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Generation and Spectroscopic Observation of a Tungsten–Carbene–Alkene Intermediate in Cyclopropane Formation

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The alkoxide-catalyzed reaction of but-3-en-1-ol with $(CO)_5W{=}C(OCH_3)C_6H_4$-*p*-CH_3 gives the (butenyloxy)carbene complex $(CO_5)W{=}C(OCH_2CH_2CH{=}CH_2)C_6H_4$-*p*-$CH_3$, **1**, which possesses a carbene ligand and an uncomplexed alkene. Upon heating at 38 °C in benzene-d_6, **1** is converted to the cyclopropane 1-(4-methylphenyl)-2-oxabicyclo[3.1.0]hexane, **10**. During the conversion of **1** to **10**, an intermediate tetracarbonyltungsten–carbene–alkene complex **15** was detected by ^1H NMR and IR spectroscopy. Intermediate **15** reacted with CO to regenerate **1** and with PEt_3 to give *cis*-$(CO)_4(PEt_3)W{=}C(OCH_2CH_2CH{=}CH_2)C_6H_4$-*p*-$CH_3$, **18**. The kinetics of the conversion of **1** to **10** are very complex. After an initial induction period, an accelerating autocatalytic decomposition of **1** occurs. A detailed mechanism for the autocatalysis is proposed in which the key steps are decomposition of tungsten–carbene–alkene intermediate **15** which reacts successively with two molecules of starting material **1** to generate $W(CO)_6$ and 2 equiv of tungsten–carbene–alkene intermediate **15**.

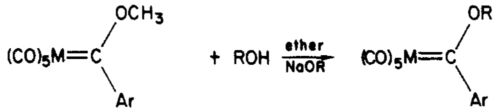
Introduction

Metal–carbene–alkene complexes have been proposed as important intermediates in the olefin metathesis reaction,[1] in the cyclopropanation of alkenes,[2] and in Ziegler–Natta polymerization of alkenes.[3] Examples of chelated[4-9] and nonchelated[10,11] metal–carbene–alkene complexes are known, but most of these complexes do not take part in olefin metathesis or cyclopropanation reactions.

Several years ago, we made a preliminary report of the observation of an unstable tungsten–carbene–alkene complex and its conversion to a cyclopropane.[12] Here we present full details of this interesting transformation and its complex kinetics.

Results

Synthesis of Metal Carbene Complexes. The syntheses of complexes **1**–**5** containing a carbene ligand and an uncomplexed alkene were accomplished in 50–75% yields by base-catalyzed alkoxy-exchange reactions of arylmethoxycarbene complexes and unsaturated alcohols. The reactions occur by nucleophilic attack of alkoxide at the electron-deficient carbene carbon atom followed by loss of methoxide. Nucleophilic attack at the carbene carbon is a characteristic reaction of metal carbene complexes. Fischer and Schubert first noted alkoxide exchange in the reaction of $(CO)_5Cr{=}C(OCH_3)CH_3$ with CD_3ONa and CD_3OD which produced fully deuterated $(CO)_5Cr{=}C(OCD_3)CD_3$.[13]



6, M = W, Ar = C_6H_4-*p*-CH_3
7, M = W, Ar = C_6H_5
8, M = Cr, Ar = C_6H_4-*p*-CH_3

1, M = W, Ar = C_6H_4-*p*-CH_3, OR = $OCH_2CH_2CH{=}CH_2$
2, M = W, Ar = C_6H_5, OR = $OCH_2CH_2CH{=}CH_2$
3, M = W, Ar = C_6H_4-*p*-CH_3, OR = $OCH_2CH{=}CH_2$
4, M = W, Ar = C_6H_4-*p*-CH_3, OR = $OCH_2CH_2CH_2CH{=}CH_2$
5, M = Cr, Ar = C_6H_4-*p*-CH_3, OR = $OCH_2CH_2CH{=}CH_2$

For example, the reaction of $(CO)_5W{=}C(OCH_3)C_6H_4$-*p*-CH_3, **6**, with but-3-en-1-ol and a catalytic amount of the sodium 3-butenyloxide in ether at 0 °C gave the (butenyloxy)carbene complex **1** in 68% yield. Since the presence of water resulted in incomplete product formation, careful exclusion of water was required. The alcohol exchange reaction is apparently reversible and complete conversion was achieved only when a 20–30-fold excess of but-3-en-1-ol was used and when Linde 4A molecular sieves were employed to selectively bind methanol produced in

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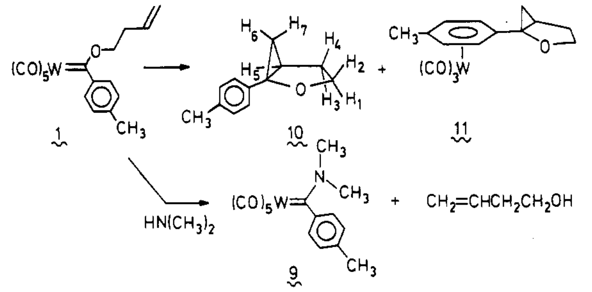
the reaction. Since these (alkenyloxy)carbene complexes were all somewhat thermally sensitive, they were successfully synthesized only at 0 °C. All of the carbene complexes could be stored indefinitely in the solid state at −20 °C without decomposition.

Carbene complexes 1, 3, and 4 were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and by their reactions with dimethylamine which led to replacement of the alkoxy group and formation of $(CO)_5W{=}C[N(CH_3)_2]C_6H_4\text{-}p\text{-}CH_3$, 9. The IR spectra of 1 and 3–5 were all consistent with their formulation as pentacarbonylmetal carbene complexes possessing approximate C_{4v} symmetry.[14] For example, the IR spectrum of 1 has ν_{CO} at 2068 (m, A_1^2), 1983 (w, B_1), 1954 (s, A_1^1), and 1943 (vs, E) cm^{-1}. In particular, the sharp medium intensity A_1^2 band in the 2050–2070 cm^{-1} range is characteristic of $(CO)_5ML$ complexes. In the ^{1}H NMR spectra of (alkenyloxy)carbene complexes 1–5, the resonances due to the three vinyl hydrogens appear between δ 5.6 and 4.9—in the same region as the starting alcohols; this provides excellent evidence that the carbon–carbon double bonds are not complexed. In the ^{13}C NMR spectra of tungsten carbene complexes 1, 3, and 4, the resonance due to the carbene carbon appears characteristically downfield between δ 319 and 317.8 and the resonances due to the trans and cis carbonyl ligands appear in a 1:4 ratio at δ 205–204 and 199–197. The ^{13}C resonances due to the two vinyl carbons appear at δ 137–132 ($CH{=}CH_2$) and 120–115 ($CH{=}CH_2$); these resonances are in the same region as those for the starting alcohols and provide further evidence that the alkene is not complexed.

Thermolysis of (Butenyloxy)carbene Complexes 1, 2, and 5. 1 rapidly decomposed at 40 °C in benzene-d_6 to produce the cyclopropane 1-(4-methylphenyl)-2-oxabicyclo[3.1.0]hexane, 10, as the sole detectable organic product in 85–95% NMR yield. 10 was isolated by TLC and characterized by ^{1}H and ^{13}C NMR spectroscopy. 10 is the formal product of cycloaddition of the carbene carbon to the vinyl group of the (butenyloxy)carbene ligand.

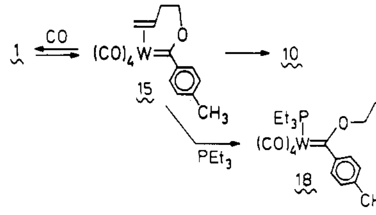


The decomposition of 1 in benzene-d_6 also resulted in the formation of several organometallic products. The principal product was $W(CO)_6$ (42% by IR). In addition, the ^{1}H NMR spectrum of the reaction mixture had minor resonances attributed to tricarbonyl[η^6-1-(4-methylphenyl)-2-oxabicyclo[3.1.0]hexane]tungsten(0), 11 (2–5% by ^{1}H NMR). The upfield portion of the ^{1}H NMR spectrum of 11 between δ 4 and 0 is very similar to that of 10, while the aromatic resonances of 11 are shifted upfield to δ 4.45 (H_3 and H_4), 4.64 (H_5), and 5.38 (H_6). The nonequivalence of these four protons, as well as their extra shielding relative to those of a free arene, is consistent with π-coordination of the arene ring to a tungsten tricarbonyl group.[15] When undeuterated benzene was used as the reaction solvent additional ^{1}H NMR resonances assigned to tricarbonyl (η^6-benzene)tungsten(0), 12 (1–2% by NMR),[9] were also seen. $W(CO)_6$ and 10 are stable under the conditions of the thermolysis, indicating that 11 and 12 are primary products of the decomposition of 1.

The related phenyl-substituted tungsten carbene complex 2 decomposed at 20 °C to give an analogous cyclopropane whose ^{1}H NMR spectrum was essentially identical with that of 10 between δ 6 and 0.

Thermal decomposition of the [(3-butenyloxy)p-tolylcarbene]chromium complex, 5, at 20–25 °C produced the same cyclopropane 10 as obtained from tungsten complex 1. In addition, $Cr(CO)_6$, tricarbonyl[(η^6-1-(4-methylphenyl)-2-oxabicyclo[3.1.0]hexane]chromium(0), 13, and tricarbonyl(η^6-benzene)chromium(0), 14[16] were also obtained. Unlike the tungsten system, the tricarbonylchromium arene complexes are formed in substantial amounts (10:13:14 = 68:27:5). The aromatic resonances of 13 are similar to those observed for 11: δ 4.45 (H_3 and H_4), 4.61 (H_5), and 5.32 (H_6). The IR spectrum of 13 shows two absorptions at 1978 and 1907 cm^{-1}, indicating a tricarbonyl complex with a normal "piano-stool" structure.[17]

Tungsten–Carbene–Alkene Complexes. When the thermolysis of 1 in benzene-d_6 was monitored continuously by ^{1}H NMR, two intermediates were observed in addition to the products already described. Both of these intermediates decomposed under the reaction conditions to produce cyclopropane 10. The maximum amount of the intermediate 15 to the minor intermediate 16 varied from about 2:1 to 4:1 during the course of the reaction. The spectral properties and the chemical behavior of the two intermediates indicated that both possess a carbene ligand and a coordinated alkene ligand.



The major intermediate 15 is formulated as a chelated tungsten–carbene–alkene complex analogous to *cis*-tetracarbonyl[(η^2-(*Z*)-*N*,2,2-trimethyl-3-butenylamino)p-tolylcarbene]tungsten(0), 17, whose structure has been determined by X-ray crystallography.[18] In the ^{1}H NMR spectrum of the major intermediate, the resonances due to the vinyl hydrogens of the complexed alkene appear at δ 3.59 ($CH{=}CH_2$), 3.14 ($CH{=}CHH$), and 2.73 ($CH{=}CHH$) with J_{trans} = 13.7 Hz, J_{cis} = 8.7 Hz, and J_{gem} too small to observe. The upfield shift of 2.0–2.5 ppm of these vinyl resonances relative to their position in the uncomplexed alkene of the precursor carbene complex 1, as well as the absence of any geminal coupling, is consistent with π-coordination of the vinyl group to tungsten. Similar upfield chemical shifts for the terminal vinyl hydrogens of (butenylamino)carbene–alkene complex 17 were observed:[18] δ 3.4 (H_6, J = 9.4 Hz) and 3.15 (H_7, J = 14.1 Hz).

The thermolysis of 1 was also monitored by IR in hexane, and evidence for intermediates was again obtained. After several hours all of the absorptions due to the starting material (with the exception of the band at 2068 cm^{-1} which was substantially reduced in intensity) had been replaced by new bands at 2030 (s), 1982 (vs, $W(CO)_6$),

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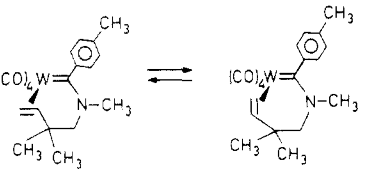
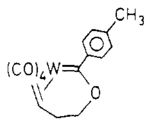
1967 (w), 1947 (s), 1928 (s), 1915 (sh), and 1908 (s) cm^{-1}. Eventually all of these bands, with the exception of the 1982 cm^{-1} band, disappeared as well. The four strong absorptions at 2030, 1947, 1928, and 1908 cm^{-1} are assigned to major intermediate **15** and support its formulation as a cis-disubstituted tetracarbonylmetal complex.[14]

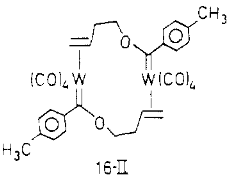
The ^{1}H NMR spectrum of minor intermediate **16** has upfield resonances for the terminal vinyl protons at δ 2.86 (J_{cis} = 8.6 Hz) and 2.78 (J_{trans} = 14.3 Hz). Therefore, minor intermediate **16** must also have both an alkene and a carbene ligand coordinated to tungsten. In a preliminary report, we had proposed that **15** and **16-I** were both mononuclear tungsten–carbene–alkene complexes that differed in the relative orientations of the carbene and the alkene ligands. Two extreme conformations are possible, one in which the carbene and alkene ligands are parallel and one in which they are perpendicular. In support of this conformational hypothesis, the solid-state structure of the chelated (butenylamino)carbene complex **17** consists of two different conformations in the unit cell. In one molecule, the alkene and carbene ligand are in a nearly parallel conformation; in the other molecule, the ligands are in a nearly perpendicular conformation.



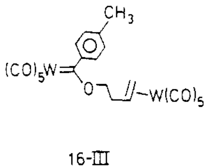
17 17



16-I



16-II



16-III

The ratio of the major intermediate **15** to minor intermediate **16** changed somewhat during the course of the conversion of **1** to cyclopropane **10** and was substantially different immediately after treatment of the mixture of **15** and **16** with CO (see below). This implies that interconversion of **15** and **16** occurs only slowly on the laboratory time scale. This stands in sharp contrast to the rapid interconversion of the parallel and perpendicular conformations of butenylamino carbene complex **17** which was shown to be fast on the NMR time scale at room temperature.[18] Either there are major rate differences for interconversion of conformational isomers of chelated (butenyloxy)- and (butenylamino)carbene complexes or other structures have to be considered for the minor intermediate **16**. Two possible alternative structures for **16** are the dimeric tungsten–carbene–alkene complex **16-II** or the dinuclear complex **16-III** in which W(CO)$_5$ is complexed to the alkene. If the minor intermediate **16** was a dimer then more of this compound should have been formed at higher concentrations. However, the ratio of major intermediate **15** to minor intermediate **16** did not change significantly when the concentration of **1** was raised from 0.06 to 0.36 M.

Further support for the structural assignments of intermediate tungsten–carbene–alkene complexes **15** and **16** was provided by trapping experiments with CO and triethylphosphine. In both cases, the alkene ligand was replaced by the incoming CO or triethylphosphine ligand and an unchelated (butenyloxy)carbene complex was formed.

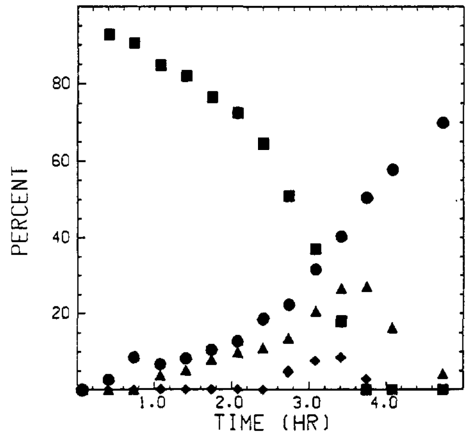


Figure 1. Percent composition of mixture from decomposition of 1 at 25 °C in benzene-d_6: ■, 1: ●, 10: ▲; 15: ◆, 16.

These trapping experiments were facilitated by the fact that **15** and **16**, generated in situ in benzene-d_6 by the thermolysis of **1**, appeared to reach their maximum concentrations at a time when nearly all of the starting carbene complex **1** had decomposed.

15 and **16** generated from the decomposition of **1** at 38 °C (**15**:**16**:**1**:**10** = 29:11:11:49), were treated with 2.7 equiv of triethylphosphine at 5 °C. No reaction was observed at room temperature, but at 38 °C complete decomposition of the carbene–alkene complexes took place in less than 5 min and a new carbene complex, **18**, was formed. The structure of **18** was assigned as *cis*-$(CO)_4(PEt_3)W{=}C(OCH_2CH_2CH{=}CH_2)C_6H_4\text{-}p\text{-}CH_3$ on the basis of its ^{1}H NMR and IR spectra. Heating a solution of **1** and triethylphosphine in benzene-d_6 to 38 °C for 1 h did not result in the formation of any **18**.

No reaction of **15** and **16** with 1 atm of CO at room temperature was seen. However, **15** and **16**, generated from the decomposition of **1** at 21 °C (**15**:**16**:**1**:**10** = 29:11:5:51), did react under 6 atm of CO pressure over 30 min at room temperature to regenerate **1** (**15**:**16**:**1**:**10** = 4:8:25:61). It is obvious from the large decrease in the ratio of **15**:**16** after exposure to CO that **15** and **16** do not rapidly interconvert at room temperature. It should also be noted that the major intermediate **15** is more reactive toward CO than the minor intermediate.

Rate of Decomposition of 1. The decomposition of **1** in benzene-d_6 was followed by ^{1}H NMR and displayed complex, but reproducible, kinetic behavior that can be described as having three stages (Figure 1). During an initial induction period, only slow disappearance of **1** was seen. In the second stage of the reaction, an accelerating autocatalytic decomposition of **1** was observed. During this stage, the concentrations of the intermediate tungsten–carbene–alkene complexes **15** and **16** and of the product cyclopropane **10** increased rapidly. The concentrations of tungsten–carbene–alkene complexes **15** and **16** reached their maximum combined concentrations of about 35% just prior to total disappearance of starting material. During the third and final stage of the reaction, the intermediate tungsten–carbene–alkene complexes decomposed to cyclopropane **10** with approximate first-order kinetics. Interestingly, the rate of appearance of intermediates **15** and **16** during the autocatalytic stage was very similar to the rate of their disappearance during the final stage of the reaction.

The rate of decomposition of **1** is independent of its initial concentration at 21 °C. Virtually identical induction and autocatalytic reaction stages were observed when the starting concentration of **1** was increased from 0.06 to 0.36

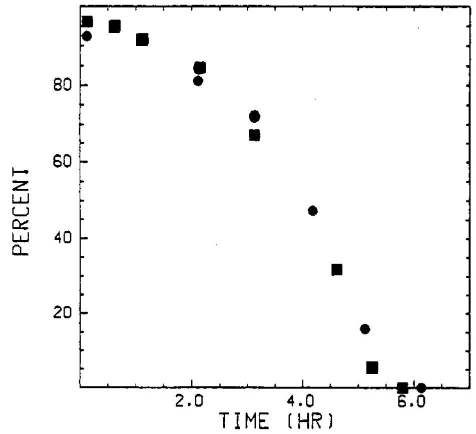


Figure 2. Percent starting material in decomposition of 1 at 21 °C in benzene-d_6: ●, 0.06 M initial concentration of 1: ■, 0.36 M initial concentration of 1.

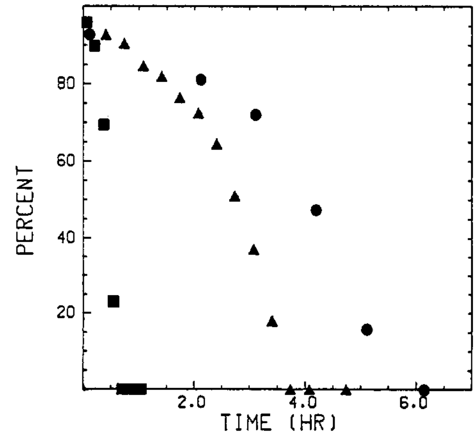
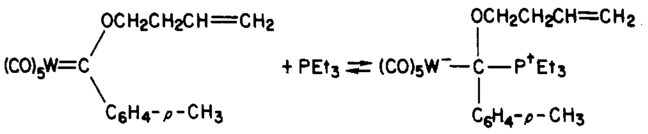


Figure 3. Percent starting material in decomposition of 1 in benzene-d_6 at 40 °C (■), 25 °C (▲), and 21 °C (●).

M (Figure 2). The rate of decomposition of 1 was strongly temperature dependent. The time required for 50% decomposition of 1 in benzene-d_6 varied from 24 min at 40 °C to 2.6 h at 25 °C to 3.5 h at 21 °C. At each temperature an induction period followed by an autocatalytic decomposition was observed. Decomposition of 1 was complete after 45 min at 40 °C, 3.8 h at 25 °C, and 5.8 h at 21 °C (Figure 3).

The rate of decomposition of 1 is strongly solvent dependent. Decomposition in dichloromethane-d_2 is faster than in benzene-d_6. At 38 °C, complete decomposition of 1 occurred in less than 27 min in CD_2Cl_2, but only 50% decomposition of 1 was seen after 38 min in C_6D_6. In the better coordinating solvents acetonitrile-d_3 and carbon disulfide, the decomposition of 1 to cyclopropane **10** was much slower and neither an induction period nor the tungsten–carbene–alkene intermediates **15** and **16** were seen. In CD_3CN at 38 °C, only 50% decomposition of 1 was observed after 1.2 h; in CS_2 at 38 °C, less than 20% decomposition of 1 was seen after 3.7 h.

Triethylphosphine, norbornadiene, and carbon monoxide all inhibited the decomposition of 1 in benzene-d_6. The ^1H NMR spectrum of a 1:1.2 mixture of 1 and triethylphosphine in benzene-d_6 at 38 °C showed only broad absorptions where the resonances of 1 would normally have been observed, due to reversible formation of an adduct of 1 with triethylphosphine.[19] After 40 min, less than 10% conversion of 1 to 10 had occurred.



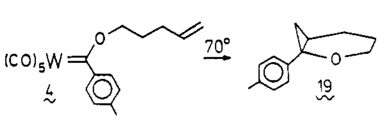
In the presence of 3 equiv of norbornadiene in benzene-d_6, 1 underwent only 50% decomposition after 20 h at 22–26 °C. Cyclopropane **10** (44% after 87 hours) was the major product, but a complex mixture was observed by NMR. The major organometallic products were $W(CO)_6$ and (η^4-norbornadiene)$W(CO)_4$[20] (40% after 87 h). No tungsten–carbene–alkene complexes were observed at any point during the reaction.

The extent of CO inhibition of the decomposition of 1 was pressure dependent. Thermolysis of 1 in benzene-d_6 at 23 °C under 0.7 atm of CO required 5.5 h for 50% decomposition. Under these conditions, the tungsten–carbene–alkene intermediates **15** and **16** were still detected in addition to cyclopropane **10**. A similar thermolysis at 21 °C under 6.7 atm of CO required over 14 h for 50% decomposition of 1. No carbene–alkene complexes were observed in this reaction, and the decomposition of 1 did not appear to be autocatalytic. CO inhibition was also effective at higher temperatures. For example, only 30% decomposition of 1 occurred after 90 min at 50 °C under 5.3 atm of CO.

Reaction of 1 with ^{13}CO. To test for possible reversible loss of CO, 1 was maintained at 24 °C in benzene-d_6 for 5 h under 5.6 atm of 90% enriched ^{13}CO. Under these conditions, 20% of 1 was converted to cyclopropane **10**. The remaining 1 was treated with dimethylamine and was converted to (dimethylamino)carbene complex **9**, which was found to contain 0.13 ^{13}CO/W by ^{13}C NMR analysis. The $W(CO)_6$ formed from decomposition of 1 was shown by mass spectrometry to contain only 0.58 ^{13}CO/W with the labeling pattern: 61.4% l_0, 26.4% l_1, 6.8% l_2, 3.8% l_3, 1.6% l_4.

Somewhat more ^{13}CO incorporation was observed in a second experiment in which 1 was maintained at 24 °C in benzene-d_6 for 10 h under 8.2 atm of 90% enriched ^{13}CO. Under these conditions, 29% 1 was converted to cyclopropane **10**. The remaining 1 was converted to **9** which was shown by ^{13}C NMR to contain 0.23 ^{13}CO/W in the cis position. Mass spectral analysis of $W(CO)_6$ formed from the decomposition of 1 had 0.70 ^{13}CO/W with the labeling pattern: 52.2% l_0, 35.2% l_1, 5.9% l_2, 4.0% l_3, 2.1% l_4, 0.6% l_5.

Thermolysis of (Pentenyloxy)carbene Complex 4. The (pentenyloxy)carbene complex 4 was substantially more thermally stable than the (butenyloxy)carbene complex 1 and decomposed slowly at 70 °C in benzene-d_6. The cyclopropane, 1-(4-methylphenyl)-2-oxabicyclo[4.1.0]heptane, **19**, was formed in 85 ± 5% NMR yield and was isolated in 53% yield by preparative TLC. When the thermolysis of 4 at 70 °C was monitored by ^1H NMR, an induction period of several hours followed by a more rapid autocatalytic decomposition of 4 was observed. However, no spectral evidence for a tungsten–carbene–alkene complex was obtained.



Thermolysis of (Allyloxy)carbene Complex 3. The thermal decomposition of the (allyloxy)carbene complex

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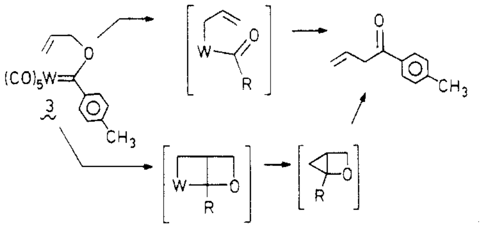
[19] Fischer, H.; Fischer, E. O.; Kreiter, C. G.; Werner, H. *Chem. Ber.* **1974**, *107*, 2459–2467.

[20] King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837–1846.

3 in benzene-d_6 at 50 °C led to a complex mixture of products. The major product was identified as *p*-tolyl allyl ketone by comparison of its ^{1}H NMR spectrum with that of an independently synthesized sample.[21]



One possible route to *p*-tolyl allyl ketone involves migration of the allyl group to tungsten in a Claisen-type rearrangement and then reductive coupling of the allyl and aroyl groups. Alternatively, a strained [2.1.0]oxabicyclopentane might be formed and then rearrange to the ketone.

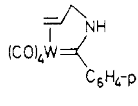
Discussion

Cyclopropane Formation. Metal–carbene–alkene complexes and metallacyclobutane complexes have been invoked as intermediates in the metal-catalyzed olefin metathesis[1] and cyclopropanation reactions.[2] These mechanistic hypotheses were based on experiments that did not involve the direct observation of either of these postulated intermediates. There is now a growing body of evidence based on the actual chemistry of these species that supports the earlier mechanistic postulates. In the tungsten (butenyloxy)carbene complex system reported here, we found that the decomposition of the tungsten–carbene–alkene complexes, generated from the (butenyloxy)carbene complex **1**, led to the formation of cyclopropane **10**. We also observed that changes in the reaction conditions that inhibited the formation of the carbene–alkene complexes from **1** also inhibited the formation of **10**. Taken together, these results suggest that the (butenyloxy)carbene complex **1** is converted into the cyclopropane product **10** via the intermediate tungsten–carbene–alkene complex.

We have not been able to observe metallacyclobutanes as intermediates in the formation of **10**. Neither did we detect any products characteristic of an alkene metathesis reaction pathway. An intramolecular metathesis reaction starting from complex **1** would have required the formation of a very unstable (CO)$_x$W=CH$_2$ or (CO)$_x$W=CHR unit.

Tungsten–Carbene–Alkene Complexes. The tungsten–carbene–alkene complexes **15** and **16** observed as intermediates in the decomposition of **1** were characterized by both spectroscopic and chemical means. The observation of ^{1}H NMR signals characteristic of a metal-coordinated alkene group provided the basis of the structural assignment of **15** and **16** as carbene–alkene complexes. IR measurements indicated that the major intermediate **15** corresponded to a cis-disubstituted tetracarbonyl complex. Further support for this structural assignment was obtained by trapping the intermediates with triethylphosphine which provided the cis phosphine–carbene complex **18**.

Subsequent to our initial description of the thermal chemistry of (butenyloxy)carbene complex **1**: reports of other isolated (CO)$_4$W(carbene)(alkene) complexes, including **17** and **22–27**, have appeared.[9,18,22] Most of these complexes have been characterized in the solid state by X-ray crystallography and serve as valuable models for the possible structures of our metastable carbene–alkene complexes **15** and **16**. In addition, thermolysis of **17** and **26** produced cyclopropanes.[9a,18]



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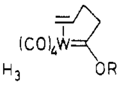

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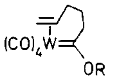

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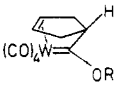

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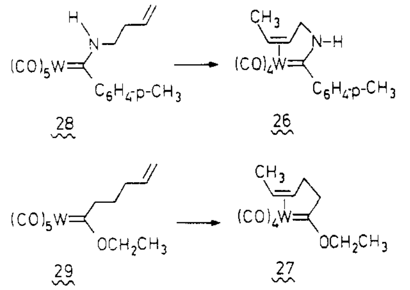
Earlier, in an attempt to prepare a (butenylamino)carbene complex from **28**, we observed double-bond migration and formation of the substituted (allylamino)carbene complex **23**.[18] Apparently, this smaller ring chelate system is more stable. Rudler also observed double-bond migration in the preparation of **25** from **29**.[9c,d] In contrast, we have seen no evidence for double-bond migration in the decomposition of either (butenyloxy)carbene complex **1** or (pentenyloxy)carbene complex **4**.



Previously, we had assigned the same formula to both intermediates **15** and **16-I**, arguing that they differed with respect to the conformation of their chelated (butenyloxy)carbene ligands. These structural differences were believed to be a consequence of two possible preferred alignments of the alkene and carbene ligands; the so-called "parallel" and "perpendicular" conformations. Subsequently, such conformational alternatives were observed by X-ray crystallography. Rudler and co-workers have prepared (CO)$_4$W=C(OCH$_2$CH$_3$)(η^2-CH$_2$CH$_2$CH$_2$CH=CH$_2$), **24**, in which the carbene and alkene ligands are parallel[9a] and (CO)$_4$W=C(OCH$_2$CH$_3$)(η^2-c-C$_5$H$_7$), **25**, in which the carbene and alkene ligands are perpendicular.[9b] (CO)$_4$W=C[η^2-(*Z*)-N(CH$_3$)(CH$_2$C(CH$_3$)$_2$CH=CH$_2$)]C$_6$H$_4$-*p*-CH$_3$, **17**, exists in both the parallel and perpendicular conformations in the solid state, but these conformations were found to rapidly interconvert on the NMR time scale at room temperature. No similar rapid interconversion of **15** and **16** was observed between 20 and 40 °C.

Since aminocarbene complexes are expected to be much more rigid than the analogous oxycarbene complexes, the NMR results just cited make it seem unlikely that **15** and **16-I** could correspond to the two conformations that were observed for **17**. Another possibility is that the major intermediate **15** corresponds to a mixture of mononuclear tetracarbonyl carbene–alkene complexes rapidly equilibrating between parallel and perpendicular conformations. In this case, the minor intermediate **16**, which also contains an η^2-(3-butenyloxy)carbene ligand, might be a dinuclear species in which the butenyloxy ligand serves as a bridging ligand between two tungsten centers.

16 could be a dinuclear dimer **16-II** of the major carbene–alkene complex **15**. A trans arrangement of the carbene and alkene ligands might prevent formation of cyclopropanes other than **10**. A relatively slow equilibration of the monomer **15** and dimer would result in a relatively rapid growth of the monomer **15** followed by an increase in the dimer **16-II** after substantial quantities of the monomer had accumulated, consistent with our observation that **16** is observed only in the presence of **15**.

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(21) Makosza, M.; Goetzen, T. *Org. Prep. Proced. Int.* **1973**, *5*, 203–207.

(22) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417–2423.

Scheme I

Induction

$$1 \xrightarrow{k_1} 15 + CO \qquad \text{step 1}$$

Autocatalysis

$$15 \xrightarrow{k_2} 10 + W(CO)_4 \qquad \text{step 2}$$

$$1 + W(CO)_4 \xrightarrow{k_3} 15 + W(CO)_5 \qquad \text{step 3}$$

$$1 + W(CO)_5 \xrightarrow{k_4} 15 + W(CO)_6 \qquad \text{step 4}$$

The reaction of the tungsten–carbene–alkene complexes with CO gave a mixture containing more **16** than **15**. This would be possible if the dimer were less reactive toward CO than the monomer. According to this equilibrating monomer–dimer model, increasing the starting concentration of **1**, should have resulted in an enhanced yield of the dimer **16-II** relative to the monomer **15**. However, **15** and **16** were formed in essentially the same ratios when the starting concentrations of **1** was increased from 0.06 to 0.36 M.

Another possible dinuclear structure for the minor intermediate, which we now favor, is **16-III** which utilizes the butenyloxy ligand as a bridge between two $W(CO)_5$ centers. Such a complex could disproportionate to $W(CO)_6$ and the tetracarbonyl alkene–carbene complex **15**. The tungsten–alkene linkage of **15** might be more reactive toward CO than that of **16-III** due to the labilizing effect of the cis carbene ligand present in **15**. Accumulation of **16-III** late in the reaction could become favorable due to the increased formation of $W(CO)_5$ fragments by the rapidly decomposing starting material.

Kinetics of the Conversion of 1 to 10. The best model we have been able to devise to explain the induction period and autocatalytic decomposition of **1** is shown in Scheme I. Step 1 involves unimolecular loss of CO from **1** which leads to tungsten–carbene–alkene complex **15**. This is the major reaction of **1** during the induction period and results in the initial formation of **15**. Loss of CO from $(CO)_5W{=}C(OCH_3)C_6H_5$ and related carbene complexes is slow at 25–40 °C[23] and accounts for the slow production of **15** during the induction period.

Steps 2, 3, and 4, constitute the autocatalytic portion of the reaction. The slow step in this sequence is the conversion of the tungsten–carbene–alkene complex **15** to cyclopropane **10** and a very reactive solvated $W(CO)_4$ fragment. The $W(CO)_4$ fragment is proposed to abstract CO from starting material **1** to regenerate 1 equiv of tungsten–carbene–alkene complex **15** and a reactive $W(CO)_5$ fragment. The $W(CO)_5$ fragment is proposed to abstract CO from **1** to generate a second equivalent of **15**.

The net effect of steps 2–4 is that the decomposition of one molecule of tungsten–carbene–alkene complex **15** leads to the formation of 2 equiv of **15** along with one molecule of cyclopropane **10** and $W(CO)_6$. Thus, while starting material **1** is available, the concentrations of **15** and **10** should be approximately equal and rise at the same rate. The macroscopic first order-rate constant for the appearance of **15** is actually the microscopic first-order rate constant for the decomposition of **15**. During the autocatalytic portion of the reaction, the major source of additional **15** is from the autocatalytic decomposition and not from the very slow CO dissociation from **1**.

When all of the starting material **1** has been depleted, decomposition of tungsten–carbene–alkene complex **15** continues to produce cyclopropane **10**. In this model, the rate constant for disappearance of **15** in the absence of **1** is equal to the rate constant for formation of **15** in the presence of **1** during the autocatalytic period. Thus, the exponential rise in the concentration of **15** in the presence of **1** should be mirrored in the exponential decay of **15** after **1** has been consumed.

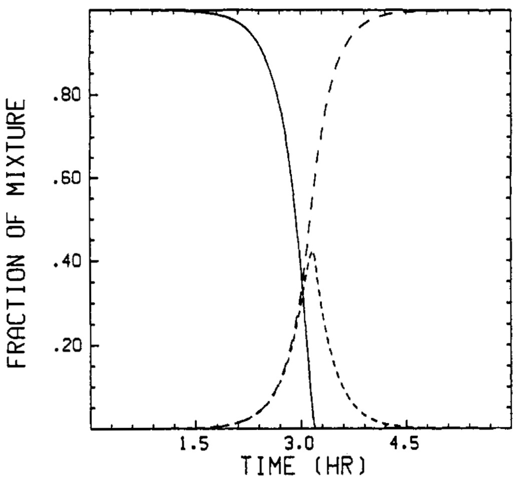

Figure 4. Calculated composition of mixture in decomposition of **1** by mechanism of Scheme I with $k_1 = 10^{-8}$ s^{-1}, $k_2 = 10^{-3}$ s^{-1}, $k_3 = 10$ M^{-1} s^{-1}, and $k_4 = 10^{-1}$ M^{-1} s^{-1}: **1**, (—); **15**, (- - -), **10**, (-- -).

There is good qualitative agreement between this scheme and our observed results. Introduction of any agent that can trap the reactive $W(CO)_4$ and $W(CO)_5$ intermediates effectively shuts down the autocatalytic decomposition and greatly inhibits the decomposition of **1**. The reactions were much slower in the coordinating solvents CD_3CN and CS_2. Ligands such as CO, PEt_3, and norbornadiene also greatly slowed the decomposition and eliminated the autocatalytic acceleration of the decomposition. ^{13}CO and PEt_3 not only intercepted the $W(CO)_4$ and $W(CO)_5$ reactive intermediates but also reacted with the tungsten–carbene–alkene complex **15** to displace the alkene ligand and generate an unreactive $(CO)_4LW{=}C(OR)R'$ (L = CO, PEt_3) complex.

The ability of $W(CO)_4$ and $W(CO)_5$ to abstract CO from **1** to generate additional **15** is supported by observations of the decomposition of **1** in the presence of added ^{13}CO. If $W(CO)_4$ and $W(CO)_5$ reacted only with ^{13}CO in solution, then a great deal of $W(^{12}CO)_4(^{13}CO)_2$ should have been formed. In fact, the $W(CO)_6$ formed had less than one ^{13}CO per molecule. This implies the existence of a source of unlabeled CO ligands and requires a kinetically competitive intermolecular transfer of CO from starting material **1**.

A quantitative model for Scheme I was constructed. The rate constant k_1 for loss of CO from **1** was estimated from the ^{13}CO exchange rate of $(CO)_5W{=}C(OCH_3)C_6H_5$[23] to be 1×10^{-8} s^{-1}. The rate constant k_2 for the conversion of tungsten–carbene–alkene complex **15** to cyclopropane **10** was taken to be 1×10^{-3} s^{-1} by comparison with the observed approximate rate of disappearance of carbene–alkene complexes **15** and **16** when all of **1** had been consumed. The rates of abstraction of CO from **1** by both $W(CO)_4$ and $W(CO)_5$ were assumed to be much faster ($k_3 = 10$ M^{-1} s^{-1}, $k_4 = 0.1$ M^{-1} s^{-1}). Figure 4 shows the calculated concentrations of **1**, **10**, and **15** using this model. The model reproduces an induction period, an autocatalytic decomposition when excess **1** is available, and an exponential decrease in intermediate **15** after **1** has been depleted. The calculated maximum concentration of intermediate **15** of 42% is in qualitative agreement with the observed maximum concentration of **15** + **16** of 35%.

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[23] Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87–94.

Experimental Section

General Data. All reactions were carried out in flame-dried glassware under a nitrogen atmosphere. Benzene, tetrahydrofuran, and diethyl ether were distilled from purple solutions prepared from sodium and benzophenone immediately prior to their use. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5 under a nitrogen atmosphere. Norbornadiene (Aldrich) was filtered through alumina prior to its use. Carbon monoxide of 90% ^{13}C enrichment was used as purchased (Mound Laboratories). Preparative column chromatography was performed by using 60–200 mesh silica gel. Preparative thin-layer chromatography (TLC) was performed by using Merck PF-254 silica gel.

^1H NMR spectra were obtained on a Bruker WH-270 or a JEOL MH-100 spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX-60, a JEOL FX-200, or a Varian XL-100 spectrometer. Accurate integration of fourier transform ^1H NMR spectra was achieved by using a 30-s pulse repetition rate in conjunction with a 45° pulse angle. ^{13}C NMR spectra, suitable for integration, were obtained from samples that contained 0.09 M Cr(acac)$_3$ "shiftless" relaxation reagent;[24a] this reagent reduces carbon T_1 relaxation times and suppresses nuclear Overhauser enhancement of the observed signals.[24] A pulse angle of 90° and a pulse repetition rate of 9 s were used in conjunction with a reversed gated broad-band ^1H-decoupling procedure in which the decoupler was on during the data acquisition period and off between acquisition periods. This scheme serves to negate nuclear Overhauser enhancements if the time between pulses is greater than five times the longest carbon T_1 relaxation time in the molecule.[25] Integration of ^{13}C NMR spectra was performed by using an Ott Type 31 planimeter.

Fourier transform infrared spectra were obtained on a Digilab FTS-20 interferometer. High-resolution mass spectra were obtained on a AEI-MS-902 mass spectrometer. UV–visible spectra were obtained on a Cary 118 spectrophotometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Pentacarbonyl[(3-butenyloxy)*p*-tolylcarbene]tungsten(0), 1. But-3-en-1-ol (2.40 mL, 27.8 mmol) was dried for several hours over activated Linde 4-Å molecular sieves, and ether (10 mL) was added by vacuum transfer. Sodium (15 mg, 0.65 mmol) was added to the solution at room temperature. After 1 h, generation of the sodium alkoxide was complete and the solution was transferred via cannula to a solution of $(CO)_5W{=}C(OCH_3)C_6H_4\text{-}p\text{-}CH_3$, **6**[26] (0.50 g, 1.09 mmol), in 20 mL of ether over activated molecular sieves. After 24 h at ice bath temperature, the reaction mixture was filtered and the solvent evaporated under vacuum to yield a dark red oil. The oil was filtered through a short silica gel column (12 g of silica gel; 2-cm diameter column) using hexane as the eluent. The red band was collected under a nitrogen atmosphere, concentrated to approximately 4–8 mL volume, and cooled to −78 °C to yield an orange-red powder. Solvent was withdrawn by pipette at −78 °C, and the red powder was warmed to room temperature under high vacuum to give pure **1** (0.367 g, 68%), mp 53 °C dec. Solid **1** decomposes over a period of several hours at room temperature but has been stored for months at −20 °C. To avoid decomposition during workup, the above procedure was performed in less than 1 h: IR (hexane) 2068 (m), 1983 (w), 1954 (s), 1943 (vs) cm^{-1}; ^1H NMR (100 MHz, C_6D_6) δ 7.56 (d, J = 8 Hz, 2 H), 6.83 (d, J = 8 Hz, 2 H), 5.6 (m, 1 H, $CH{=}CH_2$), 5.0 (m, 2 H, $CH{=}CH_2$), 4.67 (t, J = 6 Hz, 2 H, OCH_2), 2.22 (dt, J = 6, 6 Hz, 2 H, OCH_2CH_2), 1.96 (s, 3 H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (25 MHz, THF-d_8, 0 °C, 0.07 M Cr(acac)$_3$) δ 319.0 (carbene), 205.0 (trans CO), 199.1 (cis CO), 153.2, 145.3 (ipso, para), 135.4 ($CH{=}CH_2$), 130.1, 129.8 (ortho, meta), 118.7 ($CH{=}CH_2$), 84.4 (OCH_2), 34.5 (OCH_2CH_2), 21.6 ($ArCH_3$).

Addition of excess dimethylamine (ca. 0.2 mL) to a solution of **1** (32.7 mg, 0.066 mmol) in acetone-d_6 at −78 °C produced a yellow solution whose ^1H NMR spectrum corresponded to a mixture of excess dimethylamine, but-3-en-1-ol, and the (dimethylamino carbene complex **9** (100 ± 5% by ^1H NMR).

Pentacarbonyl[(3-butenyloxy)phenylcarbene]tungsten(0), 2. The reaction of but-3-en-1-ol with $(CO)_5W{=}C(OCH_3)C_6H_5$, **7**,[27] gave $(CO)_5W{=}C(OCH_2CH_2CH{=}CH_2)C_6H_5$, **2**, as a red solid: ^1H NMR (270 MHz, C_6D_6) δ 7.5 (m, 2 H), 7.0 (m, 3 H), 5.6 (m, 1 H, $CH{=}CH_2$), 4.9–5.0 (m, 2 H, $CH{=}CH_2$), 4.60 (t, J = 6.3 Hz, 2 H, OCH_2), 2.18 (dt, J = 6.4 Hz, 2 H, OCH_2CH_2).

Pentacarbonyl[(allyloxy)*p*-tolylcarbene]tungsten(0), 3. The alkoxide-catalyzed reaction of allyl alcohol (3.0 mL, 44 mmol) with **6** (0.50 g, 1.09 mmol) gave $(CO)_5W{=}C(OCH_2CH{=}CH_2)C_6H_4\text{-}p\text{-}CH_3$, **3**, as a red solid (0.268 g, 51%): mp 85 °C dec; IR (hexane) 2064 (m), 1986 (w), 1958 (s), 1946 (vs) cm^{-1}; ^1H NMR (100 MHz, C_6D_6) δ 7.55 (d, J = 8 Hz, 2 H), 6.79 (d, J = 8 Hz, 2 H), 5.6–5.8 (m, 1 H, $CH{=}CH_2$), 5.09–5.14 (m, 2 H, $CH{=}CH_2$), 5.00 (dm, J = 10 Hz, 2 H, OCH_2), 1.91 (s, 3 H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (15 MHz, $(CD_3)_2CO$, 0.07 M Cr(acac)$_3$) δ 318.6 (carbene), 204.0 (trans CO), 197.9 (cis CO), 153.0, 144.2 (ipso, para), 132.2 ($CH{=}CH_2$), 129.6, 128.3 (ortho, meta), 120.4 ($CH{=}CH_2$), 85.2 (OCH_2), 21.6 ($ArCH_3$). The reaction of **3** with excess dimethylamine gave allyl alcohol and the (dimethylamino)carbene complex **9** (100 ± 5% by ^1H NMR).

Pentacarbonyl[(4-pentenyloxy)*p*-tolylcarbene]tungsten(0), 4. The alkoxide-catalyzed reaction of pent-4-en-1-ol (2.50 g, 29.0 mmol) with **6** (0.51 g, 1.11 mmol) gave $(CO)_5W{=}C(OCH_2CH_2CH_2CH{=}CH_2)C_6H_4\text{-}p\text{-}CH_3$, **4** (0.28 g, 49%), as red crystals at −78 °C that melted to yield a red oil at room temperature: IR (hexane) 2068 (m), 1986 (w), 1956 (s), 1944 (vs) cm^{-1}; ^1H NMR (100 MHz, C_6D_6) δ 7.56 (d, J = 8.3 Hz, 2 H), 6.82 (d, J = 8.1 Hz, 2 H), 5.6 (m, 1 H, $CH{=}CH_2$), 4.9 (m, 2 H, $CH{=}CH_2$), 4.63 (t, J = 6.0 Hz, 2 H, OCH_2), 1.8–2.0 (m, 2 H, $CH_2CH{=}CH_2$), 1.92 (s, 3 H, $ArCH_3$), 1.56 (quintet, J = 6.9 Hz, 2 H, $CH_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR (15 MHz, CD_3CN, 0.07 M Cr(acac)$_3$) δ 318 (carbene), 204 (trans CO), 197 (cis CO), 152, 143 (ipso, para), 137 ($CH{=}CH_2$), 129, 127 (ortho, meta), 115 ($CH{=}CH_2$), 84 (OCH_2), 30 (CH_2), 28 (CH_2), 21 ($ArCH_3$). The reaction of *4* with excess dimethylamine gave the (dimethylamino)carbene complex **9** (100 ± 5% by ^1H NMR).

Pentacarbonyl[(3-butenyloxy)*p*-tolylcarbene]chromium(0), 5. The alkoxide-catalyzed reaction of but-3-en-1-ol (3.0 mL, 34.7 mmol) with $(CO)_5Cr{=}C(OCH_3)C_6H_4\text{-}p\text{-}CH_3$, **8**[28] (0.50 g, 1.53 mmol), gave $(CO)_5Cr{=}C(OCH_2CH_2CH{=}CH_2)C_6H_4\text{-}p\text{-}CH_3$, **5** (0.32 g, 57%), as a red powder: IR (hexane) 2058 (m), 1990 (m), 1964 (sh), 1956 (s), 1946 (sh) cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 7.20 (d, J = 8.3 Hz, 2 H), 6.81 (d, J = 8.1 Hz, 2 H), 5.5 (m, 1 H, $CH{=}CH_2$), 4.97 (m, 2 H, $CH{=}CH_2$), 4.43 (t, J = 5.3 Hz, 2 H, OCH_2), 2.12 (dt, J = 6.5 Hz, 2 H, OCH_2CH_2), 1.94 (s, 3 H, $ArCH_3$).

Pentacarbonyl[(dimethylamino)*p*-tolylcarbene]tungsten(0), 9. A solution of anhydrous dimethylamine (2 mL, 30 mmol) in 4 mL of THF at −78 °C was added to a solution of **6** (0.50 g, 1.09 mmol) in ether at 0 °C. Shaking the mixture produced an instantaneous color change from red to yellow. Evaporation of the solvent, extraction of the residue with pentane, and evaporation of the pentane gave $(CO)_5W{=}C[N(CH_3)_2]C_6H_4\text{-}p\text{-}CH_3$, **9**, as a yellow solid (0.472 g, 92%): mp 81 °C; IR (hexane) 2064 (m), 1971 (w), 1934 (vs), 1930 (sh) cm^{-1}; ^1H NMR (270 MHz, $(CD_3)_2CO$) δ 7.24 (d, J = 7.7 Hz, 2 H), 6.78 (d, J = 8.1 Hz, 2 H), 3.99 (s, 3 H, NCH_3), 3.14 (s, 3 H, NCH_3), 2.33 (s, 3 H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (50 MHz, CD_3CN, 0.07 M Cr(acac)$_3$) δ 253.7 (carbene), 205.5 (trans CO), 199.6 (cis CO, $J_{^{183}W-^{13}C}$ = 129 Hz), 152.0, 136.6 (ipso, para), 129.7, 120.7 (ortho, meta), 54.6 (NCH_3), 45.0 (NCH_3), 21.1 ($ArCH_3$); MS, calcd for $C_{15}H_{13}NO_5{}^{184}W$ 471.0304, found 471.0302; MS, m/e (%), M 474 (0.4), 473 (8.8), 472 (1.5), 471 (12.8), 470 (4.2), 469 (9.3), M − CO 446 (2.5), 445 (27.9), 444 (2.6), 443 (31.8), 442 (13.4), 441 (20.3), M − 3CO 390 (3.6), 389 (36.5), 388 (4.4), 387 (100.0), 386 (63.0), 385 (81.6).

Anal. Calcd for $C_{15}H_{13}NO_5W$: C, 38.24; H, 2.78; N, 2.97; W, 39.02. Found: C, 38.44; H, 2.78; N, 3.20; W, 38.77.

Thermolysis of Carbene Complexes. The thermolysis of various carbene complexes were carried out in sealed NMR tubes.

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Dry degassed solvents and liquid reagents were vacuum transferred into an NMR tube containing the starting carbene complex, internal standard (usually 1,4-bis(trimethylsilyl)benzene) and any other solid reagent. The tube was then sealed under vacuum and stored at −78 or −197 °C until ready for use.

Some thermolyses were conducted under a CO atmosphere. Use of a vacuum line and NMR tube of known volume in conjunction with the known solubility of CO in benzene[29] (assuming Henry's law and ideal gas behavior) allowed determination of the total amount of CO in the sealed reaction vessel as well as its concentration in the reaction solution.

Thermolysis of 1. A sealed NMR tube containing a 0.20 M solution of 1 in benzene-d_6 and 1,4-bis(trimethylsilyl)benzene was heated at 40.0 ± 0.2 °C for 6 h in a constant temperature bath. The red solution became heterogeneous and black. The ^{1}H NMR spectrum of the sample showed no starting material. The major product was identified as 1-(4-methylphenyl)-2-oxabicyclo[3.1.0]hexane, 10 (95 ± 5% from 1 by ^{1}H NMR). Additional minor ^{1}H NMR resonances were assigned to tricarbonyl[η^6-1-(4-methylphenyl)-2-oxabicyclo[3.1.0]hexane]tungsten(0), 11 (3–5% from 1 by ^{1}H NMR). The IR spectrum of the residue obtained by evaporating the reaction solvent showed a strong absorption at 1983 cm^{-1} (hexane) which was attributed to $W(CO)_6$ (ca. 42% from 1 by IR).

In a separate experiment employing benzene as the reaction solvent (in place of benzene-d_6) one additional reaction product, tricarbonyl(η^6-benzene)tungsten(0), 12 (3–5% from 1 by ^{1}H NMR), was identified: ^{1}H NMR (270 MHz, C_6D_6) δ 4.20 (s).[20]

Pure 10 was isolated as a colorless oil by preparative TLC (hexane/silica gel): ^{1}H NMR (270 MHz, C_6D_6) δ 7.32 (d, J = 8 Hz, 2 H), 7.02 (d, J = 8 Hz, 2 H), 3.95 (td, J = 9, 2.5 Hz, 1 H, OC*H*H, H_1), 3.40 (td, J = 9, 7.4 Hz, 1 H, OCH*H*, H_2), 2.13 (s, 3 H, ArC*H*$_3$), 1.80 (m, 1 H, OCH_2C*H*H, H_3), 1.54 (dddd, J = 11.9, 7.4, 2.5, 0.6 Hz, 1 H, OCH_2CH*H*, H_4), 1.42 (dt, J = 9, 5 Hz, 1 H, cyclopropyl CH, H_5), 1.13 (dd, J = 6, 5 Hz, 1 H, cyclopropyl C*H*H, H_7), 0.91 (ddd, J = 9, 6, 1 Hz, 1 H, cyclopropyl CH*H*, H_6); ^{13}C{^{1}H} NMR (15 MHz, CD_3CN) δ 138.0, 135.6 (ipso, para), 128.5, 124.5 (ortho, meta), 69.0 (O cyclopropyl C), 66.5 (OCH_2), 28.7 (OCH_2CH_2), 24.7 ($ArCH_3$), 19.9 (cyclopropyl CH), 16.7 (cyclopropyl CH_2); MS, calcd for $C_{12}H_{14}O$ 174.1045, found 174.1041; MS, *m/e* (%) 174 (31), 173 (11), 159 (16), 120 (7), 119 (100), 91 (39), 65 (14), 44 (7).

Signals in decomposition mixture assigned to minor component 11: ^{1}H NMR (270 MHz, C_6D_6) δ 5.38 (dm, J = 6 Hz, 1 H, aromatic C*H*), 4.64 (dm, J = 7 Hz, 1 H, aromatic C*H*), 4.45 (d, J = 6.6 Hz, 2 H, aromatic C*H*), 3.82 (td, J = 8.9, 3.2 Hz, 1 H, OC*H*H, H_1), 3.18 (td, J = 9.3, 7.2 Hz, 1 H, OCH*H*, H_2), 1.65 (s, 3 H, ArC*H*$_3$). The signals due to the other five hydrogens of the bicyclohexane ring were obscured by the signals due to 10.

Thermolysis of 5. A sealed tube containing a 0.11 M solution of 9 in benzene was heated at 39 ± 2 °C for 15 h. Preparative TLC of the mixture (hexane:silica gel and then ether/hexane (10/90):silica gel) produced two bands. The faster moving band was pure 10. The slower moving band was a mixture of three compounds identified as 10, tricarbonyl (η^6-benzene)chromium(0), 14,[16] and tricarbonyl(η^6-1-(4-methylphenyl)-2-oxabicyclo[3.1.0]hexane)chromium(0), 13,[30] by ^{1}H NMR. Observation of 10 in the slower moving band is a consequence of air oxidation of the arene complex 13.[31]

In a separate experiment a 0.15 M solution of 5 in benzene-d_6 was heated to 40 °C for 24 h. The ^{1}H NMR spectrum of the product mixture showed only a 2.5:1 mixture of 10 and 13.

For 14: IR (hexane) 1988 (m), 1920 (m) cm^{-1};[16] ^{1}H NMR (270 MHz, C_6D_6) δ 4.3 (s, 6 H).

For 13: IR (hexane) 1978 (m), 1907 (m) cm^{-1};[15,17] ^{1}H NMR (270 MHz, C_6D_6) δ 5.32 (d, J = 5.9 Hz, 1 H), 4.61 (d, J = 6.5 Hz, 1 H), 4.45 (d, J = 6.8 Hz, 2 H), 3.88 (m, 1 H), 3.23 (m, 1 H), 1.90 (m, 1 H), 1.55 (s, 3 H), 1.39 (m, 1 H), 1.10 (m, 1 H), 0.97 (m, 1 H), 0.64 (m, 1 H).

Thermolysis of 4. A sealed tube containing a 0.20 M solution of 4 in benzene was heated at 70.0 ± 0.2 °C in a constant temperature bath for 13 h. Preparative TLC (hexane:silica gel) of the product mixture gave two products: $W(CO)_6$ and 1-(4-methylphenyl)-2-oxabicyclo[4.1.0]heptane, 19 (53%, colorless oil).

For 19: ^{1}H NMR (270 MHz, C_6D_6) δ 7.21 (d, J = 8 Hz, 2 H), 7.04 (d, J = 8 Hz, 2 H), 3.61 (dtd, J = 10.7, 3.2, 1.0 Hz, 1 H, OC*H*H, H_2), 3.18 (ddd, J = 11.6, 10.7, 2.0 Hz, 1 H, OCH*H*, H_1), 2.15 (s, 3 H, ArC*H*$_3$), 1.6–1.0 (m, 7 H); ^{13}C{^{1}H} NMR (15 MHz, CD_3CN) δ 142, 135 (ipso, para), 129, 123 (ortho, meta), 64 (OCH_2), 60 (O cyclopropyl C), 21.8, 21.3, 20.4, 19.9, 19.7 (ring C, $ArCH_3$); MS, calcd for $C_{13}H_{16}O$ 188.1201, found 188.1198; MS, *m/e* (%), 188 (11), 187 (14), 174 (8), 173 (75), 145 (9), 131(5), 120 (6), 119 (100), 115 (5), 91 (50), 65 (18), 44 (12).

Tungsten–Carbene–Alkene Complexes 15, 16, 20, and 21. A sealed NMR tube initially containing a 0.1 M solution of 1 in benzene-d_6 was maintained at 22–25 °C in the NMR probe, and the ^{1}H NMR spectrum of the solution was recorded periodically over 6 h. At intermediate times, two species in addition to 1 and the ultimate products 10 and 11 were detected. These two metastable intermediates 15 and 16, which were not formed in equal amounts ([15] > [16]), persisted after all of 1 had decomposed. Furthermore, the subsequent decomposition of 15 and 16 was accompanied by the formation of additional 10 and 11. A separate experiment employing dichloromethane-d_2 as a reaction solvent also generated 15 and 16 as metastable products of the decomposition of 1. As before, the ultimate product mixture consisted solely of 10 and 11.

In another experiment a 0.03 M solution of 1 in hexane was maintained at 23 °C while periodically removing aliquots from the solution for measurement of the reaction mixture's IR spectrum. After 19 h all of the bands due to 1 (with the exception of the band at 2068 cm^{-1}) had disappeared and were replaced by new bands; IR (Nujol, hexane) 2030 (m), 1982 (vs), 1967 (vw), 1947 (m), 1928 (s), 1915 (m), 1908 (m) cm^{-1}. After several hours all of the bands but the one at 1982 cm^{-1} (due to $W(CO)_6$) had disappeared. The bands at 2030, 1947, 1928, and 1908 are attributed to the major metastable species 15 observed by ^{1}H NMR in the decomposition of 1.

On the basis of its IR and ^{1}H NMR spectra, the major metastable intermediate 15 is assigned the structure *cis*-tetracarbonyl[η^2-(3-butenyloxy)*p*-tolylcarbene]tungsten(0). The minor metastable intermediate 16 also contains a carbene ligand and coordinated alkene ligand; it is either a conformational isomer of 15 or a dinuclear species (see Results and Discussion).

For 15: ^{1}H NMR (270 MHz, C_6D_6) δ 7.90 (d, J = 8 Hz, 2 H), 6.89 (d, J = 8 Hz, 2 H), 4.30 (ddd, J = 11.3, 6.3, 4.0 Hz, 1 H, OC*H*H, H_2), 3.59 (dddd, J = 13.7, 8.5, 8.5, 6.3 Hz, 1 H, C*H*═CH_2, H_5), 3.14 (d, J = 8.7 Hz, 1 H, CH═C*H*H, H_6), 2.73 (d, J = 13.7 Hz, 1 H, CH═CH*H*, H_7), 1.93 (s, 3 H, ArC*H*$_3$), 0.61 (dddd, J = 14.4, 8.5, 6.1, 3.5 Hz, 1 H, OCH_2C*H*H, H_4), not observed (H_1, H_3); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 7.79 (d, J = 8 Hz, 2 H), 7.24 (d, J = 8 Hz, 2 H), 5.10 (ddd, J = 11.3, 6.3, 4.0 Hz, 1 H, OC*H*H, H_2), 4.77 (ddd, J = 11.3, 7.3, 3.6 Hz, 1 H, OCH*H*, H_1), 4.32 (dddd, J = 13.7, 8.5, 8.5, 6.3 Hz, 1 H, C*H*═CH_2, H_5), 3.42 (d, J = 13.7 Hz, 1 H, CH═CH*H*, H_7), 3.10 (dddd, J = 14.0, 7.0, 7.0, 3.6 Hz, 1 H, OCH_2CH*H*, H_3), 2.36 (s, 3 H, ArC*H*$_3$), 1.61 (dddd, J = 14.4, 8.5, 6.6, 3.6 Hz, 1 H, OCH_2C*H*H, H_4), not observed (H_6).

For 16: ^{1}H NMR (270 MHz, C_6D_6) δ 7.56 (d, J = 8 Hz, 2 H), 6.81 (d, J = 8 Hz, 2 H), 4.46 (m, 2 H, OC*H*$_2$, H_1, H_2), 2.86 (d, J = 8.8 Hz, 1 H, CH═C*H*H, H_6), 2.78 (d, J = 14.3 Hz, 1 H, CH═CH*H*, H_7), 2.60 (m, 1 H, OCH_2CH*H*, H_3), 1.92 (s, 3 H, ArC*H*$_3$), not observed (H_4, H_5).

A similar experiment utilizing a solution of 2 in benzene-d_6 provided almost identical results to those previously obtained from the decomposition of 1. The metastable intermediates 20 and 21 and the ultimate cyclopropane product differed from those obtained previously in that these new products contained a phenyl group in place of the *p*-tolyl group.

For 20: ^{1}H NMR (270 MHz, C_6D_6) δ 4.30 (ddd, J = 11.3, 6.8, 3.7 Hz, 1 H, OC*H*H, H_2), 4.00 (ddd, J = 11.3, 7.6, 3.6, 1 H, OCH*H*, H_1), 3.63 (dddd, J = 13.8, 8.6, 8.6, 6.3 Hz, 1 H, C*H*═CH_2, H_5), 3.13 (d, J = 8.4 Hz, 1 H, CH═C*H*H, H_6), 2.77 (d, J = 13.6 Hz, 1 H, CH═CH*H*, H_7), 2.08 (dddd, J = 14.0, 7.0, 7.0, 3.5 Hz, 1 H,

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OCH_2CHH, H_3), 0.67 (dddd, *J* = 14.4, 8.1, 6.5, 3.2 Hz, 1 H, OCH_2CHH, H_4), not observed (aromatic).

For **21**: ^1H NMR (270 MHz, C_6D_6) δ 4.43 (m, 2 H, OCH_2, H_1, H_2), 3.84 (m, 1 H, $CH{=}CH_2$, H_5), 2.79 (d, *J* = 8.8 Hz, 1 H, $CH{=}CHH$, H_6), 2.73 (d, *J* = 14.2 Hz, 1 H, $CH{=}CHH$, H_7), 2.56 (m, 1 H, OCH_2CHH, H_3), not observed (H_4 aromatic).

Reaction of 15 and 16 with Triethylphosphine. A 0.14 M solution of **1** in benzene-d_6 was warmed at 37–38 °C for 46 min. At this point, the ^1H NMR spectrum of the mixture showed four compounds **1**, **10**, **15**, and **16** (**1**:**10**:**15**:**16** = 11:49:29:11). The mixture was cooled to 5 °C, and triethylphosphine (1.1 equiv relative to starting **1**) was added. When the mixture was reheated to 37–38 °C, the same four compounds (**1**:**10**:**15**:**16** = 4:58:32:6) were observed. After 5 min only two compounds were observed, **10** and a new product, **18**, identified as *cis*-tetracarbonyl(triethylphosphine)[(3-butenyloxy)*p*-tolylcarbene]tungsten(0) (**10**:**18** = 64:36). Preparative TLC of the mixture (hexane:silica gel) gave a slow-moving brown band which was rechromatographed (ether/hexane (10/90): silica gel) to obtain pure **18** as a brown oil. A fast-moving band from the first TLC was found to contain $W(CO)_6$ and pentacarbonyl(triethylphosphine)tungsten(0).[32]

For **18**: IR (hexane) 2017 (m), 1925 (s), 1918 (s), 1890 (s) cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 7.52 (d, *J* = 8 Hz, 2 H), 6.89 (d, *J* = 8 Hz, 2 H), 5.73 (m, 1 H, $CH{=}CH_2$), 5.02 (m, 2 H, $CH{=}CH_2$), 4.60 (t, *J* = 6 Hz, 2 H, OCH_2), 2.35 (dt, *J* = 6, 6 Hz, 2 H, OCH_2CH_2), 1.97 (s, 3 H, $ArCH_3$), 1.34 (quintet, *J* = 7.7 Hz, 6 H, PCH_2), 0.69 (dt, *J* = 15.4, 7.7 Hz, 9 H, PCH_2CH_3).

For pentacarbonyl(tgriethylphosphine)tungsten(0):[32] IR (hexane) 2066 (m), 1946 (s), 1937 (vs) cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 1.15 (quintet, *J* = 7.7 Hz, 2 H, PCH_2), 0.59 (dt, *J* = 15.4, 7.7 Hz, 3 H, CH_3).

Reaction of 15 and 16 with CO. A sealed NMR tube containing a 0.21 M solution of **1** and 1,4-bis(trimethylsilyl)benzene in benzene-d_6 was maintained at 21.1 °C for 5.7 h at which time almost all of **1** had decomposed (5% **1**, 51% **10**, 29% **15**, and 11% **16** based on starting **1**). The brown solution was cooled to 0 °C and transferred to a Fisher-Porter bottle which was then pressurized with CO (*p*(CO) = 60 psig at 0 °C). After 30 min at 23 °C, the mixture became bright red and was found by ^1H NMR to contain very little of the tungsten–alkene–carbene complexes (25% **1**, 61% **10**, 4% **15**, and 8% **16** based on starting **1**).

Reaction of 1 with ^{13}CO. A sealed NMR tube containing **1** (0.149 mmol, 0.51 M), 1,4-bis(trimethylsilyl)benzene, and 90% enriched ^{13}CO (0.47 mmol, 0.042 M at 24 °C) in benzene-d_6 was agitated constantly for 5 h at room temperature. The ^1H NMR spectrum of the mixture showed only **1** (80% from starting **1**) and **10** (20% from starting **1**). The mixture was then treated with excess dimethylamine at 0 °C to give a yellow solution which was then subjected to preparative TLC (hexane and then hexane/dichloromethane (2/1):silica gel). From this TLC was obtained $W(CO)_6$ and the (dimethylamino)carbene complex **9**.

Incorporation of labeled CO into $W(CO)_6$ was established by mass spectroscopy (40 eV, average of four scans of the molecular ion region): MS, *m/e* (%) 350 (17.1 ± 1.3), 351 (15.8 ± 0.5), 352 (23.7 ± 1.1), 353 (10.4 ± 0.9), 354 (20.3 ± 2.3), 355 (8.8 ± 0.3), 356 (3.0 ± 0.5), 357 (0.9 ± 0.2), 358 (trace). This mass spectrum was consistent with label incorporation corresponding to 61.4% l_0, 26.4% l_1, 6.8% l_2, 3.8% l_3, and 1.6% l_4.

Incorporation of labeled CO into **9** (derived from recovered **1**) was determined by ^{13}C NMR spectroscopy (50 MHz, CD_3CN, 0.09 M $Cr(acac)_3$) using the integrated areas of the aryl resonances as internal standards: δ 205.5 (1.36 C, trans CO), 199.6 (11.8 C, cis CO), 152.0 (0.90 C, aryl), 136.6 (0.97 C, aryl), 129.7 (2.13 C, aryl).

In a related experiment, **1** (0.157 mmol, 0.56 M), 1,4-bis(trimethylsilyl)benzene, and 90% enriched ^{13}CO (0.485 mmol, 0.062 M at 24 °C) in benzene-d_6 were maintained at 24 °C for 10 h. Only two compounds were observed in the final mixture: **1** (71% from starting **1**) and **10** (28% from starting **1**). $W(CO)_6$ and the (dimethylamino)carbene complex **9** were obtained by using the workup procedure described above.

For $W(CO)_6$: MS, *m/e* (%), 350 (14.8 ± 1.0), 351 (16.2 ± 0.5), 352 (22.5 ± 0.3), 353 (12.9 ± 0.8), 354 (17.4 ± 0.6), 355 (12.2 ± 0.9), 356 (2.9 ± 0.2), 357 (0.8 ± 0.2), 358 (0.2 ± 0.2). This mass spectrum was consistent with a label incorporation corresponding to 52.2% l_0, 35.2% l_1, 5.9% l_2, 4.0% l_3, 2.1% l_4, and 0.6% l_5.

For **9** (derived from recovered **1**): ^{13}C NMR (50 MHz, CD_3CN, 0.09 M $Cr(acac)_3$) δ 205.5 (1.80 C, trans CO), 199.6 (21.0 C, cis CO), 152.0 (0.96 C, aryl), 136.6 (1.01 C, aryl), 129.7 (2.03 C, aryl).

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