Generation and Reactions of (Phenylmethylcarbene)pentacarbonyltungsten(0)

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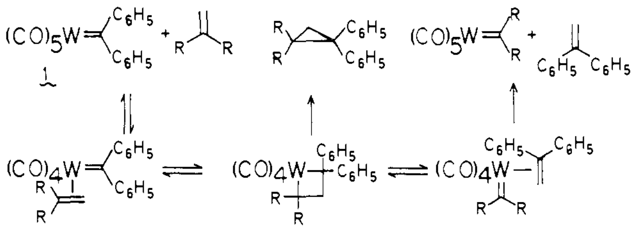
Abstract: The stereochemistry of metathesis can be explained on the basis of the stereochemistry of an intermediate puckered metallocyclobutane. To test this hypothesis, an attempt was made to study the reactions of (phenylmethylcarbene)pentacarbonyltungsten(0) (**4**) with alkenes. Reaction of CH_3Li with $(CO)_5WC(OCH_3)C_6H_5$ (**5**) at −78 °C gave the adduct $(CO)_5WC(OCH_3)(CH_3)C_6H_5^-$ (**6**), which was characterized by IR and NMR. Addition of 1.0 equiv of HCl to **6** gave styrene (47%), which is formally a hydrogen shift product of phenylmethylcarbene, and *cis*- and *trans*-1-methyl-1,2-diphenylcyclopropanes (**7c** and **7t**) (26%, cis/trans = 7.0), which are formally the cyclopropanation products of phenylmethylcarbene and styrene. Low temperature NMR studies indicated that (π-styrene)pentacarbonyltungsten(0) (**12**) was an initial product but decomposed above 0 °C. At attempt to trap $(CO)_5WC(CH_3)C_6H_5$ (**4**) with $P(C_6H_5)_3$ gave $P(C_6H_5)_3CH(C_6H_5)CH_3^+(CO)_5WBr^-$ (**10**). Generation of **4** in the presence of *p*-methylstyrene gave no 1-methyl-1-phenyl-2-*p*-tolylcyclopropane (**9**) (<0.25%), the expected cross product from the reaction of **4** with *p*-methylstyrene. Generation of the labeled carbene complex $(CO)_5WC(CH_3)(C_6H_4\text{-}p\text{-}CH_3)$ in the presence of tungsten-styrene complex **12** gave no 1-methyl-1-*p*-tolyl-2-phenylcyclopropane (**15**) (<0.5%), the expected cross product incorporating styrene. Generation of $(CO)_5WC(CD_3)C_6H_5$ (**4-*d*₃**) gave trideuterated styrene and pentadeuterated cyclopropane, **7c-*d*₅**, with deuterium in the methyl group and the methylene group of the cyclopropane. These results demonstrate that cyclopropane **7** is not formed from any styrene precursor. The carbene complex **4** was found to be a poor model for studies of the stereochemistry of metathesis since the products were not formed by an intermediate metallocycle. A mechanism involving the reaction of the α-anion of a carbene complex, **18**, with the carbene complex **4** is proposed to explain the formation of the *cis*-cyclopropane, **7c**.

We recently reported that the nonheteroatom stabilized carbene complex, $(CO)_5WC(C_6H_5)_2$ (**1**),[1] reacts with alkenes to give cyclopropanes, olefin scission products, and new carbene complexes.[2] A mechanism (Scheme I) involving the equilibrium between a metallocyclobutane and a metal complex bearing both an alkene and a carbene ligand was proposed to explain our results. Earlier, a similar equilibration had been suggested by Herrisson and Chauvin[3] as a sufficient mechanism for the olefin metathesis reaction.[4]

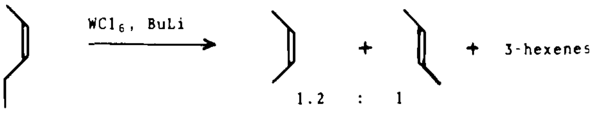
Scheme I



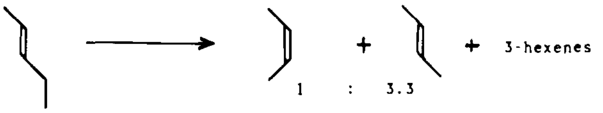
Other previously considered mechanisms for olefin metathesis involved the pairwise exchange of alkylidene groups of a pair of alkenes complexed to a metal; the pairwise exchange was proposed to proceed via either a quasi-cyclobutane complex,[5] a tetracarbene complex,[6] or a metallocyclopentane intermediate.[7] The recent demonstrations that the olefin metathesis reaction proceeds via a nonpairwise exchange of alkylidene groups is consistent only with the equilibration between a metallocyclobutane and a metal complex bearing both carbene and alkene ligands.[3,8] The observation of high molecular weight products in the metathesis of cyclic alkenes even at low conversions has been cited as evidence in favor of a chain mechanism for metathetical polymerization involving metal carbene complexes as intermediates.[9]

We have been trying to explain the characteristics of the olefin metathesis reaction on the basis of model reactions of isolable metal–carbene complexes with alkenes. The olefin metathesis reaction shows a pronounced structural selectivity.[4] The relative rates of metathesis decrease in the order: (1) the degenerate exchange of methylene units between terminal alkenes[10] > (2) cross metathesis of terminal and internal alkenes[3,11] > (3) metathesis of internal alkenes > (4) metathesis of terminal alkenes to give ethylene and internal alkenes. The observations that $(CO)_5WC(C_6H_4\text{-}p\text{-}CH_3)_2$ is relatively more reactive toward terminal alkenes than internal alkenes and that there is a high selectivity for transfer of the least substituted alkylidene unit of an alkene to the carbene ligand help to explain the structural selectivity found in catalytic olefin metathesis reactions.[12]

The moderate stereospecificity observed in the metathesis of 2-pentenes at low conversions[13,14] is one of the key characteristics of catalytic metathesis. Any mechanism purporting to account for the metathesis reaction must provide a reasonable basis for understanding this phenomenon. Metallocyclobutanes have been shown to exist in puckered conformations by x-ray crystallography.[15,16] A consideration of the steric interactions within a metallocyclobutane leads to a rational explanation of the retention of stereochemistry found in the kinetically formed products of olefin metathesis.

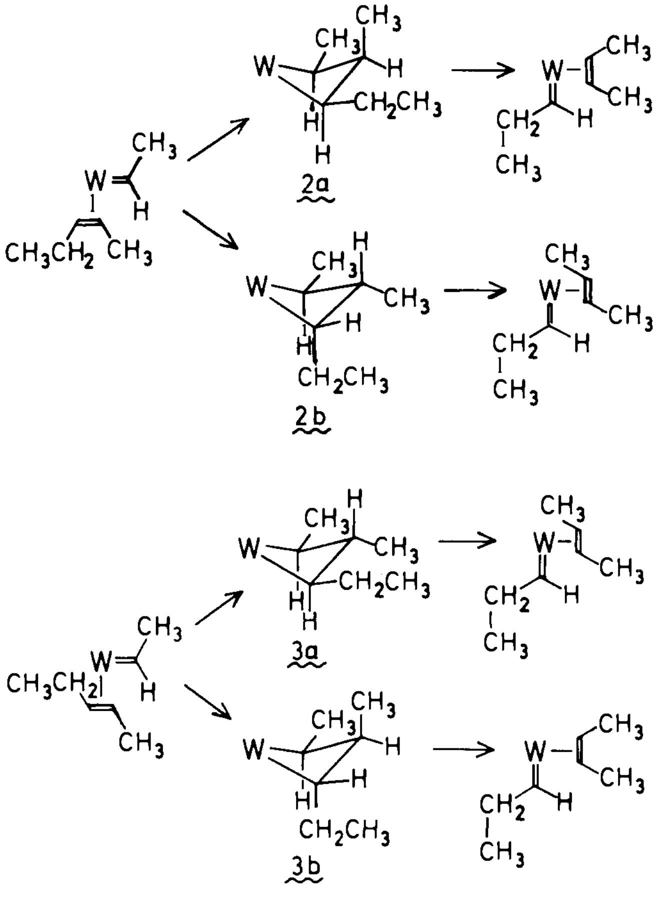


(ref. 13)



The x-ray crystal structure of $(C_3H_6)Pt(C_6H_5N)_2Cl_2$, a metallocyclobutane, indicates that the four-membered ring is puckered: the angle between the plane of the three carbon atoms and the plane of the platinum and two attached carbon atoms is 12.5°.[15] As a consequence of the ring puckering, the substituents on the ring occupy pseudoaxial and pseudoequatorial positions. The most important steric interaction in the metallocyclobutane would be expected to be a 1,3-diaxial interaction between the substituents attached to the carbons bonded to the metal.[17]

Scheme II

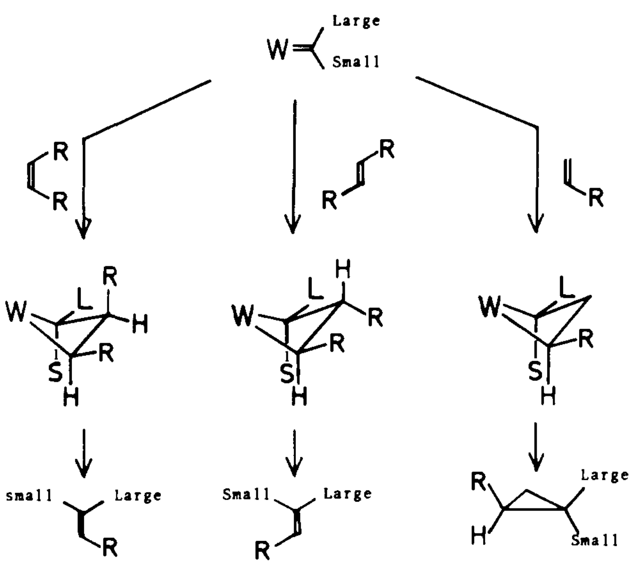


A metal complex bearing both a *cis*-2-pentene and an ethylidene ligand can rearrange to form two stereochemically different metallocyclobutane intermediates (Scheme II). Intermediate **2a** is more stable than intermediate **2b** which has a destabilizing 1,3-diaxial interaction between ethyl and hydrogen. Consequently, cyclization to give **2a** should be preferred and *cis*-2-butene which arises from decomposition of **2a** should be the kinetically favored product. Similarly, the greater stability of **3a** relative to **3b** explains the preferred formation of *trans*-2-butene from *trans*-2-pentene.[18]

A study of the reactions of cis and trans disubstituted alkenes with an isolable metal-carbene complex in which the carbene ligand possesses one sterically large and one sterically small substituent is essential to test the stereochemical implication of a puckered metallocyclobutane intermediate. The puckered metallocyclobutane hypothesis predicts that the "large-small" metal carbene system will react with cis alkenes to give new cis olefins and with trans alkenes to give new trans olefins. In addition, the preferential formation of *cis*-cyclopropanes from the reaction of a "large-small" carbene complex with a 1-alkene would be expected. The reactions of $(CO)_5WC(C_6H_4\text{-}p\text{-}CH_3)_2$ with alkenes indicate that the least substituted end of an alkene becomes transferred to the carbene ligand;[12] therefore, the central carbon of the metallocyclobutane would be expected to be the least substituted carbon atom.

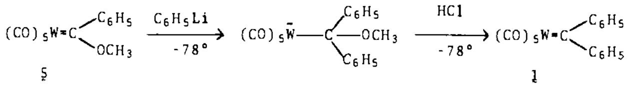
We have now begun model studies designed to account for the stereoselectivity observed in the metathesis reaction. Here we report the generation and reactions of a "large-small" carbene complex, $(CO)_5WC(CH_3)C_6H_5$ (**4**).[19] While **4** decomposes at low temperature to give styrene and the less stable *cis*-1-methyl-1,2-diphenylcyclopropane expected from consideration of the most stable metallocyclobutane, detailed studies of this reaction indicate that the cyclopropane does not arise via an intermediate metallocyclobutane.

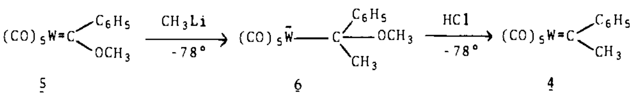
Scheme III

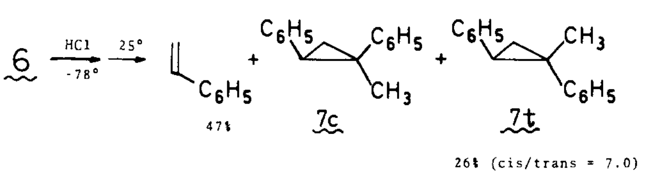


Results and Discussion

Generation of $(CO)_5WC(CH_3)C_6H_5$ (4). Our attempted synthesis of the "large-small" carbene complex (phenylmethylcarbene)pentacarbonyltungsten(0) (**4**) was patterned after the preparation of $(CO)_5WC(C_6H_5)_2$ (**1**). CH_3Li was added to an ether solution of $(CO)_5WC(OCH_3)C_6H_5$ (**5**) at −78 °C. The orange color of **5** faded over 30 min to give a yellow homogeneous solution of the 1:1 adduct $(CO)_5WC(OCH_3)(CH_3)(C_6H_5)^-$ (**6**), which was characterized by spectral data (vide infra). One equivalent of HCl in ether was added to the solution of **6** at −78 °C in order to eliminate methanol and form the desired carbene complex, **4**. A deep red color similar to that of the diphenylcarbene complex, **1**, formed immediately upon addition of HCl. While **1** is a stable compound and has been isolated by column chromatography, the red color attributable to **4** faded within 30 min at −78 °C. The products observed after warming the reaction mixture to room temperature were styrene (47%), which is formally a hydrogen shift product of phenylmethylcarbene, and *cis*- and *trans*-1-methyl-1,2-diphenylcyclopropane (26%), **7c** and **7t**, which are formally the cyclopropanation products of phenylmethylcarbene and styrene. The thermodynamically *less stable* cis isomer **7c** was the major isomer present with a cis/trans ratio of 7.0.







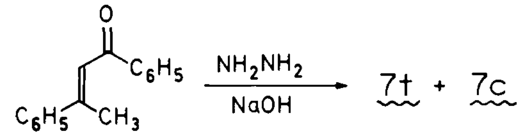
Stereochemical Assignment of 7c and 7t. Since the stereochemical assignment of cyclopropanes **7c** and **7t** was critical in relation to the puckered metallocyclobutane hypothesis for the stereospecificity of olefin metathesis, a rigorous assignment of stereochemistry was required.[20] A 1:2 mixture of **7c** and **7t**

Table I. Variation of Cyclopropane Yield with Amount of Added HCl

$(CO)_5WC(OCH_3)C_6H_5$ (**5**)	Active CH_3Li (mmol)	Total base (mmol)	Added HCl (mmol)	(equiv)[a]	% **7**[d]	Cis/trans	% styrene[e]
0.217[b]	0.24	0.30	0.08	0.00	7	2.3	44
0.238[b]	0.26	0.33	0.14	0.20	8	4.6	57
0.246[b]	0.30	0.37	0.25	0.50	45	5.6	27
0.227[b]	0.25	0.31	0.25	0.74	36	3.4	26
0.232[b]	0.26	0.32	0.32	1.00	26	7.0	47
0.176[c]	0.22	0.29	0.28	0.94	57	4.2	12

[a] An equivalent of HCl = [mmol of added HCl − (mmol of total base − mmol of **5**)]/mmol of **5**. [b] Dry HCl in ether added in ~15 s. [c] Dry HCl in ether added in 16 aliquots, each after allowing the dark red color to fade. [d] Yields shown are GC yields based on octadecane internal standard. [e] Yields shown are GC yields based on undecane internal standard.

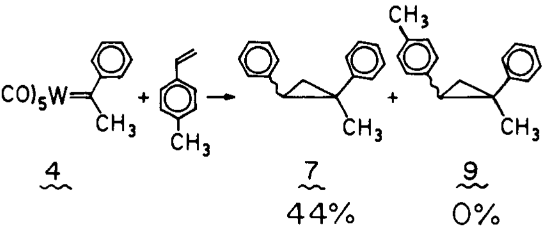
was prepared from dypnone and hydrazine using Newman's procedure.[21] The stereochemical assignments were made on



the basis of (1) NMR chemical shifts, (2) equilibration, and (3) stereospecific synthesis of **7t**. In the NMR spectra of cyclopropanes, methyl groups cis to a phenyl group resonate at higher field than methyl groups trans to a phenyl group.[22] The methyl resonances of **7c** at δ 1.52 and of **7t** at δ 1.11 support the assigned stereochemistry. Equilibration of **7c** (99.1% isomeric purity), **7t** (98.6% isomeric purity), and a mixture of **7t** and **7c** (**7t**/**7c** = 1.9) with a KOH/Me_2SO solution at 100 °C for 20 h gave in all cases 70 ± 1% of trans isomer **7t** and 30 ± 1% of cis isomer **7c**.[23] **7t** was synthesized stereospecifically from *E*-1,2-diphenylpropene[24] via the Rawson-Harrison[25] variation of the Simmons-Smith[26] procedure.

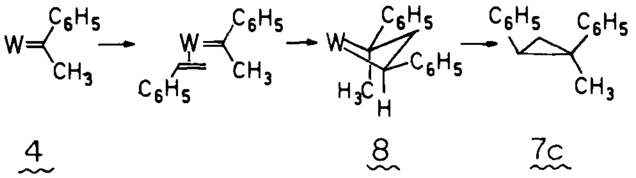
Crossover Experiments with Styrene. The preferential formation of the thermodynamically less stable **7c** from the reaction of **4** was intriguing in that it was consistent with the intermediacy of a puckered metallocyclobutane, **8**, having the sterically large phenyl groups in equatorial positions (Scheme IV). The aryl substituted carbon of the alkene would be expected to bond preferentially to the metal in light of the reactions of $(CO)_5WC(C_6H_4\text{-}p\text{-}CH_3)_2$ with styrene which led predominantly to $CH_2{=}C(C_6H_4\text{-}p\text{-}CH_3)_2$.[12] The reaction of **4** with styrene, possible via an intermediate tungsten-carbene-alkene complex, could give metallocyclobutane, **8**. Reductive elimination from **8** would give **7c**.

To test this hypothesis, **4** was generated in the presence of *p*-methylstyrene. No 1-methyl-1-phenyl-2-*p*-tolylcyclopropane (**9**) (<0.25%), the expected cross product from the reaction of **4** with added *p*-methylstyrene, was obtained. Only cyclopropanes **7c** and **7t** (44%) arising entirely from the carbene complex **4** were observed. These results indicate that styrene is not a precursor of cyclopropanes **7c** and **7t**.



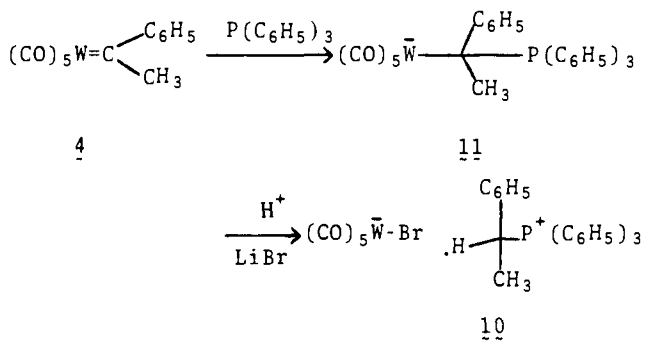
HCl Dependence. When **4** was generated by the addition of HCl to **6**, the yields of styrene and cyclopropane **7** were found to vary as a function of the amount and rate of addition of HCl (Table I). When the HCl was added rapidly (~15 s), an apparent maximum in the yield of cyclopropane **7** (45%) was obtained with ~0.5 equiv of HCl. This indicates that only 0.5 equiv of **4** is required to produce the maximum amount of **7**. In another experiment slow addition of HCl, accomplished by the addition of small aliquots and allowing the red color of **4** to fade, resulted in an even higher yield of **7** (58%). This experiment in effect keeps the concentration of anionic intermediate **6** high during the reaction and suggests that **6** might be involved in the formation of **7**. No correlation between the rate or amount of HCl added in the reaction and the ratio of **7c** to **7t** could be found, as the **7c**/**7t** ratio varied between runs but was always greater than or equal to those shown in Table I.

Scheme IV



Characterization of Intermediates. In an attempt to observe intermediates, the reaction mixtures were examined at low temperature by NMR. Addition of CH_3Li to a solution of **5** in THF-d_8 at −78 °C produced a yellow homogeneous solution of which a spectrum was observed at −63 °C which was consistent with the structure of $(CO)_5WC(OCH_3)(CH_3)C_6H_5^-$ (**6**). A unique aromatic proton at δ 6.45 was upfield of the other aromatic protons at δ 6.95. This is similar to the spectrum of $(CO)_5WCH_2C_6H_5^-$ [27] in which the para proton (δ 6.49, m, 1 H) is upfield of the ortho and meta protons (δ 6.95, m, 4 H). The methoxy resonance of **5** appears at δ 4.88 which is characteristic of a partial positive charge on the oxygen, while the methoxy resonance of **6** appears at δ 2.84 which is indicative of the negative charge on the molecule. The $C\text{-}CH_3$ group of **6** appears at δ 2.12. The room temperature NMR spectrum of **6** was the same as the spectrum obtained at −63 °C. The IR spectrum of this solution at 25 °C had bands at 2039 (w), 1939 (w), 1893 (s), and 1842 (m) cm^{-1}. This is similar to the infrared spectrum of the pentacarbonyltungsten anion $(CO)_5WCH_2C_6H_5^-$:[27] 2036 (w), 1937 (w), 1893 (s), 1846 (m) cm^{-1}.

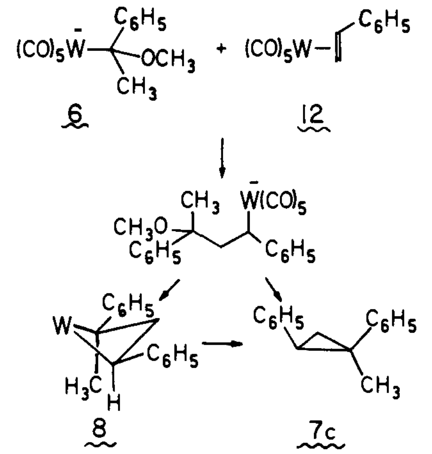
Addition of CF_3CO_2H to the solution of anion **6** at −78 °C produced a deep red color which faded too rapidly to observe any spectral evidence for the carbene complex **4**. An attempt to trap **4** with $P(C_6H_5)_3$ was made by adding an ether solution of $P(C_6H_5)_3$ to a solution of **4** at −78 °C. The deep red color of **4** immediately faded to yellow and a yellow precipitate was formed upon warming to room temperature. Recrystallization of the yellow solid from CH_2Cl_2/hexane gave $P(C_6H_5)_3CH(C_6H_5)CH_3^+(CO)_5WBr^-$ (**10**) (15%) which could arise from the protonation of **11**, the $P(C_6H_5)_3$ adduct of **4**.[28] The IR of **10** in THF had bands at 2065 (w), 1953 (w), 1922 (s), and 1859 (m) cm^{-1} which is similar to that reported



for $(CH_3CH_2)_4N^+(CO)_5WBr^-$ in THF[27]: 2068 (w), 1955 (w), 1918 (s), 1859 (m) cm^{-1}. The NMR ($CDCl_3$) of **10** was similar to that of $P(C_6H_5)_3CH(C_6H_5)CH_3{}^+Br^-$ with the major difference being the chemical shift of the methine proton, δ 5.14 for **10** with $(CO)_5WBr^-$ as a counterion and δ 6.51 with Br^- as the counterion.

The NMR spectrum at −63 °C of the yellow homogeneous solution resulting from the decomposition of **4** indicated the presence of (π-styrene)pentacarbonyltungsten(0) (**12**), as determined by comparison with an authentic sample. An authentic sample of **12** was obtained by the photolysis at 3500 Å of a solution of styrene and $W(CO)_6$ in hexane. Removal of the hexane in vacuo followed by sublimation under high vacuum at 40 °C gave **12** (36%). The NMR shifts of the vinyl protons in **12** were substantially different from those of free styrene: in going from free styrene to its $W(CO)_5$ complex, the shift of the α-vinyl hydrogen changes from δ 6.61 to 6.08, the shift of the cis β-vinyl hydrogen changes from δ 5.63 to 4.82, and the shift of the trans β-vinyl hydrogen changes from δ 5.08 to 4.23. The presence of **12** which was found to be stable in THF below 0 °C indicated the possibility that styrene complex **12** might be a precursor to the cyclopropane **7**. For example, attack of the tungsten anion **6** on the tungsten olefin complex **12** could lead to cyclopropane formation (Scheme V).

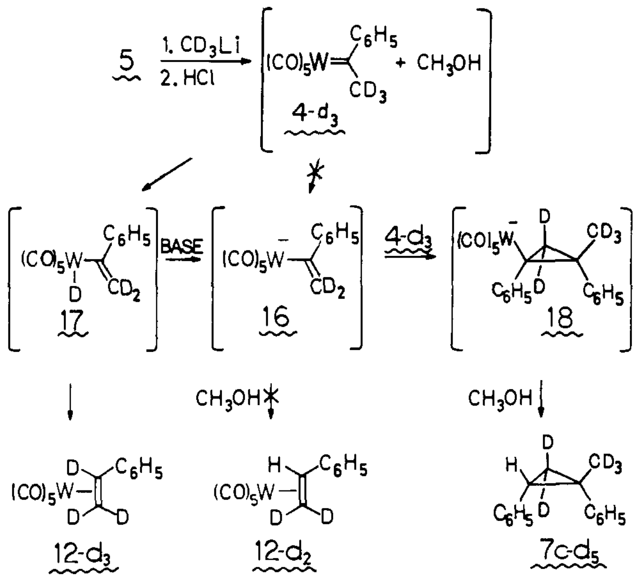
Scheme V

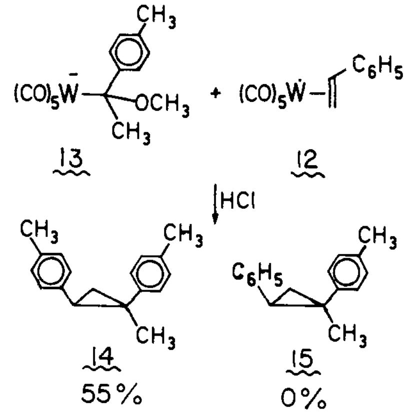


Crossover Experiment with Tungsten–Styrene Complex. To determine whether the tungsten–styrene complex **12** was a precursor of cyclopropane **7**, solutions of $(CO)_5WC(OCH_3)(CH_3)(C_6H_4\text{-}p\text{-}CH_3)^-$ (**13**) and **12** were mixed at −78 °C, and HCl was added. Analysis of the cyclopropanes indicated that only 1-methyl-1,2-di-*p*-tolylcyclopropane (**14**) (55%) resulting from **13** was formed. None of the cross product incorporating styrene, 1-methyl-1-*p*-tolyl-2-phenylcyclopropane (**15**) (<0.5%) was detected. This demonstrates that the tungsten–styrene complex, **12**, is not a precursor of cyclopropanes in these reactions.

Deuterium Labeling Experiments. To test for the possibility that the tungsten–styrene complex, **12**, might be formed via protonation of the anion, **16**, of carbene complex **4**, the reactions of the deuterated carbene complex **4-*d*₃** in the presence of CH_3OH were studied. If carbene anion **16** were an intermediate, a β,β-dideuterated styrene complex would be obtained (Scheme VI). Addition of CD_3Li to **5** followed by HCl gave styrene (>95% d_3) and **7c** (98 ± 2% d_5). The deuterium in **7c-*d*₅** was located in the methyl group and in the methylene group of the cyclopropane.

Scheme VI



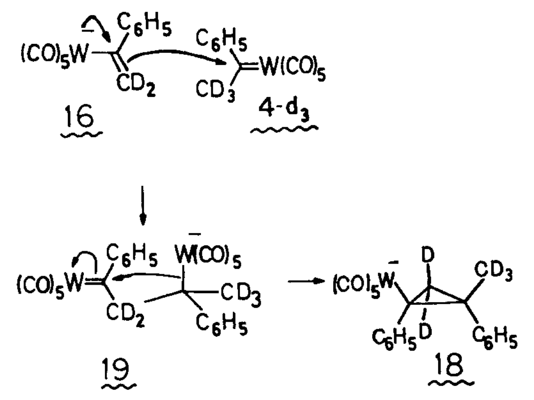


The formation of styrene-d_3 from $(CO)_5WC(CD_3)C_6H_5$ (**4-*d*₃**) rules out the intervention of carbene anion **16** in the formation of styrene. The complete retention of label in styrene-d_3 indicates an intramolecular hydrogen shift. This is consistent with a β-hydride elimination to give an (α-styryl)-tungsten(II) hydride intermediate, **17**, followed by reductive elimination from **17** to give the tungsten-olefin complex, **12-*d*₃**.

The formation of cyclopropane **7c-*d*₅** from **4-*d*₃** confirms the previous results that cyclopropane is not formed from any styrene precursor, as the styryl fragment of the cyclopropane is dideuterated, while the styrene produced in the reaction is trideuterated. The presence of cyclopropane **7-*d*₅** also implicates a (cyclopropyl)tungsten anion, **18**, as a precursor to cyclopropane. The presence of **18** also explains the preferential formation of the thermodynamically less stable cis isomer, **7c.** In the more stable isomer of **18**, the bulky $W(CO)_5$ group is trans to the β-phenyl ring. Protonation of this isomer leads to the observed *cis*-cyclopropane, **7c.**

Proposed Mechanism. The formation of the cyclopropyltungsten anion **18** can be explained by a mechanism consistent with the observed data (Scheme VII). The (α-styryl)-

Scheme VII



tungsten(II) hydride intermediate, **17**, formed by a β-hydride elimination from **4** could either reductively eliminate to give the styrene complex **12** or in the presence of a base such as **6** could deprotonate to give an (α-styryl)tungsten anion **16**. Anions generated α to oxygen stabilized carbene complexes are stable species[29] and are reactive toward electrophiles.[30] The carbene carbon atom of alkoxy substituted carbene complexes is electrophilic and is subject to attack by nucleophiles such as lithium reagents,[1,31] amines,[32] and phosphines.[33] Therefore the attack of the nucleophilic carbene anion **16** on the electrophilic carbene carbon atom of **4** appears reasonable.[34] The resulting adduct **19** can close to the (cyclopropyl)tungsten anion **18** with loss of $W(CO)_5$. At this point only 0.5 equiv of acid has been consumed in forming the maximum yield of **18**. Protonation of **18** would then lead to the observed *cis*-cyclopropane, **7c**.

Initially, we attempted to prepare **4**, a nonheteroatom stabilized carbene complex with a sterically large and small substituent, to use as a model compound for studies of stereospecificity of the olefin metathesis reaction. However, **4** decomposed more rapidly than it reacted with olefins, and metallocyclobutanes were shown not to be intermediates in its decomposition. The extreme instability of **4** was traced to the high reactivity of the methyl hydrogens which readily underwent β-elimination. We are now studying preparations of $(CO)_5WCH(C_6H_5)$ which is not subject to decomposition by a similar pathway and which may prove useful in model studies of the stereospecificity of the olefin metathesis reaction.

Experimental Section

General. All reactions involving organometallic reagents were carried out in flame dried flasks under a nitrogen atmosphere. Ether and THF used for solvents were distilled from sodium and benzophenone under a nitrogen atmosphere prior to use. Solutions were transferred by syringe or cannula (hypodermic wire) under positive nitrogen pressure. Melting points, determined on a Thomas Hoover capillary melting point apparatus, and boiling points are uncorrected. NMR spectra were recorded on a Jeolco MH-100 or Bruker WH-270 spectrometer. Chemical shifts are reported in δ downfield from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 267 spectrometer in the solvent specified and are reported in wavenumbers (cm^{-1}). Mass spectra were recorded on an AE 1-MS-903 mass spectrometer at 70 eV unless otherwise noted. Analytical vapor phase chromatography was carried out on either a Hewlett-Packard 5750 or 5700A gas chromatograph with flame ionization detector and either disk integrator or Hewlett-Packard 3380A integrator-recorder. Preparative vapor phase chromatography was carried out on a Varian Aerograph 90P gas chromatograph with a thermal conductivity detector. Photolyses were carried out in a Srinivasan-Griffin photochemical reactor at 3500 Å. Methyllithium was purchased from Alpha-Ventron and titrated prior to use.

Reaction of $(CO)_5WC(OCH_3)C_6H_5$, 5, with CH_3Li Followed by HCl. A series of experiments was carried out to determine the effect of varying amounts of added HCl on the yields of products. CH_3Li (0.77 mL, 0.39 M active base, 0.30 mmol active base, 0.49 M total base, 0.38 mmol total base) was added slowly to a solution of **5** (109 mg, 0.246 mmol) in 6 mL of ether at −78 °C. The orange color of **5** faded over 30 min to give a yellow homogeneous solution. Dry HCl in ether (0.89 mL, 2.82 M, 0.25 mmol, 0.5 equiv) was added in ~15 s. A deep red color resulted immediately but faded to yellow within 15 min. The reaction mixture was warmed to room temperature and quenched with 2 mL of water. GC analysis (10% UC W-98, 20 in. × ⅛ in.) showed 27% styrene (65 °C, undecane internal standard) and 45% 1-methyl-1,2-diphenylcyclopropane (**7**), cis/trans = 5.6 (150 °C octadecane internal standard). Styrene and cyclopropanes **7c** and **7t** were identified by GC retention times, and NMR spectra of samples collected by preparative GC (20% UC W-98 and 10– QF-1) were identical with those of authentic samples.

Yields of similar runs using 0.0, 0.20, 0.74, and 1.0 equiv of HCl are listed in Table I.

Another experiment was carried out to observe the effect of slow addition of HCl to **6** on the yields of products. CH_3Li (0.71 mL, 0.32 M active base, 0.23 mmol of total base, 0.41 M total base, 0.29 mmol of total base) was added slowly to a solution of **5** (78 mg, 0.176 mmol) in 4 mL of ether at −78 °C giving a yellow homogeneous solution of **6**. Small aliquots of dry HCl in ether (6.2 μL, 2.82 M, 0.017 mmol) were added successively forming a deep red color which was allowed to fade. The additions were repeated until the final addition of HCl produced no color change (16 additions, 99.2 μL, 0.28 mmol). The time for the deep red color to fade was steady for additions 1 through 4 (2–3 s), increased slightly for additions 5 through 7 (12–22 s), and increased rapidly for additions 6 through 16 (61–346 s). The reaction mixture was then warmed to room temperature and quenched with 2 mL of water. GC analysis (10% UC W-98, 20 in. × ⅛ in.) showed 12% styrene (78 °C, undecane internal standard) and 57% 1-methyl-1,2-diphenylcyclopropane (**7**), cis/trans = 4.2 (159 °C, octadecane internal standard).

Crossover Experiment with Styrene. *p*-Methylstyrene (0.50 mL, 3.80 mmol) was added to a solution of **5** (87 mg, 0.20 mmol) in 6 mL of ether and cooled to −78 °C. CH_3Li (0.93 mL, 0.39 M active base, 0.36 mmol of active base, 0.49 M total base, 0.46 mmol of total base) was added to the solution and stirred for 15 min to give a yellow homogeneous solution. Dry HCl in ether (0.89 mL, 2.82 M, 0.25 mmol) was added over ~15 s. A deep red color formed immediately and faded to yellow in 15 min. The reaction mixture was warmed to room temperature and quenched with 2 mL of water. GC analysis (10% UC W-98, 20 in. × ⅛ in.) showed 28% styrene (65 °C, undecane internal standard) and 44% 1-methyl-1,2-diphenylcyclopropane (**7**), cis/trans = 22 (150 °C, octadecane internal standard). No 1-methyl-1-phenyl-2-*p*-tolylcyclopropane (**9**) (<0.25%) could be detected.

Crossover Experiment with Tungsten–Styrene Complex 12. CH_3Li (1.96 mL, 0.14 M active base, 0.27 mmol of active base, 0.32 M total base, 0.62 mmol of total base) was added slowly to a solution of $(CO)_5WC(OCH_3)(C_6H_4\text{-}p\text{-}CH_3)$ (115 mg, 0.25 mmol) in 10 mL of ether at −78 °C and stirred for 0.5 h to give a yellow homogeneous solution of $(CO)_5WC(OCH_3)(CH_3)(C_6H_4\text{-}p\text{-}CH_3)^-$ (**13**). (Styrene)$W(CO)_5$ (**12**) (120 mg, 0.28 mmol) was dissolved in ether at −23 °C, cooled to −78 °C, transferred to the flask containing the tungsten anion **13**, and stirred for 15 min. Ten 25-μL aliquots of HCl in ether (0.25 mL, 2.50 M, 0.63 mmol) were added successively allowing the deep red color to fade between additions. The reaction mixture was warmed to room temperature and quenched with 5 mL of water. GC analysis (10% UC W-98, 10 ft × ⅛ in., 187 °C, octadecane internal standard) showed 55% *cis*-1-methyl-1,2-di-*p*-tolylcyclopropane (**14c**) and no detectable 1-methyl-1-*p*-tolyl-2-phenylcyclopropane (**15**) (<0.5%).

Generation of $(CO)_5WC(CD_3)C_6H_5$, 4-d_3. CD_3Li (3.50 mL, 0.40 M active base, 1.40 mmol of active base, 0.45 M total base, 1.57 mmol of total base) made from iodomethane-d_3 and lithium metal was added to a solution of **5** (497 mg, 1.12 mmol) in 20 mL of ether at −78 °C and stirred to give a yellow solution. Sixteen 40-μL aliquots of HCl in ether (0.64 mL, 2.82 M, 1.80 mmol) were added successively allowing the red color formed to fade between additions. The reaction mixture was warmed to room temperature and quenched with water. The ether layer was separated and concentrated. *cis*-1-Methyl-1,2-diphenylcyclopropane (**7c-d_5**) was collected by preparative GC (10% QF-1, 5 ft × ¼ in., 170 °C). NMR (CCl_4) δ 6.9 (m, 8 H), 6.6 (m, 2 H), 2.11 (br s, 1 H, benzylic cyclopropyl). Mass spectral analysis (14 eV) showed 98 ± 2% d_5 and 2 ± 2% d_4 cyclopropane.

In a similar experiment CD_3Li (3.15 mL, 0.40 M active base, 0.45 M total base, 1.42 mmol of total base) was added to a solution of **5**

(505 mg, 1.14 mmol) in 15 mL of ether at −78 °C and stirred to give a yellow homogeneous solution. HCl in ether (0.50 mL, 2.82 M, 1.41 mmol) was added to the solution to form a deep red color which faded to yellow <45 min. The reaction mixture was warmed to room temperature and quenched with aqueous $NaHCO_3$. The ether layer was separated. The volatile material was bulb to bulb distilled under high vacuum, and then concentrated. Styrene-d_3 was then collected by preparative GC (20% UC W-98, 20 in. × ⅜ in., 55 °C). NMR (CCl_4): δ 7.2 (m). No vinyl protons were seen (<5%).

Spectral Observation of $(CO)_5WC(OCH_3)(CH_3)C_6H_5^-$ (6). CH_3Li (0.06 mL, 1.02 M active base, 0.061 mmol of active base, 1.06 M total base, 0.064 mmol of total base) was added to an orange THF-d_8 solution of **1** (23 mg, 0.052 mmol) at −78 °C in an NMR tube and mixed until a yellow color resulted. A spectrum of **6** was recorded on a WH-270 Bruker NMR spectrometer at probe temperature −63 °. NMR (THF-d_8): δ 6.95 (m, 4 H, *o*- and *m*-H), 6.45 (m, 1 H, *p*-H), 2.84 (s, 3 H, O-CH_3), 2.16 (s, 3 H, C-CH_3). No change was observed upon warming the sample to room temperature. IR (THF): 2039 (w), 1939 (w), 1893 (s), 1842 (m) cm^{-1}.

Spectral Observation of $(CO)_5W$(styrene) (12) from 4. Trifluoroacetic acid (8 μL, 0.108 mmol) was added to the THF-d_8 solution of **6** at −78 °C. The initial deep red color rapidly faded to yellow to give a spectrum at −63 °C containing the tungsten styrene cmplex **12** by comparison with an authentic sample.

(Styrene)$W(CO)_5$ (12). A solution of styrene (59 mg, 5.70 mmol) and tungsten hexacarbonyl (500 mg, 1.42 mmol) in 50 mL of hexane was photolyzed at 3500 Å for 4.5 h in a Pyrex tube until 23.6 mL of carbon monoxide (0.96 mmol) had evolved. The hexane was removed under aspirator vacuum giving a yellow residue which was sublimed at 40 °C (0.05 mm) to give moderately air sensitive crystals of **12** (22 mg, 0.51 mmol, 36%). IR (heptane): 2082 (m), 1971 (s), 1955 (vs) cm^{-1}. NMR (THF-d_8, −79 °C, Bruker-270): δ 7.51 (d, J = 6.5 Hz, 2 H, *o*-H), 7.37 (t, $J \sim$ 7 Hz, 2 H, *m*-H), 7.22 (t, J = 7.3 Hz, 1 H, *p*-H), 6.08 (d of d, J = 15.1, 9.9 Hz, $H(C_6H_5)C{=}C$), 4.82 (d, J = 15.1 Hz, 1 H, cis vinyl H), 4.23 (d, J = 9.9 Hz, 1 H, trans vinyl H). The complex was found to be stable in THF up to 0 °C. Above 0 °C, the decomposition of **12** to free styrene was observed.

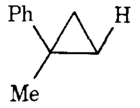
Reaction of $(CO)_5WC(CH_3)C_6H_5$ (4) with $P(C_6H_5)_3$. CH_3Li (1.12 mL, 1.23 M active base, 1.38 mmol of active base, 1.46 M total base, 1.64 mmol of total base) was added to a solution of **5** (556 mg, 1.25 mmol) in 10 mL of ether at −78 °C. CF_3CO_2H (0.12 mL, 1.64 mmol) was added to the solution and stirred 1 min to give a deep red solution. $P(C_6H_5)_3$ (262 mg, 1.64 mmol) in ether at −78 °C was transferred to the reaction mixture. The red color immediately faded to yellow and a yellow precipitate formed upon warming to room temperature. Recrystallization from CH_2Cl_2/hexane at −25 °C gave yellow crystals of $P(C_6H_5)_3CH(C_6H_5)CH_3^+(CO)_5WBr^-$ (**10**) (143 mg, 15%), mp 130–135 °C dec. NMR ($CDCl_3$): δ 7.6 (m, 18 H), 6.97 (br d, $J \sim$ 7 Hz, 2 H), 5.14 (d of q, J = 14, 7 Hz, 1 H), 1.91 (d of d, J = 18, 7 Hz, 3 H). IR(THF): 2065 (w), 1953 (w), 1922 (s), 1859 (m) cm^{-1}. Anal. Calcd for $C_{31}H_{24}BrO_5PW$: C, 48.28; H, 3.14; Br, 10.36; P, 4.01; W, 23.84. Found: C, 48.31; H, 3.30; Br, 10.57; P, 3.86; W, 23.71.

A sample of $P(C_6H_5)_3CH(C_6H_5)CH_3^+Br^-$ was prepared in 88% yield from $P(C_6H_5)_3$ and $C_6H_5CHBrCH_3$ in refluxing xylene[36] for comparison of NMR spectra. NMR ($CDCl_3$): δ 7.7 (m, 15 H), 7.16 (br s, 5 H), 6.51 (d of q, J = 14, 7 Hz, 1 H), 1.81 (d of d, J = 19, 7 Hz, 3 H).

***cis*- and *trans*-1-Methyl-1,2-diphenylcyclopropane (7c and 7t).**[20] Following a procedure similar to Newman's,[21] 1,3-diphenyl-2-butene-1-one (dypnone, 4.4 g, 0.02 mol), sodium hydroxide (3 g, 0.13 mol), hydrazine (97%, 3 mL, 2.94 g, 0.092 mol), and 45 mL of diethylene glycol were heated to 160 °C for 2 h. Solvent and water were removed by distillation until ~5 mL of water was collected. The temperature was then maintained at reflux (~180–200 °C) for 20 h. Cooling to room temperature and addition of 150 mL of water caused an oil to separate which was extracted into ether. The ether layer was washed with water and saturated sodium chloride and dried (K_2CO_3). Distillation of the residue gave a mixture of **7c** and **7t** (2.9 g, 70%, bp 83–89 °C at 0.05 mmHg, lit.[20] 83–90 °C at 0.05 mmHg). **7c** and **7t** were separated by preparative gas chromatography (10% QF-1, 5 ft × ¼ in., 150 °C).

7c (shorter retention time). NMR ($CDCl_3$): δ 7.0 (m, 8 H), 6.75 (m, 2 H), 2.21 (d of d, J = 8.7, 6.1 Hz, 1 H, CH), 1.52 (s, 3 H, CH_3), 1.50 (m, 1 H, partially obscured by s at 1.52, A), 1.24 (d of d, J = 8.7, 5.0 Hz, 1 H, B). Exact mass: 208.1246 (calcd for $C_{16}H_{16}$, 208.125 29).

7t (longer retention time). NMR ($CDCl_3$): δ 7.3 (m, 10 H), 2.41 (d of d, J = 8.8, 6.3 Hz, 1 H, CH), 1.45 (d of d, J = 8.8, 5.0 Hz, 1 H, A), 1.24 (d of d, J = 6.3, 5.0 Hz, 1 H, B), 1.11 (s, 3 H, CH_3). Exact mass: 208.1239 (calcd. for $C_{16}H_{16}$, 208.125 29).



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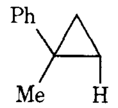


B

Equilibration of *cis*- and *trans*-1-Methyl-1,2-diphenylcyclopropane.[23] The 1-methyl-1,2-diphenylcyclopropane synthesized by the method of Newman[21] was found to consist of 34.5% cis and 65.5% trans isomers by gas chromatograph (10% UC W-98, 6 ft × ¼ in., 190 °C). A sample of this mixture (39.5 mg, 0.190 mmol) and 1.0 mL of a solution prepared from potassium *tert*-butoxide (497.9 mg, 4.44 mmol) in 4.5 mL of dimethyl sulfoxide were heated to 100 °C in a sealed tube for 20 h. GC analysis indicated 70.5% **7t** and 29.5% **7c** (29.0 mg, 74% recovered).

A sample of **7c** (20 mg, 0.096 mmol) was isolated by preparative gas chromatography (10% QF-1, 5 ft × ¼ in., 150 °C, 200 mL/min) and found to be 99.1% *cis*- and 0.9% *trans*-1-methyl-1,2-diphenylcyclopropane by analytical GC (10% UC W-98, 6 ft × ¼ in., 190 °C). After equilibration GC analysis indicated 69.1% **7t** and 30.9% **7c** (29% recovered).

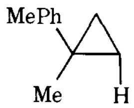
A sample of trans isomer **7t** (42 mg, 0.202 mmol) was collected by preparative GC and was found to be 98.6% **7t** and 1.4% **7c** by analytical GC (10% UC W-98). After equilibration GC analysis indicated 69.6% **7t** and 30.4% **7c** (41% recovered).

(*E*)-1,2-Diphenylpropene (20).[24] Reaction of benzylmagnesium chloride prepared from magnesium (5.3 g, 0.218 mol) and benzyl chloride (25.0 g, 0.198 mol) with acetophenone (15 g, 0.125 mol) gave 1,2-diphenyl-2-propanol which was dehydrated by refluxing in 20% H_2SO_4. Recrystallization from absolute ethanol gave (*E*)-1,2-diphenylpropene, **20** (8.0 g, 33%, mp 78.5–80 °C). NMR (CCl_4): δ 7.2 (m, 10 H), 6.72 (q, J = ~1 Hz, 1 H), 2.22 (d, J = ~1 Hz, 3 H). UV (CH_3CH_2OH): 271 (ϵ 2.09 × 10^4) indicates this to be the *E* isomer.[35] GC analysis indicates >99.9% isomeric purity.

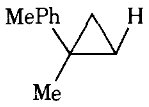
***trans*-1-Methyl-1,2-Diphenylcyclopropane (7t).** Following the Rawson-Harrison procedure,[25] zinc dust (17.0 g, 0.26 mol), cuprous chloride (3.4 g, 0.343 mol), and 40 mL of ether were refluxed 1 h. (*E*)-1,2-Diphenylpropene, **20** (2 g, 0.0103 mol) and diiodomethane (11.0 mL, 36.6 g, 0.137 mol) were added. After 10 h at reflux additional CH_2I_2 (11.0 mL, 0.137 mol) was added. After an additional 15 h at reflux, the reaction mixture was quenched with water and the ether layer separated, washed with 10% HCl, water, and saturated $NaHCO_3$, and dried (K_2CO_3). Distillation gave *trans*-1-methyl-1,2-diphenylcyclopropane (**7t**) (0.8 g, 37%; bp 82–90 °C, 0.05 mm). GC analysis indicates 99% isomeric purity. The NMR spectrum of **7t** was identical with the spectrum of **7t** prepared by the method of Newman.[21] Exact mass: 208.1247 (calcd for $C_{16}H_{16}$, 208.125 29).

***cis*- and *trans*-1-Methyl-1,2-di-*p*-tolylcyclopropane (14c and 14t).** Following the procedure outlined for **7c** and **7t**, the reaction of 1,3-di-*p*-tolyl-2-butene-1-one[37] (5.00 g, 20.0 mmol), 97% hydrazine (3.0 mL, 0.092 mol), and crushed sodium hydroxide gave **14c** and **14t** (3.15 g, 67%). GC analysis (10% UC W-98, 20 in. × ⅛ in., 155 °C) showed 68.5% *trans*- and 31.5% *cis*-1-methyl-1,2-di-*p*-tolylcyclopropane (**14t** and **14c**). Samples of **14t** and **14c** were collected by preparative GC (10% QF-1, 5 ft × ¼ in., 155 °C) for spectral identification.

14c (shorter retention time). NMR (CCl_4): δ 6.83 (s, 4 H), 6.72 (d, J = 8 Hz, 2 H), 6.48 (d, J = 8 Hz, 2 H), 2.22 (s, 3 H, $ArCH_3$), 2.18 (s, 3 H, $ArCH_3$), 2.06 (d of d, J = 8.9, 6.2 Hz, 1 H, CH), 1.47 (s, 3 H, CH_3), 1.36 (m, 1 H, partially obscured by s at δ 1.47, D), 1.13 (d of d, J = 8.9, 4.6 Hz, 1 H, C). Exact mass: 236.1574 (Calculated for $C_{18}H_{20}$ 236.1565).



C



D

14t (longer retention time). NMR (CCl_4): δ 7.10 (d, J = 8 Hz, 2 H), 6.99 (br s, 4 H), 6.94 (d, J = 8 Hz, 2 H, partially obscured by s at δ 6.99), 2.30 (s, 6 H, $ArCH_3$), 2.24 (d of d, 1 H, partially obscured by s at δ 2.30, CH), 1.29 (d of d, J = 8.6, 4.9 Hz, D), 1.05 (m, 1 H, partially obscured by s at δ 1.03, C), 1.03 (s, 3 H, CH_3). Exact mass: 236.1571 (calcd for $C_{18}H_{20}$ 236.1565).

(*E*)-1-*p*-Tolyl-2-phenylpropene (21).[24] Reaction of *p*-methylbenzylmagnesium bromide made from magnesium (4.86 g, 0.20 mol) and α-chloro-*p*-xylene (28.1 g, 0.20 mol) with acetophenone (20.0 g, 0.16 mol) gave 1-*p*-tolyl-2-phenyl-2-propanol which was dehydrated by refluxing in 20% H_2SO_4. Recrystallization from absolute ethanol gave (*E*)-1-*p*-tolyl-2-phenylpropene (**21**) (3.02 g, 9%, mp 53-54 °C). NMR ($CDCl_3$): δ 7.15 (m, 9 H), 6.66 (br s, 1 H, vinyl H), 2.28 (s, 3 H, Ar-CH_3), 2.21 (d, J = 1 Hz, 3 H). UV (CH_3CH_2OH): 276 ($\epsilon = 1.89 \times 10^4$).[35] GC analysis showed >96% isomeric purity.

(*E*)-1-Methyl-1-phenyl-2-*p*-tolylcyclopropane (9E). Using the same procedure as for **7t**, **21** was converted to (*E*)-1-methyl-1-phenyl-2-*p*-tolylcyclopropane (**9E**) (39%, bp 105-125 °C, 0.15 mmHg). GC analysis showed >98% isomeric purity but indicated the presence of 10% impurities. Samples for spectral data were collected by preparative GC (10% QF-1, 5 ft × ¼ in., 155 °C). NMR (CCl_4): δ 7.15 (m, 9 H), 2.33 (s, 3 H, ArCH_3), 2.32 (d of d, J = 8.8, 6.2 Hz, 1 H, partially obscured by s at δ 2.33, CH), 1.36 (d of d, J = 8.8, 5.0 Hz, 1 H, A), 1.11 (d of d, J = 6.2, 5.0 Hz, 1 H, partially obscured by s at δ 1.08, B), 1.08 (s, 3 H, CH_3). Exact mass: 222.140 79 (calcd for $C_{17}H_{18}$ 222.140 85).

Equilibration of 9E and 9Z.[23] **9E** (99 mg, 0.45 mmol) and a 1.5-mL solution of potassium *tert*-butoxide (489 mg, 4.36 mml) in 4.5 mL of Me_2SO was heated to 100 °C for 20 h. GC analysis (10% UC W-98, 6 ft × ⅛ in., 200 °C) showed 80% (*E*)- and 20% (*Z*)-1-methyl-1-phenyl-2-*p*-tolylcyclopropane (**9E** and **9Z**). A sample of **9Z** (shorter retention time) was collected by preparative GC (10% QF-1, 5 ft × ¼ in., 155 °C) for spectral identification. NMR (CCl_4): δ 7.01 (s, 5 H), 6.74 (d, J = 8 Hz, 2 H), 6.52 (d, J = 8 Hz, 2 H), 2.18 (s, 3 H, ArCH_3), 2.12 (d of d, J = 9.0, 6.7 Hz, 1 H, partially obscured by s at δ 2.18, CH), 1.51 (s, 3 H, CH_3), 1.44 (d of d, J = 6.7, 5.3 Hz, 1 H, partially obscured by s at δ 1.51, A), 1.17 (d of d, J = 9.0, 5.3 Hz, 1 H, B). Exact mass: 222.140 57 (calcd for $C_{17}H_{18}$ 222.140 85).

(*E*)-1-Phenyl-2-*p*-tolylpropene (22).[24] Reaction of benzylmagnesium chloride (33.0 mL, 1.97 M, 65.0 mmol) with *p*-methylacetophenone (6.70 g, 50.0 mmol) gave 1-phenyl-2-*p*-tolyl-2-propanol which was dehydrated by refluxing in 20% H_2SO_4. Recrystallization from absolute ethanol gave (*E*)-1-phenyl-2-*p*-tolylpropene (**22**) (5.73 g, 55%, mp 66-66.5 °C). NMR (CCl_4): δ 7.30 (d, J = 8 Hz, 2 H), 7.24 (s, 5 H), 7.04 (d, J = 8 Hz, 2 H), 6.72 (br s, 1 H, vinyl H), 2.34 (s, 3 H), 2.21 (d, J = 1.4 Hz, 3 H). UV (CH_3CH_2OH): 275 ($\epsilon = 1.67 \times 10^4$).[35] GC indicates >99% isomeric purity.

(*E*)-1-Methyl-1-*p*-tolyl-2-phenylcyclopropane (15E). Using the same procedure as for **7t**, **22** was converted to (*E*)-1-methyl-1-*p*-tolyl-2-phenylcyclopropane (**15E**) (28%, b.p. 95-105 °C, 0.05 mm). GC analysis showed >96% isomeric purity but indicated the presence of 10% impurities. Samples for spectral data were collected by preparate GC (10% QF-1, 5 ft × ¼ in., 195 °C). NMR (CCl_4): δ 7.20 (s, 5 H), 7.16 (d, J = 8 Hz, 2 H, partially obscured by s at δ 7.20), 6.99 (d, J = 8 Hz, 2 H), 2.30 (s, 3 H, Ar-CH_3), 2.30 (d of d, J = 8.6, 6.7 Hz, 1 H, partially obscured by s at δ 2.30, CH), 1.33 (d of d, J = 8.6, 4.9 Hz, 1 H, D), 1.11 (d of d, J = 6.7, 4.9 Hz, 1 H, partially obscured by s at δ 1.08, C), 1.08 (s, 3 H, CH_3). Exact mass: 222.1401 (calcd for $C_{17}H_{18}$ 222.1408).

Equilibration of 15E and 15Z.[23] **15E** (97 mg, 0.44 mmol) and a 1.5-mL solution of potassium *tert*-butoxide (503 mg, 4.48 mmol) in 4.5 mL of Me_2SO was heated to 100 °C for 20 h. GC analysis (10% UC W-98, 20 in. × ⅛ in., 200 °C) showed 67.5% (*E*)- and 32.5% (*Z*)-1-methyl-1-*p*-tolyl-2-phenylcyclopropane (**15E** and **15Z**). A sample of **15Z** (shorter retention time) was collected by preparative GC (10% QF-1, 5 ft × ¼ in., 165 °C) for spectral identification. NMR (CCl_4): δ 6.9 (m, 8 H), 6.6 (m, 1 H), 2.20 (s, 3 H, Ar-CH_3), 2.08 (d of d, J = 9.0, 6.2 Hz, 1 H, CH), 1.47 (s, 3 H, CH_3), 1.38 (m, 1 H, partially obscured by s at δ 1.47, D), 1.14 (d of d, J = 9.0, 5.1 Hz, 1 H, C). Exact mass: 222.1403 (calcd for $C_{17}H_{18}$ 222.1408).

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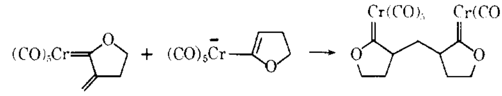

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