Tetrahedron Vol. 49, No. 25, pp. 5507-5530, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Preparation of Seven-Membered Rings by the Reaction of Cyclopropylcarbene-Tungsten and Molybdenum Complexes with Alkynes

James W. Herndon*, Metin Zora, Paren P. Patel, Gautam Chatterjee, Julius J. Matasi, and Seniz U. Tumer

Department of Chemistry and Biochemistry

University of Maryland

College Park, Maryland 20742-2021 USA

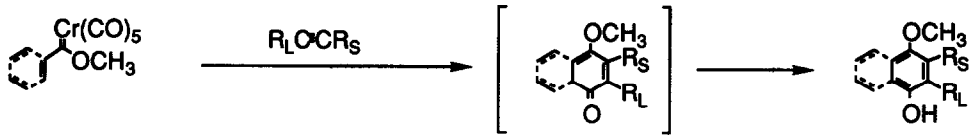
(*Received in USA* 18 *February* 1993; *accepted* 9 *April* 1993)

Summary: The reaction between alkynes and cyclopropylcarbene-tungsten and molybdenum complexes has been examined. Depending upon the conditions of the reaction, either cycloheptadienones or furanones are obtained. The scope, limitation, and mechanistic rationale for observed selectivities are discussed.

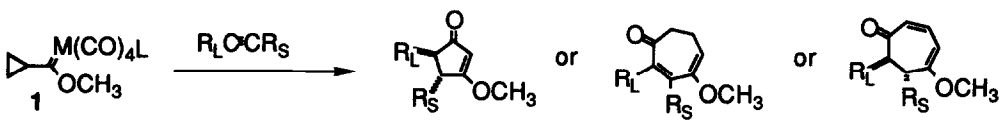
Introduction

The cycloheptane ring system is an important structural feature in a variety of biologically-important molecules,[1] including cholchicine, phorbol, and the guaianolides and pseudoguaianolides. As part of a program to develop new cycloaddition reactions for the preparation of carbocyclic seven-membered rings,[2] the reaction between cyclopropylcarbene-metal complexes and alkynes was examined. Conceptually, if a cyclopropane ring replaces the α,β–unsaturated component of the Dötz reaction (Scheme 1),[3] a well-known six-membered ring-forming reaction, then by a similar reaction pathway a seven-membered ring (e.g. **3**, Scheme 2) could form. As reported earlier, the direct analog of the Dötz reaction, where cyclopropylcarbene-*chromium* complexes and alkynes were coupled, failed to produce a seven-membered ring.[4] From this reaction, only five-membered rings were realized (e.g. **2**) and ethylene was expelled in the reaction process. As reported in preliminary communications, cyclopropylcarbene-tungsten[5] and molybdenum[6] complexes did in fact produce cycloheptadienones (e.g. **3** and **4**), or furanones (e.g. **5**) upon reaction with alkynes, depending upon the conditions of the reaction. Reported in this paper is a more detailed account of these studies.

Scheme 1. The Dötz Reaction:



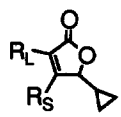
Scheme 2. Reaction of Cyclopropylcarbene-Group VI Metal Complexes and Alkynes:



2 (from **1a**) 3 (from **1b**) 4 (from **1c**)

All Carbene Complexes
(lowercase letters)
a M = Cr, L = CO
b M = Mo, L = CO
c M = W, L = CO
d M = Mo. L = PPh_3
e M = W, L = PPh_3

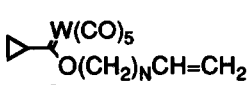
Compounds **2-5**
(uppercase letters)
A R_L, R_s = Ph
B R_L, R_S = n-C_3H_7
C R_L = Ph, R_S = CH_3
D R_L = Ph, R_S = $Si(CH_3)_3$



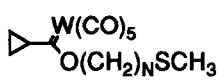
5 (from **1b, c**)

Results

Initially, the reaction between simple cyclopropylcarbene complex **1c** and diphenylacetylene was examined at 100 °C in dioxane. From this reaction cycloheptadienone **3A** was obtained in 21% yield, accompanied by a substantial amount of unreacted carbene complex, and a trace amount of rearranged cycloheptadienone **4A**. This reaction never went to completion at this temperature, however as the reaction time was extended the proportion of cycloheptadienone **4A** increased. The reaction would proceed to completion at 140 °C in xylene, however under these condition only isomerized compound **4A** was obtained. Even after extensive chromatographic purification, the ^{1}H NMR spectrum of cycloheptadienone **3A** or **4A** revealed a large excess of aromatic-containing compounds, probably due to polymerization or oligomerization of diphenylacetylene.[7] By addition of phosphine ligands to the reaction mixture, the extent of this side reaction was suppressed. The most beneficial effects on the alkyne-carbene coupling reaction were realized with tris(o-tolyl)phosphine or 1,2-bis(diphenylphosphino)benzene as additives. Addition of triphenylphosphine retarded the alkyne-carbene coupling reaction, while tributylphosphine or 1,2-bis(diphenylphosphino)ethane completely inhibited the reaction. Triphenylphosphine-substituted complexes **1d** and **1e** were noticeably less reactive than the corresponding pentacarbonyl complexes **1b** and **1c**.

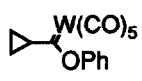


6

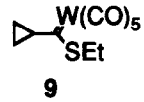


7

Complexes **6-7**, N = 2 or 3



8



9

Since excessive reaction temperatures were required for this reaction, other complexes which might be more reactive than **1c** were examined. Complexes **6-7**, which have an internal ligation site, were prepared[8] in anticipation that the internal ligand could displace CO at a reduced temperature,[8] which could then be displaced by the alkyne. Complexes **6-7** were no more reactive than was complex **1c**. Complex **8**,[9] where electron donation from oxygen is reduced, decomposed prior to reaction with diphenylacetylene. Thiocarbene complex **9**[10] similarly decomposed without incorporation of diphenylacetylene.

Since molybdenum carbene complexes typically display greater reactivity than either chromium- or tungsten-carbene complexes,[11] molybdenum carbene complex **1b** was prepared and examined in its reactions with diphenylacetylene. Complex **1b** was considerably more reactive than **1c**, and reaction with diphenylacetylene at 65 °C in the presence of triphenylphosphine led to cycloheptadienone **3A** in 65% yield. In this case there were no complications from rearrangement of **3A** to **4A**. In the ^{1}H NMR spectrum of cycloheptadienone **3A** obtained by this method, the aromatic region integrated for only ten hydrogens, and thus competing reactions of diphenylacetylene did not appear to be a problem. In the absence of triphenylphosphine, diphenylacetylene and complex **1b** provided compound **3A** in 52% yield.

Shown in the Table is the reaction for a variety of alkynes and carbene complexes **1b** and **1c**. In reactions with alkynes other than diphenylacetylene, furanones (**5**, Scheme 2) were observed if a phosphine additive was omitted from the reaction. As noted in Entries H and I, furanones were the major products of the no-phosphine reaction between molybdenum complex **1b** and 4-octyne or 1-phenylpropyne. Furanones were also observed in no-phosphine reactions of these alkynes and tungsten complex **1c**, however these reactions mixtures were very complex and the yield was not quantified. Terminal alkynes did not lead to cycloheptadienones, but internal alkynes reliably led to cycloheptadienones. This problem might be alleviated by employing a trimethylsilyl-substituted alkyne (entry G) since the trimethylsilyl group in cycloheptadienone **3D** can be replaced by a hydrogen.[12] Since the molybdenum carbene complexes were reactive at lower temperatures, the major products of these reactions were typically cycloheptadienone **3** and not **4**. In all cases except one (Entry F), compound **4** was obtained as a single isomer assigned as the trans isomer.

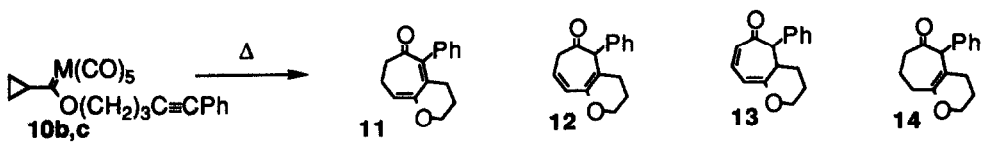
TABLE. Reaction of Various Alkynes with Carbene Complexes 1b and 1c.

Entry	Complex	R_L	R_S	Solvent, Conditions, Additive	Yield 3	Yield 4
A	Mo (**1b**)	Ph	Ph	THF, 65 °C/3 h, PPh_3	65%	0%
B	W (**1c**)	Ph	Ph	p-Xylene, 140 °C/24 h, DPPBz[b]	9%	55%
C	Mo (**1b**)	*n*-C_3H_7	*n*-C_3H_7	THF, 65 °C/ 5 h, PPh_3	23%	23%
D	W (**1c**)	*n*-C_3H_7	*n*-C_3H_7	p-Xylene, 140 °C/24 h, DPPBz[b]	0%	45%
E	Mo (**1b**)	Ph	CH_3	THF, 65 °C/ 5 h, PPh_3	45%	10%
F	W (**1c**)	Ph	CH_3	p-Xylene, 140 °C/24 h, DPPBz[b]	3%	61%[a]
G	Mo (**1b**)	Ph	$Si(CH_3)_3$	THF, 65 °C/ 5 h, PPh3	48%	0%
H[c]	Mo (**1b**)	*n*-C_3H_7	*n*-C_3H_7	THF, 65 °C/ 5 h, No Additive	12%	7%
I[d]	Mo (**1b**)	Ph	CH_3	THF, 65 °C/ 5 h, No Additive	15%	4%

[a]This product was obtained as an 85:15 trans:cis ratio. [b]DPPBz = 1,2-bis(diphenylphosphino)benzene. [c]The major product was furanone **5B** in 17% yield. [d]The major product was furanone **5C** in 25% yield.

The intramolecular reaction proceeded similarly (Scheme 3). The requisite alkyne-containing carbene complexes were prepared using the acetoxy exchange procedures established for cyclopropylcarbene-chromium complexes.[13] The molybdenum procedure was somewhat inefficient, however an efficient method for synthesis of complexes such as **10b** has recently been reported.[14] From thermolysis of complex **10b** and **10c** reaction, the unconjugated isomer **12** was the major product (63% from **10c** and 55% from **10b**). None of the expected carbonyl-conjugated cycloheptadienones **11** or **13** were observed. In the cyclization of the tungsten complex, an additional compound, tentatively identified as the monohydrogenation product **14**, was a significant impurity if the reaction was allowed to continue for an excessive time (>20 h) at 140 °C.

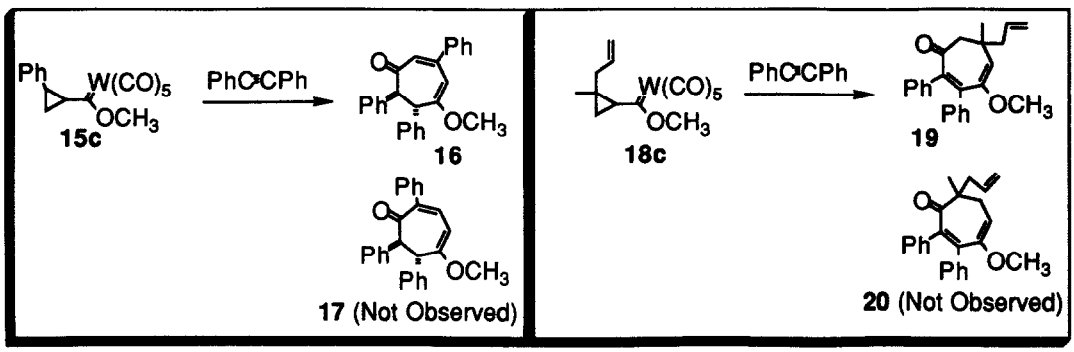
Scheme 3. Intramolecular Coupling of Cyclopropylcarbene-Molybdenum(Tungsten) Complexes and Alkynes:

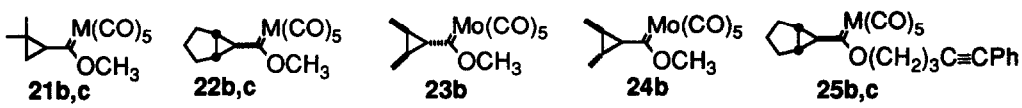


The reaction between diphenylacetylene and complexes having substituted cyclopropane rings was also examined. The reaction between phenyl-substituted carbene complex **15c** and diphenylacetylene led to

cycloheptadienone **16** in 53% yield (Scheme 4). Similarly, carbene complex **18c** led to cycloheptadienone **19**. In each of these reactions, two additional regioisomers (**17** and **20**, respectively) were possible, and these regioisomers were not observed. The reaction between the molybdenum complex **15b** and diphenylacetylene provided only a trace amount of cycloheptadienone **16**. The efficiency of the cycloaddition reaction was very sensitive to substitution on the cyclopropane ring. Complexes **21-24** produced no identifiable products in their reaction with diphenylacetylene. Similarly, no identifiable products were observed in the intramolecular reaction involving complexes **25b** and **25c**.

Scheme 4. Regiochemistry of Cyclopropane Ring Opening:





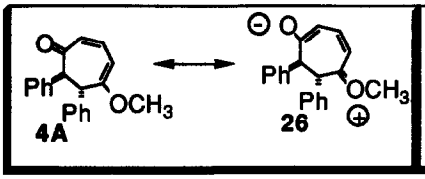
Discussion

i. Diene Isomerization

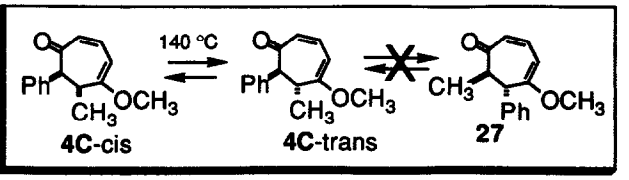
In intermolecular reactions between alkynes and cyclopropylcarbene chromium complexes, 2,3-disubstituted-2,4-cycloheptadienones (e.g. **3**) are favored at low temperature, while 6,7-disubstituted-2,4-cycloheptadienones (e.g. **4**) are favored at higher temperature. Cycloheptadienone **3A** is completely converted to **4A** upon thermolysis at 140 °C for 2 h, suggesting that **3A** is the kinetic product, while **4A** is the thermodynamic product. Cycloheptadienone **4A** is more stable due to the resonance interaction (see resonance structure **26** in Scheme 5) between the methoxy oxygen and the carbonyl group (a doubly vinylogous ester

linkage). This resonance interaction is supported by the infrared stretching frequencies of the carbonyl group, which occur at 1695 cm^{-1} in **3A**, and is lowered to 1652 cm^{-1} in **4A**. Since compound **4** is obtained as a result of a thermodynamic equilibration, the relative stereochemistry of R_L and R_S has been assigned as trans. Except in one case, the exclusive product of the reaction was the trans isomer of cycloheptadienone **4**. In this case (entry F) a 7:1 mixture of isomers was obtained. For this compound, a concern is whether these are regioisomers (e.g. **4C** and **27**, Scheme 6) or stereoisomers. To assess this, the minor isomer of **4C** was subjected to thermolysis at 140 °C, and nearly pure **4C** (major isomer) was obtained. This result confirms that these are stereoisomers (**4C**-cis and trans) and not regioisomers (**4C** and **27**).

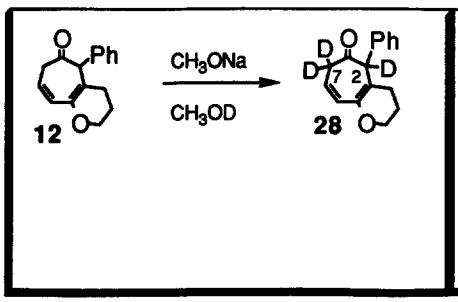
Scheme 5. Resonance Stabilization of **4A**:



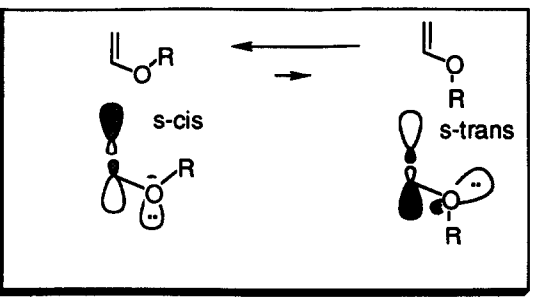
Scheme 6. Thermal Equilibration of **4C**-cis and trans:



Scheme 7. Thermal Equilibration of **12**:



Scheme 8. Stereoelectronic Effects in Enol Ethers:



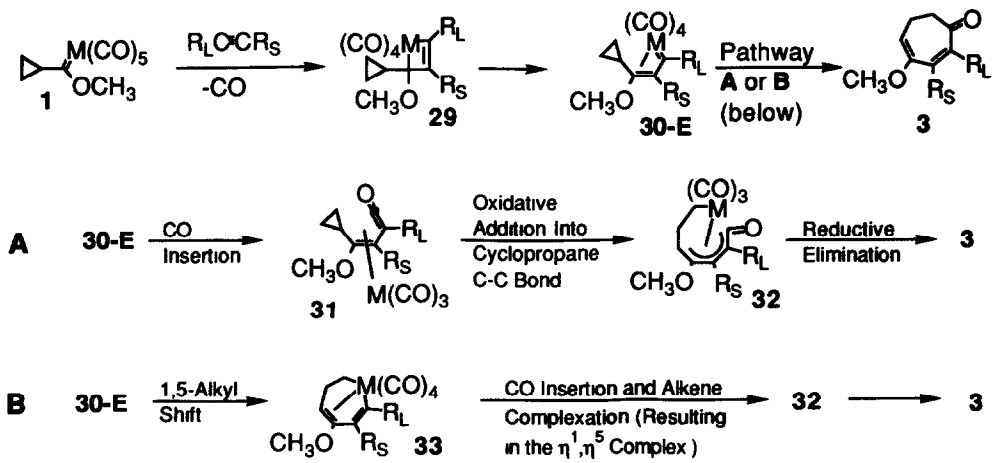
In the intramolecular case, the only product of the reaction was the isomer not conjugated to the carbonyl group. That this was in fact the thermodynamic product was verified by a deuterium labelling study. Treatment of compound **12** with triethylamine and D_2O produced no diene isomerized product, and placed deuterium at the 2- (90% incorporation) and 7-positions (40% incorporation) (Scheme 7). Why is this the thermodynamic product in this system? Interestingly, in cycloheptadienone equilibrium studies, there is only a slight preference for conjugation of the diene with the ketone.[15] This observation might be due to the more stable configuration for enol ethers, which prefer the s-cis conformation in order to maximize interaction

between the nonconjugating oxygen lone pair and the C-C σ* orbital (Scheme 8).[16] This is the conformation present in the major product **12**; the opposite configuration is present in both of the ketone-conjugated isomers, **11** and **13**, which are never observed in the reaction. An additional factor is the stability of endocyclic vs exocyclic double bonds in six-membered rings.[17]

ii. mechanism and regioselectivity of ring opening

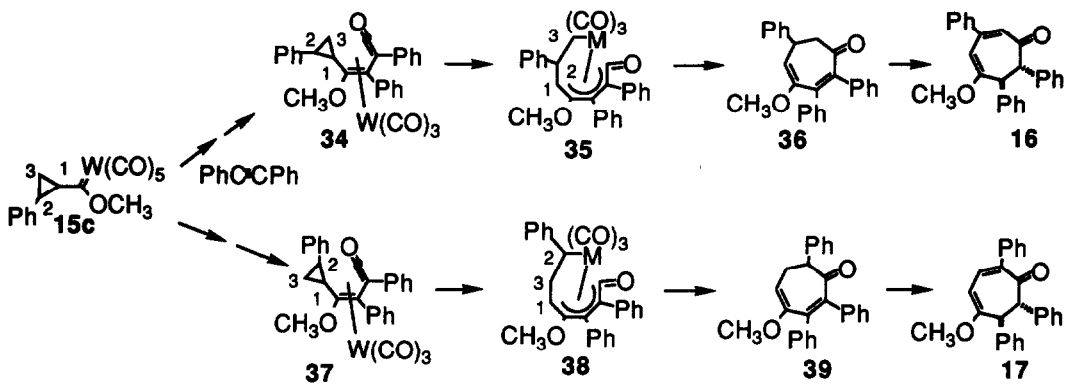
The mechanism for the reaction is depicted in Scheme 9. The regiochemistry of alkyne insertion is set in the metallacyclobutene-forming step, and the observed regiochemistry is consistent with that observed by previous investigators.[18] Two variations in this mechanism can be envisaged, which differ in their timing of CO-insertion vs cyclopropane ring opening steps. The mechanism in path A more closely resembles the currently-favored mechanism for the Dötz reaction.[19] Some evidence favoring cyclopropane ring opening as an early event (pathway B) was noted in the reaction between cyclopropylcarbene-chromium complexes and alkynes.[4] Simple cyclopropylvinylketenes (from thermolysis of 4-cyclopropyl-2-cyclobutenone derivatives)[20] do not provide cycloheptadienones in the limited number of examples studied, thus the mechanism in path A can only be operative if vinylketenes and vinylketene-metal complexes are very different in their reactivity. A possible function of the metal is to open the cyclopropane ring by an oxidative addition process as depicted in Scheme 9, path A. Cyclopropyl complex **1c** is noticeably less reactive than the corresponding methyl complex (reaction with diphenylacetylene goes to completion in a few hours in refluxing dioxane),[18] perhaps because the carbene center is more hindered in the cyclopropyl case.

Scheme 9. Mechanism of the Cycloheptadienone-Forming Reaction:



When unsymmetrical cyclopropanes are employed in the cycloaddition reaction, two regioisomeric cycloheptadienones are possible. When considering the reaction involving phenylcyclopropylcarbene complex **15c**, steric effects predict that cycloheptadienone **16** should predominate (Scheme 10). The mechanism analogous to that in Scheme 9, path A is depicted in Scheme 10, however the cyclopropane ring opening step in path B also involves initial formation of a carbon-tungsten bonded species and similar effects should be operative. Conversely, the C1-C2 bond of the cyclopropane should be considerably weaker that the C1-C3 bond,[21] and thus electronic factors predict that cycloheptadienone **17** should predominate. Clearly steric effects are more important. Similar regiochemistry is also observed in the reaction of compound **18**. Since so few substituted cyclopropylcarbene complexes are suitable substrates for the cycloheptadienone-forming reaction, this reactivity trend could not be thoroughly evaluated.

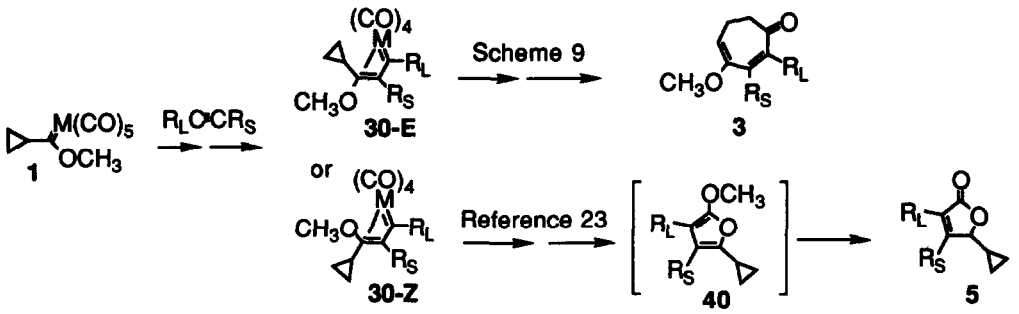
Scheme 10. Ring Opening in Complexes Having Unsymmetrically-Substituted Cyclopropane Rings:



iii. furanone vs cycloheptadienone formation

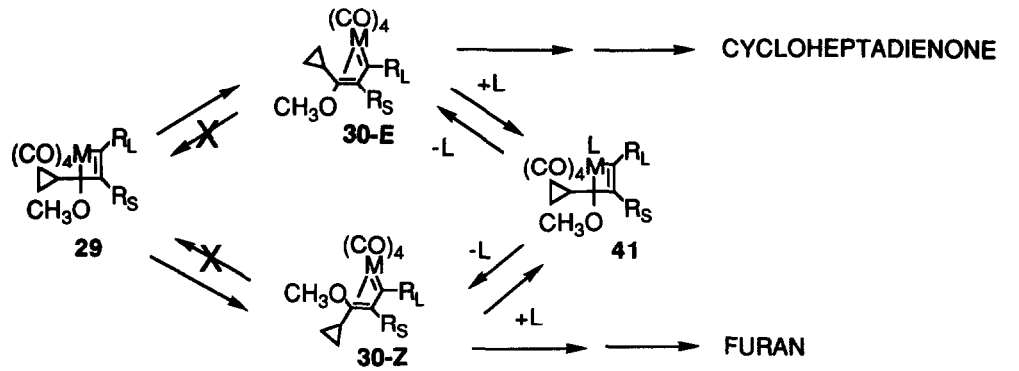
In many cases, furanone formation is a major competing reaction. The observed furanones presumably result from silica-gel hydrolysis of furan **40** (Scheme 11),[22] which has not been confirmed as an intermediate in the reaction. As noted before, it furanone formation is never a problem when diphenylacetylene is the alkyne, or when phosphine ligands are used as an additive. We shall address each of these issues separately. As suggested by previous investigators, furans form only from the Z-vinylcarbene complex intermediate **30-Z**.[23] The cycloheptadienone can form only from vinylcarbene complex **30-E**, otherwise a trans double bond in a seven-membered ring will be produced. Furanones can not form from the intramolecular reaction since only the E-vinylcarbene complex can be produced.

Scheme 11. Point of Divergence in the Cycloheptadienone/Furanone-Forming Reactions:



Why is furanone formation not observed when using diphenylacetylene? This is best explained by a steric effect. A cyclopropyl group is larger than a methoxy group. As the size of R_S in compound **30** increases, the more disfavored is the compound where R_S and cyclopropyl are cis (**30-Z**, furan precursor), and the more favored is the compound where R_S and cyclopropyl are trans (**30-E**, cycloheptadienone precursor). In the examples tested, the largest R_S group employed was phenyl, obtained from diphenylacetylene. Thus reactions involving diphenylacetylene are the least likely to produce furanones.

Scheme 12. Potential Role of Triphenylphosphine in the E-Z Isomerization of Vinylcarbene Complexes:



Why does phosphine substitution affect the ratio of furanone: cycloheptadienone? Phosphine complexation to the metal might simply alter the E:Z ratio of the vinylcarbene complexes, however increasing the steric bulk of the metal should *increase* the proportion of the sterically less congested Z-vinylcarbene complex. Alternatively, if the cyclopropane ring opening step is kinetically faster than the ring-closure step of

the furan-forming reaction, and phosphine could effect an E:Z isomerization, then the apparent result would be an increase in the cycloheptadienone: furanone ratio. A problem with the second explanation is that previous investigators have established that E-Z equilibration, most likely via reversible metallacyclobutene ring opening, does not occur during reactions between Fischer carbene complexes and alkynes. A possible role of an external ligand in inducing this process is depicted in Scheme 12. As noted in a theoretical paper by Hofmann,[24] metallacyclobutenes (e.g. **29**) are unstable relative to internally-coordinated vinylcarbene complexes (e.g. **30-E,Z**). The major source of this instability, coordinative unsaturation in metallacyclobutenes such as **29**, is alleviated if an external ligand is present, which stabilizes metallacyclobutene **41**. Thus in the presence of a phosphine ligand, the conversion of the vinylcarbene complex to a metallacyclobutene is more energetically favorable. This reversible ring opening step would in essence allow for interconversion of the E and Z isomers of vinylcarbene complexes.

Conclusion

We have examined the seven-membered ring-forming reaction between cyclopropylcarbene-tungsten and molybdenum complexes. The reaction is general for internal alkynes, but fails for terminal alkynes. With some alkynes, furanone formation is a significant competing reaction pathway, but this can be suppressed by addition of phosphine ligand additives to the reaction. The favorable effect of phosphine has been attributed to an equilibration of the E and Z isomers of the vinylcarbene complex intermediate. As the cyclopropane ring is substituted, the reaction becomes less facile. In all cases the diene isomers obtained are subject to complete or partial thermodynamic equilibration. The reaction is a potentially powerful method for the preparation of seven-membered ring systems, however the scope and limitations exhibited by these systems is less than optimal.

Acknowledgements: We thank the National Institutes of Health (GM-40777) and the Petroleum Research Fund, Administered by the American Chemical Society for financial support of this research. We thank Dr Jill Harp and Ms. Margaret Reid for experimental support.

Experimental

General Considerations: Nuclear Magnetic Resonance (^{1}H and ^{13}C) spectra were recorded on a Bruker AF200 (200 MHz) or Bruker AF400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Nicolet 5DXC FT-IR spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are reported relative to the most intense band and are listed as: br (broad), vs (very strong), s (strong), m (medium), w (weak). Mass spectra (MS) were obtained on a VG 7070E spectrometer using electron impact (EI) or chemical ionization (CI) or on a Hewlett-Packard GC-Mass Spec 5970B with Mass Selection Detector; m/e values are reported, followed by the relative intensity in parentheses. Melting points were taken on a Fischer-Johns melting point apparatus (Model 12-144) equipped with a calibrated thermometer. Flash column chromatography was performed using thick-walled glass columns and "flash grade" silica (Bodmann 230-400 mesh). Routine thin layer chromatography (TLC) was effected by using precoated 0.25mm silica gel plates purchased from Whatman. The relative proportion of solvents in mixed chromatography solvents refers to the volume:volume ratio.

Cyclopropyl bromide,[25] 5-Phenyl-4-pentyn-1-ol,[26] and 1-bromo-2-phenylcyclopropane[27] were prepared according to literature procedures. All other commercially available reagents and reactants were obtained in reagent grade and used without purification. All reaction solvents were distilled for purity. Diethyl ether, THF and dioxane were distilled from sodium-benzophenone ketyl, dichloromethane from calcium hydride prior to use. All reactions were performed in an inert atmosphere created by a slight positive pressure (ca. 0.1 psi) of nitrogen.

General Procedure I - Preparation of Carbene Complexes: To a solution of the cyclopropyl bromide (1 eq, 0.4M) in diethyl ether at -78 °C under nitrogen was added via syringe t-butyllithium (1.7M pentane solution, 2 eq) over a period of 15 min. The mixture was stirred for 30 min at -78 °C, and then transferred via cannula to a suspension of group VI metal carbonyl hexacarbonyl (1 eq) in diethyl ether (50 mL/mole of cyclopropyl bromide) at 0 °C. This mixture was warmed to 25 °C and then stirred for 1 h. The mixture was cooled to 0 °C and methyl trifluoromethanesulfonate or methyl fluorosulfonate (3 eq) was added. The mixture was stirred at room temperature for 30 min. The reaction mixture was poured into saturated aqueous sodium bicarbonate

solution in a separatory funnel, and then extracted with hexane. The hexane layer was washed with water and saturated aqueous sodium chloride solution, respectively. After drying over anhydrous sodium sulfate, the solvent was removed on a rotary evaporator. The crude yellow oil was purified by flash chromatography on silica gel using hexane as the eluent.

*Preparation of Pentacarbonyl[cyclopropyl(methoxy)methylene]molybdenum (**1b**):* General Procedure I was followed using cyclopropyl bromide (1.200 g, 10.0 mmol), t-butyllithium (11.7 mL of a 1.7M pentane solution, 20.00 mmol), molybdenum hexacarbonyl (2.640 g, 10.00 mmol), and methyl trifluoromethanesulfonate (3.4 mL, 30.00 mmol). After chromatography, the yellow band was collected to give carbene complex **1b** (mp 54-56 °C, 1.920 g, 60%). ^{1}H NMR ($CDCl_3$): δ 4.53 (s, 3 H), 3.45 (m, 1 H), 1.38 (m, 2 H), 1.20 (m, 2 H); IR (CH_2Cl_2): 3056 (w), 2359 (w), 2069 (vs), 1942 (vs), 1456 (m), 1361 (m), 1203 (m), 1175 (m), 1038 (m), 989 (s), 957 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$): δ 346.5, 213.6, 206.0, 68.3, 41.5, 17.8; Mass Spec (CI): 322 (M, 15), 294 (14), 266 (9), 238 (5), 182 (10), 113 (5), 101 (16), 85 (100), 79 (8), 71 (14); High res. MS: calcd. for $C_{10}H_8MoO_6$ 321.9374, found 321.9398.

*Preparation of Pentacarbonyl[cyclopropyl(methoxy)methylene]tungsten (**1c**).* General Procedure I was followed using cyclopropyl bromide (1.20 g, 10.0 mmol), t-butyllithium (20.0 mmol, 9.1 mL, 1.7 M solution in pentane), tungsten hexacarbonyl (3.50 g, 10.0 mmol, in 100 mL dry diethyl ether) and methyl trifluroromethanesulfonate (3.0 mL, 26.5 mmol). After chromatographic purification, a bright yellow solid (m.p 43-44 °C, 2.3 g, 62.0%) identified as carbene **1c** was obtained. ^{1}H NMR ($CDCl_3$): δ 4.47 (s, 3H); 3.49 (m, 1H); 1.39 (m, 2H); 1.23 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 329.0, 203.6, 198.9, 197.6, 196.4, 69.3, 44.3, 17.6. IR (CH_2Cl_2): 2068 (m), 1975(w), 1935 (vs) cm^{-1}. MS: m/e 409 (M+1, 31) 408 (M, 37), 352 (29), 309 (43), 281 (56), 268 (100), 223 (68), 210 (35), 118 (9). High res. MS: Calcd. for $C_{10}H_8O_6W$: 407.9830. Found: 407.9835

*Preparation of Pentacarbonyl[2-phenylcyclopropyl(methoxy)methylene]tungsten (**15c**):* General Procedure I was followed using 1-bromo-2-phenylcyclopropane (1.1 g, 5.7 mmol), tungsten hexacarbonyl (2.0 g, 5.7 mmol), t-butyllithium (6.7 mL of 1.7 M pentane solution, 10.5 mmol) and methyl fluorosulfonate (1.4 mL, 17.7 mmol). After chromatographic purification carbene complex **15c** (1.34 g, 41%) was obtained as a yellow-orange oil. The ^{1}H NMR spectrum showed the presence of both the *cis* and *trans* isomer in about

1.5:1 ratio. A small sample was further separated into the individual stereoisomers. The product in the first fraction was identified as the cis isomer of complex **15c**. ^{1}H NMR ($CDCl_3$): δ 7.32-7.19 (m 5H), 4.01 (ddd, 1H, J = 8.9, 6.9, 5.6 Hz), 3.98 (s 3H), 3.35 (q 1H J =8.9Hz), 2.34 (ddd, 1H, J= 8.9, 6.9, 5.6 Hz), 1.53 (ddd, 1H, J = 8.9, 6.9, 5.6 Hz). ^{13}C NMR ($CDCl_3$): δ 325.3, 204.0, 198.0, 129.7, 129.0, 128.0, 126.8, 68.4, 51.3, 36.4, 17.7. IR (CH_2Cl_2): 2067 (s), 1973 (w), 1935 (vs) cm^{-1}. MS (EI): 486 (M+2, 23), 484 (25), 428 (28), 372 (68), 344 (100), 327 (71), 299 (87), 253 (49), 223 (33), 209 (18), 149 (56), 115 (23), 91 (27), 77 (35). High res. MS: Calcd. for $C_{16}H_{12}O_6W$: 484.0143. Found: 484.0134. The product in the second fraction was identified as the trans isomer. ^{1}H NMR ($CDCl_3$): δ 7.32-7.10 (m 5H), 4.52 (s 3H), 3.63 (ddd, 1H, J = 8.9, 5.1, 3.5 Hz), 2.84 (ddd, 1H, J = 8.9, 5.1, 3.5 Hz), 2.03 (ddd, 1H, J = 8.9, 5.1, 3.5 Hz), 1.69 (ddd, 1H, J = 8.9, 5.1, 3.5 Hz). IR (CH_2Cl_2): 2068 (s), 1975 (w), 1937 (vs) cm^{-1}. MS (EI): 486 (M+2, 13), 484 (18), 428 (23), 372 (55), 344 (81), 327 (68), 299 (82), 153 (50), 136 (32), 89 (53), 77 (100). High res. MS: Calcd. for $C_{16}H_{12}O_6W$: 484.0143. Found: 484.0145.

*Preparation of Pentacarbonyl[2-methyl-2-(2-propenyl)cyclopropyl(methoxy)methylene]tungsten (**18c**).* General procedure I was followed using 1-Bromo-2-propenyl-2-methylcyclopropane[28] (1.0 g, 5.7 mmol), t-butyl lithium (7.1 mL of a 1.7M pentane solution, 12.0 mmol), tungsten hexacarbonyl (2.0 g, 5.7 mmol), and methylfluorosulfonate (1.4 mL, 17.7 mmol). After chromatographic purification, a orange oil (1.9 g, 72% yield) identified as carbene **18c** was obtained as a mixture of two inseperable isomers. ^{1}H NMR ($CDCl_3$): δ 5.73 (m, 1H), 5.03 (m, 3H), 4.55 (s, 3H, major), 4.52 (s, 3H, minor), 3.45 (dd, 1H, J = 11.2, 5.8 Hz), 2.15 (m, 2H), 1.84 (m, 2H), 1.32 (s, 3H, minor), 1.06 (s, 3H, major). ^{13}C NMR ($CDCl_3$): δ 328.6 (minor), 327.0 (major), 203.7, 203.5, 199.0, 197.7, 196.5, 135.8, 134.2, 118.2, 116.6, 69.1, 58.5, 57.0, 45.1, 40.1, 39.6, 37.3, 29.8, 26.6, 25.3, 16.7. IR (CH_2Cl_2): 2067 (s), 1978 (s), 1940 (s) cm^{-1}. MS (EI): 462 (M+1, 37), 461 (21), 406 (7), 378 (30), 350 (35), 322 (100), 304 (88), 251 (63), 238 (35), 209 (15), 160 (5), 137 (5), 84 (7), 55 (9). High res. MS: Calcd. for $C_{14}H_{14}O_6W$: 461.0222. Found: 461.0207.

*Preparation of Pentacarbonyl[cyclopropyl(5-phenyl-4-pentynoxy)methylene]molybdenum (**10b**):* To a solution of tetramethylammonium pentacarbonyl(cyclopropanecarbonyl)molybdate (see below) (1.140 g, 3.00 mmol) in dichloromethane (30 mL) at -20 °C under nitrogen was added via syringe acetyl chloride (0.21 mL, 3.00 mmol). The solution was allowed to stir 10 min at -20 °C, and then 5-phenyl-4-pentyn-1-ol (0.480 g, 3.00 mmol) was added via syringe. The solution was allowed to warm to 0 °C, and stirred at this temperature

for a period of 1 h. After the solvent was removed on a rotary evaporator, crude carbene complex was purified by flash chromatography on silica gel using hexane as the eluent. The yellow fraction was collected and assigned as carbene complex **10b** (0.870 g, 65%). ^{1}H NMR ($CDCl_3$): δ 7.35-7.15 (m, 5 H), 4.86 (t, 3 H, J = 6.5 Hz), 3.38 (m, 1 H), 2.52 (t, 2 H, J = 6.5 Hz), 2.09 (quintet, 2 H, J = 6.5 Hz), 1.33 (m, 2 H), 1.14 (m, 2 H); IR (CH_2Cl_2): 2068 (vs), 1939 (vs) cm^{-1}; ^{13}C NMR ($CDCl_3$): δ 344.4, 213.6, 205.9, 131.5, 128.2, 127.8, 123.3, 87.4, 81.9, 80.7, 41.6, 28.2, 17.9, 16.3; Mass Spec (CI): 450 (M, 1), 394 (7), 364 (6), 338 (6), 308 (9), 240 (18), 212 (100), 197 (13), 183 (18), 155 (30), 142 (25), 135 (46), 115 (25), 91 (12); High res. MS: calcd. for $C_{20}H_{16}MoO_6$ 450.0000, found 450.0018.

Preparation of Tetramethylammonium Pentacarbonyl(cyclopropanecarbonyl)molybdate: To a solution of cyclopropyl bromide (1.200 g, 10.00 mmol) in diethyl ether (25 mL) at -78 °C under nitrogen was added via syringe t-butyllithium (11.7 mL of a 1.7M pentane solution, 20.00 mmol) over a period of 15 min. The mixture was stirred for 30 min at -78 °C, and then transferred via cannula to suspension of molybdenum hexacarbonyl (2.640 g, 10.00 mmol) in diethyl ether (50 mL) at 0 °C. This mixture was warmed to 25 °C and then stirred for 1 h. The solvent was removed on a rotary evaporator and residue was dissolved in a minimum amount of water and filtered through celite. To the filtrate a saturated aqueous solution of tetramethylammonium bromide (20 mL) was added, leading to immediate precipitation of the ammonium salt. The precipitate was collected by suction filtration, and then dissolved in dichloromethane and dried over anhydrous sodium sulfate. After the solvent was removed on a rotary evaporator, a yellow solid (1.900 g, 50%) was obtained. This crude yellow solid was not characterized, but was used immediately in conversion to complex **10b** (see above).

*Preparation of Pentacarbonyl[cyclopropyl(5-phenyl-4-pentynoxy)methylene]tungsten (**10c**):* To a solution of tetramethylammonium (pentacarbonyl)cyclopropanecarbonyltungstate (see below) (1.00 g, 2.14 mmol) in dichloromethane (50 mL) under nitrogen at -40 °C was added acetyl chloride (0.152 mL, 2.14 mmol), followed by a solution of 5-phenyl-4-pentyn-1-ol (0.343 g, 2.14 mmol) in dichloromethane (5 mL). The reaction mixture was stirred 2 h at -40 °C, and then allowed to warm to room temperature. The solvent was removed on a rotary evaporator, and the residue was purified by flash chromatography on silica gel using hexane as the eluent. A single yellow fraction (0.800 g, 73%) was obtained. ^{1}H NMR(CDCl3): δ 7.35-7.19 (m, 5 H), 4.82 (t, 2 H, J = 6.2 Hz), 3.41 (m, 1 H), 2.55 (t, 2 H, J = 6.8 Hz), 2.14 (m, 2 H), 1.36 (m, 2 H),

1.20 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 327.0, 203.6, 197.7, 131.6, 128.2, 127.9, 123.4, 87.4, 82.0, 81.6, 44.5, 28.3, 17.8, 16.4; IR ($CDCl_3$): 2068 (s), 1918-1947 (vs, br) cm^{-1}; Mass Spec (EI): 538 (M ^{186}W, 65), 536 (M ^{184}W, 75), 478 (37), 450 (38), 394 (50), 366 (57), 213 (100), 141 (45), 115 (55); High Res. Mass Spec (EI): Calcd for $C_{20}H_{16}O_6{}^{184}W$ 536.0456, found 536.0457.

Preparation of Tetramethylammonium Pentacarbonyl(cyclopropanecarbonyl)tungstate: To a solution of cyclopropyl bromide (2.00 g, 16.5 mmol) in diethyl ether (38 mL) at -78 °C under nitrogen was added via syringe t-butyllithium (20 mL of a 1.7M pentane solution, 34.0 mmol) over a period of 15 min. The mixture was stirred for 30 min at -78 °C, and then transferred via cannula to suspension of tungsten hexacarbonyl (5.80 g, 16.4 mmol) in diethyl ether (83 mL) at 0 °C. This mixture was warmed to 25 °C and then stirred for 1 h. The solvent was removed on a rotary evaporator and residue was dissolved in a minimum amount of water and filtered through celite. To the filtrate a saturated aqueous solution of tetramethylammonium bromide (20 mL) was added, leading to immediate precipitation of the ammonium salt. The precipitate was collected by suction filtration, and then dissolved in dichloromethane and dried over anhydrous sodium sulfate. After the solvent was removed on a rotary evaporator, a yellow solid (1.287 g, 68.5%) was obtained. This crude yellow solid was not characterized, but was used immediately in conversion to complex **10c** (see above).

General Procedure II - Reaction of Molybdenum Carbene Complexes with Alkynes: A solution of molybdenum carbene complex **1b** (1.00 mmol) and triphenylphosphine (1.00 mmol) and alkyne (1.50-2.00 mmol) in THF (30-40 mL) was refluxed under nitrogen until all carbene complex was consumed. The progress of the reaction was monitored by routine TLC for the disappearance of carbene complex and possibly phosphine-complexed carbene complex formed in situ. The mixture was then cooled to 25 °C, and the solvent was removed on a rotary evaporator. The residue was dissolved in 4:1 hexane-ethyl acetate and filtered through celite. After removal of the solvent on a rotary evaporator, final purification was achieved by flash chromatography on silica gel. Eluting with 29:1 hexane-ethyl acetate yielded unreacted alkyne and triphenylphosphine. Eluting with 19:1 hexane-ethyl acetate followed by 9:1 hexane-ethyl acetate yielded the cycloheptadienone derivatives.

General Procedure III - Reaction of Tungsten Carbene Complexes with Alkynes: A solution of carbene (1.0 eq), alkyne (1.7-2.0 eq) and phosphine (1.0 eq) in p-xylene (20 mL) was added dropwise to refluxing p-xylene (25 mL) over a period of 10 h with the help of a syringe pump. After the addition was complete, the mixture was allowed to reflux until all the carbene was consumed (as indicated by routine TLC, usually an additional 10-12 h are required). The mixture was then allowed to cool to room temperature. The solvent was removed on a rotary evaporator. The residue was treated with 1:1 hexane-ethyl acetate and filtered through a bed of celite. The solvent was removed on a rotary evaporator, and the final purification was achieved by flash chromatography on silica gel. During flash chromatography, the column was first eluted with hexane (this removes the unreacted alkyne, and phosphine), next it was eluted using 19:1 hexane-ethyl cetate which removes any unreacted carbene, followed by 9:1 hexane-ethyl acetate.

*Reaction of Carbene Complex **1b** with Diphenylacetylene (Entry A):* General Procedure II was followed using carbene complex **1b** (0.320 g, 1.00 mmol), triphenylphosphine (0.262 g, 1.00 mmol) and diphenylacetylene (0.267 g, 1.50 mmol). After chromatographic purification using 9:1 hexane-ethyl acetate, a single fraction was collected and assigned as 2,3-diphenyl-4-methoxy-2,4-cycloheptadienone (**3A**) (0.189 g, 65%). ^{1}H NMR ($CDCl_3$): δ 7.40-6.90 (m, 10 H), 5.42 (t, 1 H, J = 7.5 Hz), 3.45 (s, 3 H), 2.85 (t, 2 H, J = 7.5 Hz), 2.55 (q, 2 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$): δ 206.4, 157.4, 140.9, 137.6, 136.8, 134.6, 129.8, 129.7, 127.8, 127.3, 127.2, 101.5, 54.8, 51.0, 20.3; IR (CH_2Cl_2): 1695 (s) cm^{-1}; Mass Spec (CI): 291 (M+1, 18), 290 (19), 262 (100), 247 (6), 191 (9), 105 (16), 91 (7), 84 (12), 51 (37); High res. MS: calcd. for $C_{20}H_{18}O_2$ 290.1307, found 290.1309.

*Reaction of Carbene Complex **1c** with Diphenylacetylene (Entry B):* General Procedure III was followed using carbene complex **1c** (0.080 g, 0.20 mmol) diphenylacetylene (0.060 g, 0.33 mmol), and 1,2-bis(diphenylphosphino)benzene (0.090 g, 0.20 mmol). After purification by flash chromatography using 9:1 followed by 4:1 hexane-ethyl acetate as eluents, two fractions were isolated. The product in the first fraction (0.005 g, 5%) was identified as cycloheptadienone **3A** (see above). The product in the second fraction (0.030 g, 55%) was identified as 6,7-diphenyl-5-methoxy-2,4-cycloheptadienone (**4A**). ^{1}H NMR ($CDCl_3$): δ 7.25-7.10 (m, 10H), 6.40 (dd, 1H, J = 12.0, 8.7 Hz), 5.90 (d, 1H, J = 12.0 Hz), 5.31 (d, 1H, J = 8.7 Hz), 4.18 (q, 2H, J = 8.0 Hz), 3.56 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 198.6, 170.0, 137.4, 136.4, 130.3, 129.4, 128.8, 128.2, 127.7, 127.3, 126.7, 126.2, 98.5, 59.3, 55.6, 50.3. IR (CH_2Cl_2): 1652 (s) cm^{-1}; MS (CI): m/e 290

(M+1, 1.1), 290 (4), 262 (7), 233 (5), 215 (4), 205 (5), 178 (52), 165 (10), 152 (12), 129 (8), 105 (88), 86 (63), 84 (100), 51 (37). High res. MS: Calcd. for $C_{20}H_{18}O_2$: 290.1306. Found 290.1309.

*Reaction of Carbene Complex **1b** with 4-Octyne (Entry C):* General Procedure II was followed using molybdenum carbene complex **1b** (0.320 g, 1.00 mmol), triphenylphosphine (0.262 g, 1.00 mmol) and 4-octyne (0.220 g, 2.00 mmol). After chromatographic purification using 9:1 hexane-ethyl acetate as the eluent, two fractions were isolated. The product in the first fraction was assigned as 2,3-dipropyl-4-methoxy-2,4-cycloheptadienone (**3B**) (0.052 g, 23%). ^{1}H NMR ($CDCl_3$): δ 5.09 (t, 1 H, J = 7.3 Hz), 3.43 (s, 3 H), 2.58 (t, 2 H, J = 7.3 Hz), 2.32 (t, 2 H, J = 7.7 Hz), 2.24 (t, 2 H, J = 7.7 Hz), 2.14 (q, 2 H, J = 7.3 Hz), 1.38-1.29 (m, 4 H), 0.90-0.84 (m, 6 H); IR ($CDCl_3$): 1670 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$): δ 209.1, 157.3, 140.4, 139.3, 98.8, 54.5, 51.1, 32.1, 31.4, 23.1, 21.6, 19.8, 14.2; Mass Spec (EI): 222 (M^+, 44), 195 (18), 194 (18), 181 (11), 179 (22), 166 (16), 165 (100), 151 (43), 137 (21), 123 (14), 110 (29), 107 (13); High res. MS: calcd. for $C_{14}H_{22}O_2$ 222.1620, found 222.1619. The product in the second fraction was assigned as 6,7-dipropyl-5-methoxy-2,4-cycloheptadienone (**4B**) (0.052 g, 23%). ^{1}H NMR ($CDCl_3$): δ 6.45 (dd, 1 H, J = 12.2, 8.5 Hz), 5.74 (d, 1 H, J = 12.2 Hz), 5.05 (d, 1 H, J = 8.5 Hz), 3.60 (s, 3 H), 2.79 (m, 1 H), 2.20 (m, 1 H), 1.95 (m, 1 H), 1.4-1.1 (m, 7 H), 0.85 (m, 6 H); ^{13}C NMR ($CDCl_3$): δ 203.0, 173.0, 136.9, 123.6, 95.4, 55.1, 51.7, 43.8, 31.2, 30.1, 21.3, 20.4, 14.1, 13.9; IR (CH_2Cl_2): 1652 (s) cm^{-1}; Mass Spec (EI): 222 (M^+, 12), 179 (16), 165 (6), 151 (62), 137 (89), 109 (100), 91 (27), 77 (34), 55 (60); High res. MS: calcd. for $C_{14}H_{22}O_2$ 222.1620, found 222.1619.

*Reaction of Carbene Complex **1c** with 4-Octyne (Entry D):* General Procedure III was followed using carbene complex **1c** (0.200 g, 0.490 mmol), 4-octyne (0.108 g, 0.980 mmol), and 1,2-bis(diphenylphosphino)benzene (0.220 g, 0.490 mmol). Final purification was achieved by flash chromatography using 9:1 hexane-ethyl acetate as the eluent. A single fraction was isolated (0.049 g, 45%) and assigned as compound **4B** (see preceding experiment).

*Reaction of Carbene Complex **1b** with 1-Phenylpropyne (Entry E):* General Procedure II was followed using molybdenum carbene complex **1b** (0.320 g, 1.00 mmol), triphenylphosphine (0.262 g, 1.00 mmol) and 1-phenylpropyne (0.232 g, 2.00 mmol). After chromatographic purification using 9:1 hexane-ethyl acetate as the eluent, two fractions were isolated. The product in the first fraction was assigned as 4-methoxy-3-methyl-

2-phenyl-2,4-cycloheptadienone (**3C**) (0.103 g, 45%). ^{1}H NMR ($CDCl_3$): δ 7.35-7.10 (m, 5 H), 5.19 (t, 1 H, J = 7.5 Hz), 3.50 (s, 3 H), 2.71 (t, 2 H, J = 7.5 Hz), 2.33 (q, 2 H, J = 7.5 Hz), 1.71 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 205.3, 141.0, 137.9, 137.6, 129.3, 128.2, 127.6, 127.2, 99.5, 54.6, 50.0, 19.8, 17.8; IR (CH_2Cl_2): 1636 (vs), 1448 (m), 1361 (m), 1248 (s), 1206 (m), 1133 (m), 1087 (m), 1047 (m) cm^{-1}; Mass Spec (EI): 228 (M^+, 19), 200 (61), 185 (34), 172 (16), 157 (17), 141 (24), 129 (58), 115 (75), 87 (41), 69 (100); High res. MS: calcd. for $C_{14}H_{16}O_2$ 228.1150, found 228.1156. The product in the second fraction was assigned as 5-methoxy-6-methyl-7-phenyl-2,4-cycloheptadienone (**4C**-trans) (0.023 g, 10%). ^{1}H NMR ($CDCl_3$): δ 7.23-7.11 (m, 5 H), 6.45 (dd, 1 H, J = 12.2, 8.7), 5.95 (dd, 1 H, J = 12.2, 1.4), 5.01 (dd, 1 H, J = 8.7, 1.4), 3.66 (d, 1 H, J = 4.7), 3.51 (s, 3 H), 2.90 (qd, 1 H, J = 7.4, 4.7), 1.23 (d, 3 H, J = 7.4); irradiate δ 3.66 (PhC<u>H</u>CO): δ 5.95 (d, J = 12.2 Hz); irradiate δ 2.90 ($CH_3C\underline{H}$): δ 5.01 (d, J = 8.7 Hz), 1.23 (s); ^{13}C NMR ($CDCl_3$): δ 199.8, 174.3, 137.6, 136.7, 128.2, 127.1, 126.9, 124.9, 95.8, 58.9, 55.4, 39.3, 14.3; IR (CH_2Cl_2): 1645 (s) cm^{-1}; Mass Spec (EI): 228 (M^+, 37), 200 (41), 185 (76), 169 (21), 153 (31), 137 (30), 109 (57), 91 (100), 77 (54), 51 (23); High res. MS: calcd. for $C_{14}H_{16}O_2$ 228.1150, found 228.1164.

Reaction of Carbene Complex ***1c*** *with 1-Phenylpropyne (Entry F):* General Procedure III was followed using carbene complex **1c** (0.200 g, 0.490 mmol), 1-phenylpropyne (0.114 g, 0.98 mmol), and 1,2-bis(diphenylphosphino)benzene (0.220 g, 0.490 mmol). Final purification was achieved by flash chromatography using 9:1 hexane-ethyl acetate, followed by 4:1 hexane-ethyl acetate as the eluent. Three fractions were isolated. The product in the first fraction was assigned as compound **4C**-trans (0.058 g, 52%) (see preceding experiment). The product in the second fraction was identified as compound **4C**-cis (0.010 g, 9%, contaminated with compound **4c**-trans). ^{1}H NMR ($CDCl_3$): δ 7.4-7.1 (m, 5 H), 6.61 (dd, 1 H, J = 12.9, 8.6 Hz), 5.95 (d, 1 H, J = 12.9 Hz), 5.13 (dd, 1 H, J = 8.6, 1.4 Hz); 3.51 (d, 1 H) overlapping with (s, 3 H), 3.89 (m, 1 H), 1.13 (d, 3 H, J = 6.9 Hz). The product in the third fraction was identified as cycloheptadienone **3C** (0.003 g, 3%) (see preceding experiment).

Conversion of ***4C****-cis to* ***4C****-trans:* A solution of compound **4C**-cis (0.010 g, 0.044 mmol, contaminated with ca 10% of compound **4C**-trans) in xylene (10 mL) was heated at reflux under nitrogen for a 2h period. After removal of solvent on a rotary evaporator, a colorless liquid (0.008 g, 80%) was obtained. The ^{1}H NMR spectrum was identical to that for the major isomer **4C**-trans.

*Reaction of Carbene Complex **1b** with 1-Phenyl-2- trimethylsilylacetylene (Entry G):* General Procedure II was followed using molybdenum carbene complex **1b** (0.320 g, 1.00 mmol), triphenylphosphine (0.262 g, 1.00 mmol) and 1-phenyl-2-trimethylsilylacetylene (0.348 g, 2.00 mmol). This reaction was performed with an 0.1 M carbene solution. After chromatographic purification using 9:1 hexane-ethyl acetate as the eluent, a single fraction was collected, giving 4-methoxy-2-phenyl-3-trimethylsilyl-2,4-cycloheptadienone (**3D**) (0.137 g, 48%). ^{1}H NMR ($CDCl_3$): δ 7.30-7.10 (m, 5 H), 5.05 (t, 1 H, J = 7.3 Hz), 3.49 (s, 3 H), 2.81 (t, 2 H, J = 7.3 Hz), 2.36 (q, 2 H, J = 7.3 Hz), -0.18 (s, 9 H); ^{13}C NMR ($CDCl_3$): δ 206.8, 160.2, 152.4, 143.2, 139.0, 129.5, 128.0, 127.8, 95.8, 53.9, 51.7, 20.3, 0.1; IR (CH_2Cl_2): 1684 (s) cm^{-1}; Mass Spec (EI): 286 (M^+, 50), 271 (15), 258 (100), 239 (49), 230 (35), 213 (25), 197 (10), 185 (21), 171 (10), 165 (12), 154 (38), 141 (9), 126 (22), 115 (19); High res. MS: calcd. for $C_{17}H_{22}O_2Si$ 286.1389, found 286.1389.

*Reaction of Carbene Complex **1b** and 4-Octyne in the Absence of Phosphines (Entry H):* General Procedure II was followed using molybdenum carbene complex **1b** (0.320 g, 1.00 mmol) and 4-octyne (0.220 g, 2.00 mmol). After chromatographic purification using 9:1 hexane-ethyl acetate as the eluent, three major fractions were isolated. The product in the first fraction was cycloheptadienone **3B** (0.027 g, 12%). The product in the second fraction was cycloheptadienone **4B** (0.016 g, 7%). The product in the third fraction was assigned as 5-cyclopropyl-3,4-dipropyl-2-(5*H*)-furanone (**5B**) (0.036 g, 17%). ^{1}H NMR ($CDCl_3$): δ 4.10 (d, 1 H, J = 8.3 Hz), 2.35 (t, 2 H, J = 8.5 Hz), 2.15 (t, 3 H, J = 8.5 Hz), 1.50 (m, 4 H), 0.95-0.80 (m, 7 H), 0.80-0.35 (m, 4 H); ^{13}C NMR ($CDCl_3$): δ 174.0, 163.4, 127.0, 85.1, 28.6, 25.4, 21.6, 21.4, 16.4, 13.7, 13.0, 2.4, 1.6; IR ($CDCl_3$): 1745 (vs), 1671 (vs) cm^{-1}; Mass Spec (EI): 208 (M^+, 48), 180 (10), 179 (16), 166 (9), 165 (61), 151 (10), 140 (10), 139 (100), 137 (8), 133 (4), 123 (8), 119 (6), 107 (5); High res. MS: calcd. for $C_{13}H_{20}O_2$ 208.1463, found 208.1468.

*Reaction of Carbene Complex **1b** and 1-Phenylpropyne in the Absence of Phosphines (Entry I):* General Procedure II was followed using molybdenum carbene complex **1b** (0.320 g, 1.00 mmol) and 1-phenylpropyne (0.232 g, 2.00 mmol). After chromatographic purification using 9:1 hexane-ethyl acetate as the eluent, three fractions were isolated. The product in the first fraction was cycloheptadienone **3C** (0.034 g, 15%). The product in the second fraction was cycloheptadienone **4C** (0.009 g, 4%). The product in the third fraction was assigned as 5-cyclopropyl-4-methyl-3-phenyl-2-(5*H*)-furanone (**5C**) (mp 83-85 °C, 0.054 g, 25%). ^{1}H NMR ($CDCl_3$): δ 7.45-7.25 (m, 5 H), 4.15 (d, 1 H, J = 8.3 Hz), 2.17 (s, 3 H), 0.88 (m, 1 H),

0.71-0.48 (m, 4 H); ^{13}C NMR ($CDCl_3$): δ 172.2, 160.8, 129.8, 128.8, 128.3, 128.2, 126.3, 86.4, 13.2, 12.8, 2.4, 1.6; IR ($CDCl_3$): 1748 (vs), 1734 (vs) cm^{-1}; Mass Spec (EI): 214 (M^+, 100), 199 (10), 171 (11), 145 (58), 129 (9), 117 (89), 114 (40); High res. MS: calcd. for $C_{14}H_{14}O_2$ 214.0994, found 214.0995.

*Reaction of Carbene Complex **15c** with Diphenylacetylene:* General Procedure III was followed using carbene **15c** (0.10 g, 0.20 mmol) diphenylacetylene (0.06 g, 0.33 mmol), and 1,2-bis(diphenylphosphino)benzene (0.09 g, 0.20 mmol). After purification by flash chromatography on silica gel using 9:1 followed by 4:1 hexane-ethyl acetate as the eluting solvents, a single compound (0.040 g, 50%) identified as 5-methoxy-4,6,7-triphenyl-2,4-cycloheptadienone (**16**) was obtained. ^1H NMR ($CDCl_3$): δ 7.36-7.10 (m, 15H), 6.10 (s, 1H), 5.47 (s, 1H), 4.28 (d, 1H, J = 4.9 Hz), 4.15 (d, 1H, J = 4.9 Hz), 3.52 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 198.5, 168.8, 149.9, 143.8, 136.4, 128.9, 128.8, 128 5, 127.5, 127.3, 127.1, 126.9, 125.7, 101.6, 59.5, 55.5, 50.8, 29.6; IR (CH_2Cl_2): 1641 (s) cm^{-1}; MS (EI) 367 (M+1), 366 (21), 338 (29), 307 (10), 289 (4), 261 (20), 247 (100), 215 (25), 178 (25), 167 (61), 128 (10), 115 (77), 77 (43), 51 (20). High res. MS: Calcd. for $C_{26}H_{22}O_2$: 366.1619. Found: 366.1620.

*Reaction of Carbene Complex **18c** with Diphenylacetylene:* General procedure III was followed using carbene complex **18c** (0.23 g, 0.50 mmol) diphenylacetylene (0.16 g, 0.88 mmol), and 1,2-bis(diphenylphosphino)benzene (0.22 g, 0.50 mmol). Purification by flash chromatography using 9:1 followed by 4:1 hexane-ethyl acetate provided a single compound (0.052 g, 30%) identified as the 4-methoxy-6-methyl-2,3-diphenyl-6-(2-propenyl)-2,4-cycloheptadienone (**19**). ^1H NMR ($CDCl_3$): δ 7.20- 6.90 (m, 10H), 5.73 (ddt, 1H, 16.6, 9.4, 7.1, 7.0 Hz), 5.0 (m, 3H), 3.35 (s, 3H), 2.85 m, 2H), 2.55 (m, 2H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 203.3, 154.8, 139.9, 137.6, 135.5, 134.4, 129.8, 128.5, 128.0, 127.7, 127.5, 127.1, 126.6, 118.5, 113.9, 60.5, 55.1, 46.9, 33.7, 27.6; IR (CH_2Cl_2): 1687 (s) cm^{-1}; Mass Spec (EI): 344 (M^+, 7), 316 (5), 303 (100), 275 (57), 261(47), 243 (38), 228 (23), 215 (19), 202 (17) 191 (20); High Res. Mass Spec (El): Calcd for $C_{24}H_{24}O_2$: 344.1776; found: 366.1786.

*Thermolysis of Carbene Complex **10b**:* A solution of carbene complex **10b** (0.448 g, 1.00 mmol) in THF (20 mL) under nitrogen was refluxed until all carbene complex was consumed. The progress of the reaction was monitored by routine TLC for the disappearance of carbene complex. The mixture was then cooled to 25 °C, and the solvent was removed on a rotary evaporator. The residue was dissolved in 4:1 hexane-ethyl acetate

and filtered through celite. After removal of the solvent on a rotary evaporator, final purification was achieved by flash chromatography on silica gel using 9:1 hexane-ethyl acetate as the eluent. A single fraction was collected, giving 3,4,5,7-tetrahydro-5-phenylcyclohepta[*b*]pyran-6(2*H*)-one (**12**) (0.132 g, 55%). ^{1}H NMR ($CDCl_3$): δ 7.30-7.20 (m, 5 H), 5.96 (d, 1 H, J = 10.9 Hz), 5.52 (dt, 1 H, J = 10.9, 5.4 Hz), 4.09 (s, 1 H), 3.94 (m, 2 H), 3.17 (d, 2 H, J = 5.4 Hz), 2.00 (m, 4 H), 1.82 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 203.2, 148.8, 136.7, 128.4, 128.3, 127.9, 127.1, 123.5, 108.3, 65.6, 62.8, 43.8, 26.5, 22.8; IR ($CDCl_3$): 1697 (s) cm^{-1}; Mass Spec (EI): 240 (M^+, 26), 212 (100), 197 (12), 185 (46), 170 (19), 144 (32), 135 (69), 115 (64), 91 (23), 77 (18); High res. MS: calcd. for $C_{16}H_{16}O_2$ 240.1150, found 240.1151.

Thermolysis of Carbene Complex ***10c****:* General Procedure III was followed using carbene complex **10c** (0.500 g, 0.933 mmol) and 1,2-bis(diphenylphosphino)benzene (0.419 g, 0.933 mmol). Reflux was continued for 3 h after the addition was complete. Final purification was achieved by flash chromatography using 4:1 hexane-ethyl acetate as the eluent. A single fraction was isolated (0.141 g, 63%) and assigned as compound **12** (see preceding experiement). If the amount of reflux time was extended to 24 h, a significant amount of a new compound, tentatively identified as 3,4,5,7,8,9-hexahydro-5-phenylcyclohepta[*b*]pyran-6(2*H*)-one (**14**) (not completely separable from compound **12**) was obtained. This was a significant (>30%) portion of the cycloheptane products. ^{1}H NMR ($CDCl_3$): δ 7.32-7.05 (m, 5 H), 4.09 (s, 1 H), 4.01 (m, 1 H, $W_{1/2}$ = 18 Hz), 3.80 (m, I H, $W_{1/2}$ = 35 Hz), 2.5-1.5 (m, 10 H); ^{13}C NMR ($CDCl_3$): δ 209.6 (DEPT 0), 152.1 (DEPT 0), 137.7 (DEPT 0), 128.8 (DEPT -), 128.7.8 (DEPT -), 127.1 (DEPT -), 102.7 (DEPT 0), 65.6 (DEPT +), 64.3 (DEPT -), 41.1 (DEPT +), 31.9 (DEPT +), 26.9 (DEPT +), 26.3 (DEPT +), 20.3 (DEPT +). Mass Spec (CI): 243 (M+ 1). Note: DEPT 0 = quaternary C, DEPT + = CH_2, DEPT - = CH or CH_3.

Thermal Equilibration of Compound ***12****.* A solution of compound **12** (0.024 g, 0.10 mmol) and sodium methoxide (0.006 g, 0.10 mmol) in methanol-d_1 (2 mL) was stirred at room temperature under nitrogen for a 2h period. The reaction mixture was poured into water in a separatory funnel and extracted with diethyl ether. The ether layer was washed with water and then with saturated aqueous sodium chloride solution. After drying over magnesium sulfate, the solvent was removed on a rotary evaporator. The ^{1}H NMR spectrum showed deuterium incorporation at the 2- and 7-positions. ^{1}H NMR ($CDCl_3$): δ 7.30-7.20 (m, 5 H), 5.96 (d,

1 H, J = 10.9 Hz), 5.52 (dt, 1 H, J = 10.9, 5.4 Hz), 4.09 (br s, 0.1 H, Ph(RCH=CH)C<u>H</u>C=O, H at C-2), 3.94 (m, 2 H), 3.17 (br d, 1.2 H, J = 5.4 Hz, =CHC<u>H</u>$_2$C=O, H at C-7), 2.00 (m, 4 H), 1.82 (m, 2 H).

References

1. a. Colchicine synthesis: Muzaffar, A.; Brossi, A. *Pharmacol. Ther.* **1991**, *49*, 105-109 and references therein. b. Phorbol synthesis: Wender, P.A.; McDonald, F.E. *J. Am. Chem. Soc.* **1990**, *112*, 4956-4958 and references therein. c. Guaianolide and Pseodoguaianolide synthesis: Heathcock, C.H.; Graham, S.L.; Pirrung, M.C.; Plavac, F.; White, T.C. In *The Total Synthesis of Natural Products;* Apsimon, J.W. Ed.; Wiley: New York, 1983, pp 333-347.

2. Some representative examples seven-membered ring-forming cycloadditions include: a. Davies, H. M. L.; McAfee, M. J.; Oldenburg, C. E. M. *J. Org. Chem.* **1989**, *54*, 930-936. b. Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61-66. c. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1-19. d. Wulff, W.D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653-2655. e. Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* **1987**, *109*, 3483-3484. f. Molander, G.A.; Cameron, K.A. *J. Am. Chem. Soc.* **1993**, *115*, 830-846. h. Boger, D.L.; Brotherton, C.E. *J. Org. Chem.* **1985**, *50* 3425-3427. i. Harvey, D.F.; Lund, K.P. *J. Am. Chem. Soc.* **1991**, *113*, 5066-5068. j. Wender, P.A.; Lee, H.Y.; Wilhelm, R.S.; Williams, P.D. *J. Am. Chem. Soc.* **1989**, *111*, 8954-8957. k. Ohno, M.; Mori, K.; Hattori, T.; Eguchi, S. *J. Org. Chem.* **1990**, *55*, 6086-6091. l. Engler, T.A.; Combrink, K.D.; Takusagawa, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1573-1576.

3. For a review of the Dötz reaction, see Wulff, W.D. In *Comprehensive Organic Synthesis*; Trost, B.M.; Fleming, I.; Paquette, L.A. Eds., Pergamon: Oxford 1991, Vol. 5, pp 1065-1113.

4. Tumer, S.U.; Herndon, J.W.; McMullen, L.A. *J. Am. Chem. Soc.* **1992**, *114*, 8394-8404.

5. Herndon, J.W.; Chatterjee, G.; Patel, P.; Matasi, J.J.; Tumer, S.U.; Harp, J.J.; Reid, M.D. *J. Am. Chem. Soc.* **1991**, *113*, 7808-7809.

6. Herndon, J.W.; Zora, M. *Synlett* **1993**, 363-365.

7. Katz, T.J.; Lee, S.J. *J. Am. Chem. Soc.* **1980**, *102*, 422-424.

8. a. Dötz, K.H.; Erben, H.-G.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 692-693. b. Alvarez, C.; Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J.C.; Knobler, C. *Organometallics* **1989**, *8*, 2253-2259.

9. Fischer, E.O.; Kalbfus, W. *J. Organometal. Chem.* **1972**, *46*, C15-C18.

10. Yamashita, A.; Toy, A.; Ghazal, N.B.; Munchmore, C.R. *J. Org. Chem.* **1989**, *54*, 4481-4483.

11. Harvey, D.F.; Brown, M.F. *Tetrahedron Lett.* **1990**, *31*, 2529-2532.

12. Fleming, I. In *Comprehensive Organic Chemistry;* Barton, D.H.R.; Ollis, W.D.; Jones, N. Eds.; Pergammon: Oxford, 1979; Vol. 3, pp 613-622.

13. Herndon, J.W.; Matasi, J.J. *J. Org. Chem.* **1990**, *55*, 786-88.

14. Harvey, D.F.; Brown, M.F. *Tetrahedron Lett.* **1991**, *32*, 5223-5226.

15. ter Borg, A.P.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 1189-1196.

16. a. Larson, J.R.; Epiotis, N.D.; Bernardi, F. *J. Am. Chem. Soc.* **1978**, *100*, 5713-5716. b. Venkataraman, H.; Cha, J.K. *Tetrahedron Lett.* **1989**, *30*, 3510-3513.

17. Turner, R.B.; Garner, R.H. *J. Am. Chem. Soc.* **1958**, *80*, 1424-1430.

18. Macomber, D.W. *Organometallics* **1984**, *3*, 1589-1591.

19. Bos, M.A.; Wulff, W.D.; Miller, R.A.; Chamberlin, S.; Brandvold, T.A. *J. Am. Chem. Soc.* **1991**, *113* 9293-9319.

20. Herndon, J.W.; Zora, M.; Shen, F. Unpublished Observations

21. Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73-146.

22. Harvey, D.F.; Lund, K.P.; Neil, D.A. *J. Am. Chem. Soc.***1992**, *114* 8424-8434.

23. McCallum, J.S.; Kunng, F.-A.; Gilbertson, S.R.; Wulff, W.D. *Organometallics* **1988**, *7*, 2346-2360.

24. Hofmann, P.; Hämmerle, M., Unfried, G. *New J. Chem.* **1991**, *15*, 769-789.

25. Meek, J.S.; Osuga, D.T. In *Organic Syntheses:* Baumgarten, H.E. Ed.; Collective Vol. V; John Wiley and Sons: New York, 1973; pp 126-130.

26. Yamaguchi, M.; Nobayashi, Y.; Hirao, I. *Tetrahedron* **1984**, *40*, 4261-4266.

27. Hauser, J.W.; Grubber, M.J. *J. Org. Chem.* **1972**, *37*, 2648-2650.

28. This compound was prepared from 2-methyl-1,4-pentadiene according to the procedure in reference 27.