Hz, 2 H, $\mathrm{C_6H_4}$), 7.13 (d, *J* = 8.3 Hz, 2 H, $\mathrm{C_6H_4}$), 3.98 (td, *J* = 8.5, 5.5 Hz, $\mathrm{OC}\mathit{H}\mathrm{H}$), 3.70 (q, *J* = 7.4 Hz, $\mathrm{OCH}\mathit{H}$), 3.35 (d, *J* = 2.6 Hz, CHOMe), 3.05 (s, $\mathrm{OCH_3}$), 2.31 (s, $\mathrm{ArCH_3}$), 2.19–2.32 (m, $\mathrm{OCH_2C}\mathit{H}\mathrm{H}$), 1.97–2.06 (m, $\mathrm{OCH_2CH}\mathit{H}$ and bridgehead H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50.1 MHz, $\mathrm{CD_3CN}$) δ 137.1, 135.2 (ipso, para), 73.9 (bridgehead quaternary C), 71.1, 71.0 ($\mathrm{OCH_2}$, CHOMe), 58.1 ($\mathrm{OCH_3}$), 30.8, 30.0 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$, bridgehead H); HRMS calcd for $\mathrm{C_{13}H_{16}O_2}$ 204.1146, found 204.1152.

1-(4-Methylphenyl)-2-oxa-6-*endo*-methoxybicyclo[3.1.0]hexane (*endo*-8). *trans*-**6** was generated by photolysis (−78 °C, 28 h) of *trans*-**5** (95:5 trans:cis, 300 mg, 5.7 mmol) in 20 mL of $\mathrm{CH_2Cl_2}$. Solvent was evaporated at −15 °C under high vacuum, and THF (20 mL) was vacuum transferred into the flask. After the solution was stirred at +5 °C for 24 h, THF was evaporated. A ^{1}H NMR spectrum of the crude reaction mixture showed cyclopropanes *exo*-**8** and *endo*-**8** present in a 1:1 ratio. Preparative TLC (75:25 hexane/ether) gave *endo*-**8** as the faster moving band (R_f 0.54) and *exo*-**8** as the slower moving band (R_f 0.43). Cyclopropane *endo*-**8** was further purified by distillation on a Kugelrohr apparatus and was isolated as a clear oil (12 mg, 10%): bp 80 °C (1 mm); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.21 (d, *J* = 8.0 Hz, 2 H, $\mathrm{C_6H_4}$), 7.02 (d, *J* = 8.0 Hz, 2 H, $\mathrm{C_6H_4}$), 4.14 (ddd, *J* = 9.8, 7.7, 5.0 Hz, $\mathrm{OC}\mathit{H}\mathrm{H}$), 4.07 (q, *J* = 7.7 Hz, $\mathrm{OCH}\mathit{H}$), 3.33 (d, *J* = 7.4 Hz, CHOMe), 3.26 (s, $\mathrm{OCH_3}$), 2.13 (s, $\mathrm{ArCH_3}$), 2.12 (dddd, *J* = 12, 8.6, 4.7, 0.9 Hz, $\mathrm{OCH_2C}\mathit{H}\mathrm{H}$), 1.91 (ddt, *J* = 12, 9.5, 7.0 Hz, $\mathrm{OCH_2CH}\mathit{H}$), 1.65 (t, *J* = 7.0 Hz, bridgehead H); ^{1}H NMR ($\mathrm{CD_3CN}$) δ 7.13 (s, $\mathrm{C_6H_4}$), 4.23 (ddd, *J* = 9.5, 7.5, 4.7 Hz, $\mathrm{OC}\mathit{H}\mathrm{H}$), 3.97 (dt, *J* = 8.6, 7.5 Hz, $\mathrm{OCH}\mathit{H}$) 3.48 (d, *J* = 7.5 Hz, CHOMe), 3.40 (s, $\mathrm{OCH_3}$), 2.32 (dddd, *J* = 12.1, 9.5, 7.6, 6.4 Hz, $\mathrm{OCH_2C}\mathit{H}\mathrm{H}$), 2.29 (s, $\mathrm{ArCH_3}$), 2.16 (dddd, *J* = 12.1, 8.6, 4.7, 1.0 Hz, $\mathrm{OCH_2CH}\mathit{H}$), 1.96 (ddd, *J* = 7.5, 6.5, 1.0 Hz, bridgehead H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.76 MHz, $\mathrm{CD_3CN}$) δ 138.6, 136.9 (ipso, para); 129.7, 125.4 (ortho, meta), 73.5, 69.9 ($\mathrm{OCH_2}$, CHOMe), 72.6 (bridgehead quaternary C), 48.9 ($\mathrm{OCH_3}$), 31.1, 27.0 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$, bridgehead CH), 21.0 ($\mathrm{ArCH_3}$); HRMS calcd for $\mathrm{C_{13}H_{16}O_2}$ 204.1150, found 204.1138.

$[p\text{-}\mathrm{CH_3\text{-}C_6H_4CO_2CH_2CH_2CH_2P(C_6H_5)_3}]^+\mathrm{Br}^-$ (13). A solution of sodium 4-methylbenzoate (6.44 g, 40 mmol) and $[\mathrm{BrCH_2CH_2CH_2P(C_6H_4)_3}]^+\mathrm{Br}^-$ (8.46 g, 18 mmol) in 60 mL of acetone–water (5:1 by volume) was refluxed for 24 h. Acetone was evaporated under vacuum, and 50 mL of water and 50 mL of $\mathrm{CHCl_3}$ were added. The $\mathrm{CHCl_3}$ layer was dried ($\mathrm{MgSO_4}$), and solvent was evaporated under vacuum. The resulting viscous oil was triturated with ethyl acetate to yield **13** (7.49 g, 88%) as a chalky white powder: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.7–7.9 (m, 11 H, ArH), 7.55–7.7 (m, 6 H, ArH), 7.19 (d, *J* = 8.3 Hz, 2 H, $\mathrm{C_6H_4}$), 4.61 (t, *J* = 6.3 Hz, $\mathrm{OCH_2}$), 4.0–4.25 (m, $\mathrm{Ph_3PCH_2}$), 2.37 (s, $\mathrm{ArCH_3}$), 2.05–2.20 (m, $\mathrm{Ph_3PCH_2C}\mathit{H}_2$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50.1 MHz, $\mathrm{CDCl_3}$) δ 166.2 (C=O), 143.8, 127.2, 119.0, 117.3 ($\mathrm{C_6H_4}$), 135.5 ($\mathrm{Ph_3P}$ para), 133.7 (d, $J_{^{31}\mathrm{P-C}}$ = 12.6 Hz, $\mathrm{C_6H_5}$), 129.5 (d, $J_{^{31}\mathrm{P-C}}$ = 28.6 Hz, $\mathrm{Ph_3P}$ ipso), 63.5 (d, $J_{^{31}\mathrm{P-C}}$ = 15.8 Hz, $\mathrm{OCH_2}$), 22.0 (d, $J_{^{31}\mathrm{P-C}}$ = 50.8 Hz, $\mathrm{Ph_3PCH_2CH_2}$), 19.9 (d, $J_{^{31}\mathrm{P-C}}$ = 54.0 Hz, $\mathrm{Ph_3PCH_2CH_2}$); IR ($\mathrm{CHCl_3}$) ν(CO) 1705 $\mathrm{cm^{-1}}$. Anal. Calcd for $\mathrm{C_{29}H_{28}BrO_2P}$: C, 67.06; H, 5.43. Found: C, 66.97; H, 5.31.

5-(4-Methylphenyl)-2,3-dihydrofuran (10). A slurry of phosphonium salt **13** (2.95 g, 5.6 mmol) in 125 mL of toluene was dried by distillation of 30 mL of toluene. Sodium *tert*-amylate (0.70 g, 90%, 5.6 mmol) in 30 mL of toluene was added dropwise to the refluxing slurry. The reaction mixture was filtered at room temperature, and solvent was removed on a rotary evaporator. The residue was extracted with hexane, and the concentrated hexane extract was chromatographed (98:2 hexane/$\mathrm{NEt_3}$) to give **10** (0.52 g, 58%) as a colorless waxy solid, mp 29–34 °C, which decomposed even on storage in a freezer: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.65 (d, *J* = 8.0 Hz, 2 H, $\mathrm{C_6H_4}$), 6.96 (d, *J* = 8.0 Hz, 2 H, $\mathrm{C_6H_4}$), 5.15 (t, *J* = 2.8 Hz, C=CH), 4.16 (t, *J* = 9.4 Hz, $\mathrm{OCH_2}$), 2.40 (td, *J* = 9.4, 2.8 Hz, $\mathrm{OCH_2C}\mathit{H}_2$), 2.05 (s, $\mathrm{ArCH_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (50.1 MHz, $\mathrm{CD_3CN}$) δ 156.8, 139.2, 129.4 ($\mathrm{C{=}}\mathit{C}\mathrm{O}$, ipso, para), 129.9, 126.9 (ortho, meta), 95.5 ($\mathit{C}\mathrm{{=}CO}$), 70.6 ($\mathrm{OCH_2}$), 31.3 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 21.4 ($\mathrm{ArCH_3}$); HRMS calcd for $\mathrm{C_{11}H_{12}O}$ 160.0888, found 160.0889.

***cis*-$\mathrm{(Et_3P)(CO)_4W{=}C(OCH_2CH_2CH{=}CHOCH_3)C_6H_4\text{-}}p\mathrm{\text{-}CH_3}$ (18).** Photolysis of *trans*-**5** (60 mg, 0.13 mmol) in 8 mL of $\mathrm{CH_2Cl_2}$ for 24 h at −78 °C produced a solution of *trans*-**6**. Triethylphosphine (30 μL, 0.20 mmol) was added, and the solution was warmed to room temperature. Solvent was evaporated under vacuum. ^{1}H NMR showed an 80:20 mixture of **18**/*trans*-**5**. Preparative TLC (95:5:2 hexane/ether/$\mathrm{NEt_3}$) gave **18** (50 mg, 71%) as a deep red oil: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.51 (d, *J* = 8.2 Hz, 2 H, $\mathrm{C_6H_4}$), 6.91 (d, *J* = 8.3 Hz, 2 H, $\mathrm{C_6H_4}$), 6.31 (d, *J* = 12.7 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{OCH_3}$), 4.65 (dt, *J* = 12.7, 7.3 Hz, $\mathrm{C}\mathit{H}\mathrm{{=}CHOCH_3}$), 4.55 (t, *J* = 6.4 Hz, $\mathrm{OCH_2}$), 3.13 (s, $\mathrm{OCH_3}$), 2.27 (q, *J* = 6.5 Hz, $\mathrm{OCH_2C}\mathit{H}_2$), 1.98 (s, $\mathrm{ArCH_3}$), 1.37 (dt, $J_{^{31}\mathrm{P}-^1\mathrm{H}}$ = 7.6 Hz, $J_{^1\mathrm{H}-^1\mathrm{H}}$ = 7.6 Hz, $\mathrm{PCH_2}$), 0.71 (dt, $J_{^{31}\mathrm{P}-^1\mathrm{H}}$ = 15.7 Hz, $J_{^1\mathrm{H}-^1\mathrm{H}}$ = 7.6 Hz, $\mathrm{PCH_2C}\mathit{H}_3$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50.1 MHz, $\mathrm{CD_3CN}$, 0.07 M $\mathrm{Cr(acac)_3}$, 0 °C) δ 319.7 (W=C), 212.8 (1 CO), 207.2 (d, $J_{^{31}\mathrm{P}-^{13}\mathrm{C}}$ = 17.7 Hz, 1 CO), 203.7 (2 CO), 155.1, 141.3 (ipso, para), 155.0 ($\mathrm{CH{=}}\mathit{C}\mathrm{HOCH_3}$), 128.8, 126.6 (ortho, meta), 98.2 ($\mathit{C}\mathrm{H{=}CHOCH_3}$), 83.0 ($\mathrm{OCH_2}$), 56.1 ($\mathrm{OCH_3}$), 28.5 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 21.3 (d, $J_{^{31}\mathrm{P}-^{13}\mathrm{C}}$ = 21.0 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 8.0 ($\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$). A $^{13}\mathrm{C}\{^1\mathrm{H}\}$ INEPT experiment confirmed the assignment of the resonances at δ 150.0, 128.8, 129.9, and 98.2 as methine carbons. IR (hexane): 2016 (m), 1928 (s), 1921 (s), 1894 (s) $\mathrm{cm^{-1}}$.

Kinetics. All kinetic data were obtained by ^{1}H NMR spectroscopy. Degassed samples were sealed under vacuum and frozen at −78 °C until placed in the preequilibrated probe of a 270-MHz spectrometer. Spectra were recorded periodically by using a 30-s delay between scans to minimize the effects of different relaxation times. Concentrations were determined by integration vs. 1,4-bis(trimethylsilyl)benzene (δ 0.24 (s)), triphenylmethane (δ 5.41 (s)), or tetramethylsilane as internal standards. The following signals were monitored: for *trans*-**5**, $\mathrm{CH{=}C}\mathit{H}\mathrm{OCH_3}$ (δ 6.27 in $\mathrm{C_6D_6}$); for *endo*-**8**, $\mathrm{C}\mathit{H}\mathrm{OCH_3}$ (δ 3.33 in $\mathrm{C_6D_6}$) or $\mathrm{OC}\mathit{H}\mathrm{H}$ (δ 4.23 in $\mathrm{CD_3CN}$); for **10**, vinyl H (δ 5.15 (t) in $\mathrm{C_6D_6}$) or $\mathrm{OCH_2}$ (δ 4.46, t, in $\mathrm{CD_2Cl_2}$); for *trans*-**6**, $\mathrm{CH{=}C}\mathit{H}\mathrm{OCH_3}$ (δ 6.47 in $\mathrm{CD_2Cl_2}$), and for *cis*-**6**, $\mathrm{CH{=}C}\mathit{H}\mathrm{OCH_3}$ (δ 6.05 in $\mathrm{C_6D_6}$). The preparation of one sample is described below. Others were prepared in a similar manner.

Decomposition of *trans*-5 with 0.08 M $\mathrm{PPh_3}$. A 5-mm NMR tube was charged with *trans*-**5** (15 mg, 0.028 mmol), $\mathrm{PPh_3}$ (8.8 mg, 0.034 mmol), and 1,4-bis(trimethylsilyl)benzene (<1 mg, not weighed). $\mathrm{C_6D_6}$ (0.38 mL) was distilled into the tube under vacuum. The tube was cooled to liquid-nitrogen temperature, sealed, and stored at −78 °C until used. The sample was quickly warmed to room temperature to dissolve *trans*-**5** (0.07 M) and $\mathrm{PPh_3}$ (0.08 M) and was placed in the preheated (41.7 °C) probe of the spectrometer. Spectra were recorded every 30 min beginning 15 min after the sample had been placed in the probe. A plot of $-\ln (c/c_0)$ vs. time for *trans*-**5** gave an observed first-order rate constant of $(8.80 \pm 0.36) \times 10^{-5}\ \mathrm{s^{-1}}$ (corr = 0.997) for the first half-life.

Upon completion of the reaction, the tube was opened, $\mathrm{C_6D_6}$ was evaporated under high vacuum, and the residue was dissolved in $\mathrm{CHCl_3}$. An IR spectrum showed bands for $\mathrm{(CO)_5W(PPh_3)}$ at 2070 (m), 1985 (w), and 1940 (vs) $\mathrm{cm^{-1}}$. Analytical TLC ($\mathrm{SiO_2}$, hexane) vs. an independently prepared sample of $\mathrm{(CO)_5W(PPh_3)}$ showed a spot at R_f 0.29 for both samples.

Photolysis of *trans*-5: Generation of $\mathrm{(CO)_4W{=}C(OCH_2CH_2CH{=}CHOCH_3)C_6H_4\text{-}}p\mathrm{\text{-}CH_3}$ (*trans*-6). $\mathrm{CD_2Cl_2}$ (0.3 mL) was distilled under vacuum into a 5-mm NMR tube containing *trans*-**5** (10 mg, 0.019 mmol, 0.04 M). The tube was cooled to liquid-nitrogen temperature and sealed. Photolysis for 27 h at −78 °C gave a 91:9 mixture of *trans*-**6** and *trans*-**5** as determined by ^{1}H NMR spectroscopy.

For *trans*-**6**: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −35 °C) δ 7.74 (d, *J* = 8.3 Hz, 2 H, $\mathrm{C_6H_4}$), 7.21 (d, *J* = 8.3 Hz, 2 H, $\mathrm{C_6H_4}$), 6.47 (d, *J* = 10.7 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{OCH_3}$), 5.14 (ddd, *J* = 11.7, 5.3, 2.1 Hz, $\mathrm{OC}\mathit{H}\mathrm{H}$), 4.86 (m, 2 H.

$C\mathit{H}{=}CHOCH_3$, $OCH\mathit{H}$), 3.58 (s, OCH_3), 3.05 (dt, *J* = 15.8, 5.4 Hz, $OCH_2C\mathit{H}H$), 2.36 (s, $ArCH_3$), 1.06 (dtd, *J* = 15.8, 10.1, 2.2 Hz, $OCH_2CH\mathit{H}$).

A sample of *trans*-**6** for ^{13}C NMR analysis was prepared by photolysis of a CD_2Cl_2 (1 mL) solution of *trans*-**5** (40 mg, 0.076 mmol) in a 10-mm septum-capped NMR tube for 42 h at −78 °C under N_2 purge. $Cr(acac)_3$ (32 mg, 0.07 M) was then added, and the tube was sealed under high vacuum: $^{13}C\{^1H\}$ NMR (50.1 MHz, −45 °C) δ 311.2 (W=C), 210.9, 210.6, 207.9, 203.1 (CO), 148.7, 143.1 (ipso, para), 128.3 (ortho, meta, $CH{=}\mathit{C}HOCH_3$), 80.4 (OCH_2), 61.0 ($\mathit{C}H{=}CHOCH_3$), 60.2 (OCH_3), 28.6 ($OCH_2\mathit{C}H_2$), 21.2 ($ArCH_3$). A $^{13}C\{^1H\}$ INEPT experiment (90.56 MHz, −35 °C) confirmed the assignment of resonances at δ 128.2, 128.0 (unresolved in 50.1 MHz spectrum above), and 61.0 as methine carbons. A two-dimensional ^{13}C–^1H correlation spectrum (decoupled in F1 and F2)[22] was obtained on a Bruker AM-360 spectrometer at −35 °C. The spectrum showed the ^{13}C signal at δ 128.2 consisted of two resonances: an aromatic CH coupled to the proton at δ 7.21 and the vinyl ether carbon $CH{=}\mathit{C}HOCH_3$ coupled to the vinyl H at δ 6.47 in the ^1H NMR spectrum.

An IR spectrum of a 0.011 M solution of *trans*-**6** in CH_2Cl_2 (generated by photolysis of *trans*-**5** at −78 °C for 20 h) was obtained at −78 °C: 2015 (s), 1929 (s), 1909 (s), 1884 (s) cm^{-1}. An IR sample in hexane was prepared by evaporation of CH_2Cl_2 from a sample of *trans*-**6** (prepared by photolysis of *trans*-**5** at −78 °C for 31 h) at −15 °C under high vacuum and addition of hexane at −78 °C. The sample was warmed to −15 °C and an IR spectrum was obtained at −78 °C: 2026 (m), 1945 (m), 1918 (s) cm^{-1}.

Photolysis of *cis*-5: Generation of $(CO)_4W{=}C(OCH_2CH_2CH{=}CHOCH_3)C_6H_4$-*p*-$CH_3$ (*cis*-6). CD_2Cl_2 (0.3 mL) was distilled under high vacuum into a 5-mm NMR tube containing *cis*-**5** (12 mg, 0.023 mmol). Photolysis at −78 °C for 21 h generated a (9:1) mixture of *cis*-**6** and *cis*-**5** as determined by ^1H NMR.

For *cis*-**6**: ^1H NMR (CD_2Cl_2, −35 °C) δ 7.94 (d, *J* = 8.3 Hz, 2 H, C_6H_4), 7.27 (d, *J* = 8.1 Hz, C_6H_4), 6.92 (d, *J* = 5.2 Hz, $CH{=}C\mathit{H}OCH_3$), 5.46 (ddd, *J* = 10.8, 4.6, 2.8 Hz, $OC\mathit{H}H$), 4.31 (td, *J* = 10.9, 2.8 Hz, $OCH\mathit{H}$), 3.83 (s, OCH_3), 2.90 (dt, *J* = 8.3, 5.2 Hz, $C\mathit{H}{=}CHOCH_3$), 2.66 (ddt, *J* = 13.6, 5.3, 2.9 Hz, $OCH_2C\mathit{H}H$), 2.36 (s, $ArCH_3$), 2.20 (tdd, *J* = 13.0, 8.6, 4.7 Hz, $OCH_2CH\mathit{H}$); ^{13}C NMR (125.76 MHz, −80 °C) δ 318.2 (W=C), 214.0, 209.7, 201.0, 199.6, 197.4 (CO, cis CO of remaining *cis*-**5**), 148.3, 144.1 (ipso, para), 129.3, 128.7 (ortho, meta), 128.5 ($CH{=}\mathit{C}HOCH_3$), 82.6 (OCH_2), 61.0 ($\mathit{C}H{=}CHOCH_3$), 56.7 (OCH_3), 23.7 ($OCH_2\mathit{C}H_2$), 21.5); IR (hexane) 2024 (m), 1931 (m), 1916 (s) cm^{-1}.

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Parallel Behavior in Kinetic and NMR Effects: Secondary Deuterium Isotope Effects on the Alkaline Hydrolysis of Esters

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Abstract: β-Deuterium secondary kinetic isotope effects (β-D KIEs) on the alkaline hydrolysis of the *p*-nitrophenyl esters of acetic, propanoic, butanoic, and pentanoic acids in pH 10.70, 0.20 M carbonate buffer at 25 °C tend to increase with increasing chain length of the esters up to the pentanoate. The β-D KIEs are respectively 0.975 ± 0.004, 0.960 ± 0.002, 0.940 ± 0.001, and 0.948 ± 0.004. The activation energies of the esterolyses of the isotopically light esters follow a similar pattern, as do the ^{13}C NMR nuclear shieldings in $CDCl_3$ of the isotopically light parent carboxylic acids (20.9, 27.4, 35.9, and 33.8 (ppm)) and ^{13}C NMR one-bond isotope shifts produced by disubstitution of deuterium for hydrogen at the α-carbons of the acids (0.45, 0.55, 0.60, and 0.59 (ppm)). Correlation of nuclear shieldings and isotope shifts is known from previous work. The possibility is considered that all of the kinetics-based and NMR relationships are linked through the operation of a common ground-state feature of the ester and acid alkyl chains.

The chemical literature contains a growing number of theoretical and experimental studies of NMR isotope shifts resulting from the substitution of deuterium for hydrogen on carbon.[1] These studies complement a substantial literature concerning secondary kinetic isotope effects on organic reactions.[2] The possibility of a correlation between kinetic and NMR isotope effects has been mentioned.[1a] To the best of our knowledge, however, no experimental study of this kind has been done. Thus, having determined the β-deuterium secondary kinetic isotope effects (β-D KIEs) on the alkaline hydrolysis of the *p*-nitrophenyl esters (NPEs) of the C_2–C_5 normal alkanoic acids, we were interested in comparing them with NMR isotope shifts at α-carbon of the esters. Technical difficulties prevented determination of the shifts for the esters, but we were able to measure the nuclear shieldings, isotope shifts, and C–D coupling constants at the α-carbons of the parent acids. Here we report these kinetic and NMR investigations.

Results

Second-order rate constants for the alkaline hydrolysis of NPEs of the homologous C_2–C_5 normal alkanoic acids and their α-deuteriated versions are given in Table I, as are the β-D KIEs. The value k_{3H}/k_{3D} of 0.975 ± 0.004 found in this study for the acetate is identical within experimental error to the 0.970 ± 0.009 reported by Kovach and co-workers.[3,4]

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(4) The apparent second-order rate constants of Table I were obtained by dividing the pseudo-first-order rate constants by a_{OH}, a procedure that ignores contributions of the rate of hydrolysis by nucleophilic buffer species. The similarity of k_{3H}/k_{3D} for *p*-nitrophenyl acetate found by us (0.20 M bicarbonate/carbonate buffer) and by Kovach and co-workers[3] (unbuffered solution, ionic strength 1.0 M (KCl)) indicates that contributions to catalysis by buffer nucleophiles do not have a measureable effect on the β-D KIEs.

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