# Reactions of Pentacarbonyl(1-methoxyethylidene)molybdenum and -tungsten with α,ω-Enynes: Comparison with the Chromium Analogue and Resulting Mechanistic Ramifications

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The title reactions of the molybdenum- and tungsten-containing Fischer carbene complexes 1-Mo and 1-W with the series of enynes 2 have been examined. Significant differences are noted in comparison with previous studies with the analogous chromium Fischer carbene complex 1-Cr. Namely, selectivities for cyclopropane formation are higher and, for the first time, a trisubstituted enyne has participated in the cyclopropanation pathway. A new reaction manifold which produced cyclopentenones as the result of a Pauson–Khand-like cyclization has been identified. Simple dienes arising from reaction of nondonor-substituted alkylidenemolybdenum and -tungsten "carrier" species have also been observed. This has led to the mechanistic suggestion that the greater ability of the larger tungsten atom to access relatively hindered species of higher coordination selectively opens reaction pathways which are less accessible to the corresponding chromium and molybdenum analogues. Within this framework the seven-coordinate metallacyclobutane **15g** is a necessary intermediate in the conversion of enyne **2g** to the bicyclic cyclopropane **10g**. Likewise, to account for the formation of the unusual Pauson–Khand cyclization products, it is proposed that seven-coordinate species like 18 and 20 are important.

## Introduction

Since their initial synthesis in 1964, Fischer carbene complexes have received considerable attention as useful synthetic intermediates in the formation of, e.g., phenols and naphthols, enol ethers, cyclohexadienes, pyridines, β-lactams, cyclobutanones, cyclopentenones, indenes, cycloheptadienes, and simple or polycyclic cyclopropanes.[2] Recently we have demonstrated that the reaction of Fischer carbene complexes with enyne substrates is a viable strategy for the construction of bicyclic carbon skeletons.[3] Thus, the reactions of pentacarbonyl(1-methoxyethylidene)chromium (1-Cr) with 1,6-enynes 2 produced bicyclic cyclopropanes 3, metathesized dienes 4, bicyclic cyclobutanones 5, and furans 6 (Scheme I).[3a]

In the course of our investigations we have also discovered that the nature of the carbene donor group (heteroatom) plays a substantial role in determining the mechanistic pathway and, therefore, the product distribution in the reaction with enynes. The reactions of pentacarbonyl(1-pyrrolidinoethylidene)chromium with the enynes 2 produced only the bicyclic cyclopropanes 3.[3b,4] Similarly, bicyclic cyclopropanes were the only products isolated from the reactions of the in situ generated pentacarbonyl(1-oxidoalkylidene)chromium anions with 1,6-enynes.[3c] These results suggest that the analogues of presumed vinyl carbene intermediates 8[5] in which OMe is replaced by more strongly electron-donating substituents have sufficient electron density on the metal to prevent CO insertion and preclude the formation of vinylketene complexes like 9, presumed precursors to furans[6a,b] and cyclobutanones.[6c]

Ease of cyclopropanation depends upon the degree of alkene substitution; more highly substituted olefins enter the cyclopropanation manifold less readily. Substrates containing trisubstituted olefins have not previously been observed to undergo cyclopropanation.[3a,b] This is a significant limitation which restricts the widespread application of the above strategy to the synthesis of many polycyclic carbon skeletons.

In addition to the impact which the heteroatom can have on the reactivity of group VI metal carbene complexes, the nature of the metal itself plays a significant role.[3d] For example, the use of *tungsten* Fischer carbenes tends not to give rise to products derived from CO insertion and ketene-like intermediates.[7] Recent reports of cyclization studies with *molybdenum* carbene complexes which produce polycyclic cyclopropane-containing skeletons are also relevant.[8] We have now studied reactions of the neutral carbene complexes, pentacarbonyl(1-methoxyethylidene)*molybdenum* and *-tungsten* (1-Mo, 1-W), with the α,ω-enynes **2a–g** (Table I). These results are here compared and contrasted with those derived from analo-

(1) BASF Graduate Fellow 1991–1992.

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(7) E.g.: (a) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833. (d) See pages 236–237 in ref 2f.

(8) (a) Harvey, D. F.; Brown, M. *J. Am. Chem. Soc.* **1990**, *112*, 7806. (b) Harvey, D. F.; Brown, M. *Tetrahedron Lett.* **1990**, *31*, 2529. (c) Harvey, D. F.; Brown, M. *Tetrahedron Lett.* **1991**, *32*, 5223. (d) Harvey, D. F.; Lund, K. P.; Neil, D. A. *Tetrahedron Lett.* **1991**, *32*, 6311.

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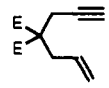
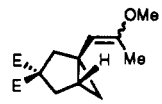
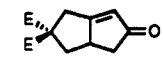
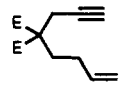
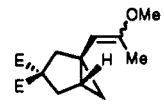
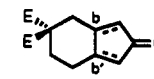
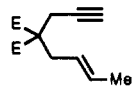
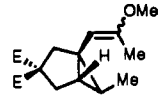
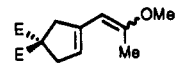
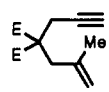
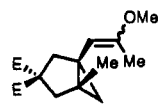
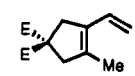
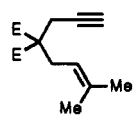
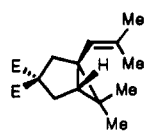
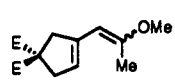
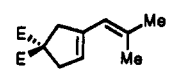
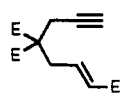
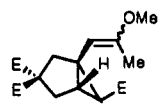
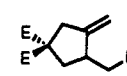
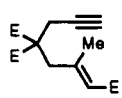
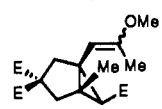
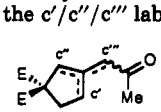
**Table I. Reaction of Pentacarbonyl(1-methoxyethylidene)molybdenum (1-Mo) and -tungsten (1-W) with Enynes 2 To Produce Cyclopropanes 10, Metathesis Enol Ethers 11, Metathesis Dienes 12, and Pausori–Khand or Reductive Cyclization Products 13**

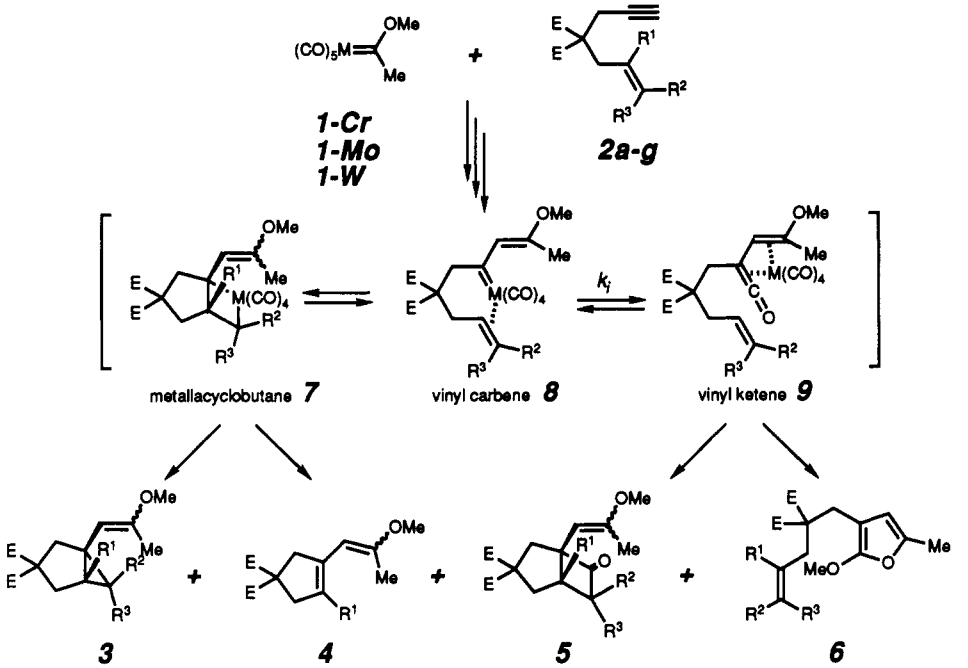
| | substrates | | yields[a] of products 11–14 | | | | |
|---|---|---|---|---|---|---|---|
| entry | enyne 2 | metal in 1 | cyclopropane 10[b] | metathesis enol ether 11[b] | ketene-derived products[c] | metathesis diene 12 | 13 |
| a |  **2a** | |  **10a** | | | |  **13a** |
| | | Cr[c] | 67 | - | - | - | - |
| | | Mo | 81 | - | - | - | - |
| | | W | 48 | - | - | - | 24 |
| b |  **2b** | |  **10b** | | | |  **13b/b′** |
| | | Cr[c] | 46 | - | 20[e] | - | - |
| | | Mo | 52 | - | 10[e] | - | - |
| | | W | 27 | - | - | - | 24 |
| c |  **2c** | |  **10c** |  **11c** | | | |
| | | Cr[c] | 2 | 30 | 13[d,e] | - | - |
| | | Mo | 23 | 28 | - | - | - |
| | | W | 24 | 6[f] | - | - | - |
| d |  **2d** | |  **10d** | | |  **12d** | |
| | | Cr[c] | 23 | - | 23[d] | - | - |
| | | Mo | 65 | - | - | - | - |
| | | W | 48 | - | - | 9 | - |
| e |  **2e** | |  **10e** |  **11c** | |  **12e** | |
| | | Cr[c] | - | 30 | 14[d,e] | - | - |
| | | Mo | - | 28 | 10[d] | 50 | - |
| | | W | 5 | 6[f] | - | 34 | - |
| f |  **2f** | |  **10f** | | | |  **13f** |
| | | Cr[c] | 65 | - | - | - | - |
| | | Mo | 73 | - | - | - | - |
| | | W | 48 | - | - | - | 5 |
| g |  **2g** | |  **10g** | | | | |
| | | Cr[c] | 2 | - | - | - | - |
| | | Mo | 53 | - | - | - | - |
| | | W | 53 | - | - | - | - |

[a] Yields stated are of material isolated by MPLC ($SiO_2$). A "-" Entry indicates that the product was not observed (i.e., less than ~2% formed). [b] A mixture of the *E*- and *Z*-enol ethers was isolated when 1-Cr was used; the hydrolyzed ketone corresponding to these enol ethers was isolated when 1-W was used; a mixture of the enol ethers and ketone was isolated when 1-Mo was used (see text). [c] See ref 2a. [d] Cyclobutanone 5.[c] [e] Furan 6.[c] [f] The isolated material was actually an ~2:2:1:1 mixture of the endocyclic and E- and Z-exocyclic enones 11c′/c″/c‴ where the position of the alkene is indicated by the c′/c″/c‴ labels.



11c′/c″/c‴

**Scheme I**




gous reactions with the *chromium*-based complex 1-Cr.[3a] The dissimilarities imply significant and important differences in mechanism. We offer the suggestion that reactions of the larger tungsten-containing carbenes are able to facilitate certain reaction paths by accessing relatively hindered, seven-coordinate intermediates.[9]

## Results

The enynes **2a–g** were treated with the molybdenum or tungsten carbene 1-Mo or 1-W (~1.1 equiv) in toluene at 120 °C (external bath) in a resealable culture tube under a nitrogen atmosphere. Typically, the enyne was consumed after 1–2 h (TLC analysis) for the molybdenum-based reactions (which also proceeded in THF at room temperature or, more conveniently, 80 °C) and 16–24 h (TLC analysis) for the tungsten-based reactions. The mixture was then allowed to stir open to the air for 30 min, and products were chromatographed on silica gel. Compared with the analogous chromium carbenes, the reactions with 1-Mo occurred at faster rates and those with 1-W at slower rates. This presumably reflects the relative strengths of association of CO ligands in 1 with the relevant metal center.[10]

The reaction of 1-Mo with enyne **2a** (entry a, Table I) produced the bicyclic cyclopropane skeleton shown as **10a** in 81% total yield. The reaction of 1-W with **2a** produced the ketone derived from hydrolysis of **10a** in 48% yield as well as the cyclopentenone **13a** (24%). In contrast to reactions with the chromium analogue 1-Cr where *E*- and *Z*-methyl enol ethers **10a** were the only cyclopropane-containing products observed,[3a] the tungsten carbene reaction conditions always produced only the corresponding "hydrolyzed" ketones, while the molybdenum carbene reaction conditions usually gave rise to a mixture of both the ketones as well as *E*- and *Z*-enol ether species. For simplicity, we have chosen throughout to represent all products having the same carbon skeleton as the enol ethers regardless of their "hydrolysis state."

The cyclopentenone **13a** is the result of a Pauson–Khand-like cyclization[11] of **2a**, an event that is unprecedented in Fischer carbene chemistry. Recognize that **13a** has not incorporated the carbene carbon of 1-W nor its substituents; we comment later on additional experiments designed to shed light on this reaction pathway.

Enyne **2b** (entry b), a one carbon longer homologue of **2a**, reacted with 1-Mo to yield the bicyclic cyclopropane (**10b**) in 52% along with a ketene derived furan (**6**) in 10%. The reaction of enyne **2b** with 1-W also produced a bicyclic ketocyclopropane (**10b**) and the corresponding Pauson–Khand product as an ~1:1 mixture of the isomeric enones **13b/b′**. The formation of the bicyclo[4.1.0]heptane **10b** would be expected to be slower than the formation of the bicyclo[3.1.0]hexane **10a**, thereby permitting increased competition from the ketene or Pauson–Khand reaction pathways.

Enyne **2c** (entry c) differs from **2a** by the presence of an additional methyl substituent on the olefin terminus. Reaction with 1-Mo gave similar amounts of bicyclic cyclopropanes **10c** and the enol ethers from metathesis **11c**. The analogous reaction with 1-W produced the bicyclic cyclopropane **10c** as the major product accompanied by the enones **11c′/11c″/11c‴**. Alkenes **11** are the result of metal–carbene/alkene metathesis within the vinylcarbene complex **8**. Products **10** and **11** arise via competitive reductive elimination vs retro 2 + 2 fragmentation of the metallacyclobutane **7** (Scheme I).

The enyne **2d** (entry d) also contains an additional alkyl substituent on the olefin but now on the internal rather than terminal carbon. Reaction of this enyne with 1-Mo gave only the cyclopropane **10d** (65%). However, the reaction of **2d** with 1-W produced the cyclopropane **10d** (48%) and the diene **12d** (9%). By analogy to the ob-

(9) For an example of an isolable 7-coordinate tungsten complex containing no chelating ligands $[(^tBuN{\equiv}C)_7W](PF_6)_2$, see: Szalda, D. J.; Dewan, J. C.; Lippard, S. *Inorg. Chem.* **1981**, *20*, 3851.

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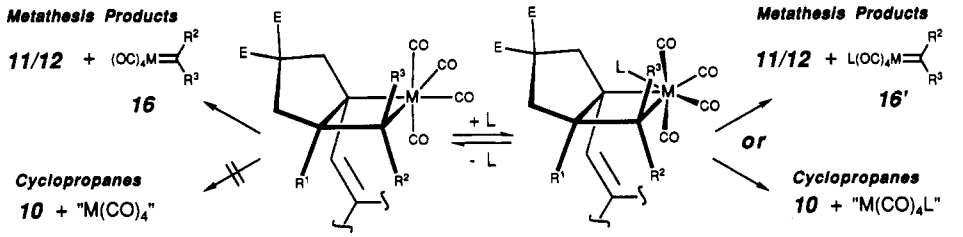
(11) (a) Pauson, P. L.; Khand, I. U. *J. Chem. Soc., Chem. Commun.* **1974**, 379. (b) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477. (c) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. (d) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

**Scheme II**




| 14 | $R^1$ | $R^2$ | $R^3$ | 15 |
|---|---|---|---|---|
| a | H | H | H | a |
| c | H | Me | H | c |
| d | Me | H | H | d |
| e | H | Me | Me | e |
| f | H | $CO_2Me$ | H | f |
| g | Me | $CO_2Me$ | H | g |

servations and suggestion by Katz,[12] this diene presumably arises from the reaction of the in situ generated, highly reactive "carrier" carbene species $(CO)_nW{=}CH_2$ with the enyne **2d**. This carbene species $(CO)_nW{=}CH_2$ is the result of retro 2 + 2 fragmentation of the metallacyclobutane intermediate **7** ($R^1$ = Me, $R^2$ = $R^3$ = H; M = W). No metathesis product **11d** was observed. This can best be explained if the chain reaction of $(CO)_nW{=}CH_2$ with enyne **2d** to produce **12d** (which regenerates $(CO)_nW{=}CH_2$) is very efficient. This would mean that only a few molecules of **7** need fragment (to produce $(CO)_nW{=}CH_2$ and **11d**) as an initiation step for the chain process which then produces **12d**.

The reaction of trisubstituted enyne **2e** with 1-Mo gave the enol ether **11c** (28%), a ketene-derived cyclobutanone **5** (10%), and the diene **12e** (50%) as the major product. The reaction of 1-W with the *tri*substituted enyne **2e** (entry e) produced a small amount of the bicyclic vinylcyclopropane **10e** (but not the corresponding ketone or enol ether), the previously mentioned alkenes **11c′/11c″/11c‴**, and, as the major product, the diene **12e**. The cyclopropane **10e** as well as the diene **12e** presumably arise from the reaction of the in situ generated carrier carbene complex $(CO)_nM{=}CMe_2$ (**16e**) with the enyne **2e**. This new carbene is presumably also the result of retro 2 + 2 cleavage of the metallacyclobutane intermediate **7**.

Substrates **2f** and **2g** (entries f and g) contain an electron-deficient alkene, an α,β-unsaturated enoate. Reaction of the *di*substituted alkene **2f** with 1-Mo gave only the cyclopropane **10f** (66%). Enyne **2f** reacted with 1-W to produce **10f** (48%) and a small amount of the reductive cyclization product **13f**. Reaction of the electronically similar but *tri*substituted enyne **2g** (entry g) with the molybdenum and tungsten carbenes 1-Mo and 1-W produced the cyclopropane **10g** as the only isolated material both in 53% yield. This is the first example of an efficient cyclopropanation of a *tri*substituted olefin in these Fischer carbene-enyne reactions. Incidentally, while the chromium carbene analogue 1-Cr reacted with the *di*substituted enyne **2f** to give bicyclic cyclopropanes in good yield (65%),[3a] reaction of the *tri*substituted analogue **2g** with 1-Cr produced only a 2% yield of the cyclopropane **10g**.

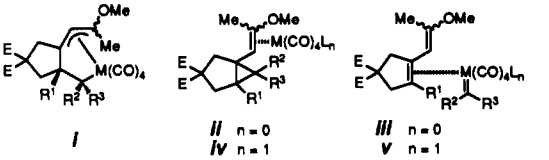
## Mechanistic Discussion

It is interesting and appropriate to speculate about the factors governing the relative rates of cyclopropanation versus retro 2 + 2 cycloaddition in the metallacyclobutane intermediates **14** (cf. **7**). The initially formed, 16-electron, six-coordinate metallacyclobutane **14** seemingly requires the addition of a seventh ligand L, to produce the 18-electron species **15** prior to undergoing reductive elimination to a cyclopropane **10** with concomitant formation of the transient 16-electron $M(CO)_4L$ species (Scheme II). In this and subsequent mechanistic discussion, we use L to represent any viable two-electron donor ligand—a suitable solvent molecule, another carbon monoxide ligand, or two electrons from the adjacent C–C π-bond. In other words, included among the structures which **15** represents is the $\eta^3$-allyl species in which L is the alkene π-electron density (see structure i in footnote 13).

In the absence of prior seven-coordination, cyclopropane formation from within **14** would require the expulsion of the highly energetic 14-electron fragment $M(CO)_4$.[13] On the other hand, a retro 2 + 2 process within **14** would produce the more palatable, if still transient, 16-electron carbene complex **16**.[13] Moreover, fragmentation from within the more crowded intermediate **15** should be further favored, relative to **14**, by the accompanying relief of steric strain. This analysis (i) supports the idea that formation of **15** is a necessary prerequisite for the reductive elimination reaction which forms cyclopropane-containing materials **10**[14a] but (ii) suggests that metathesis can be consummated from either of the 6- or 7-coordinate species **14** or **15** to generate **11/12** and **16** or **16′**, respectively.[13] Similar arguments have been made by Casey[14b] to explain the partitioning between cyclopropanation vs metathesis in the reaction of ethyl vinyl ether with pentacarbonyl(1-

(12) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.

(13) A reviewer has made the entirely reasonable suggestion that reductive elimination or metathesis from within **14** (or the $\eta^3$-allyl complex i) could initially form the 16- and 18-electron complexes ii and iii, respectively, each of which could undergo subsequent external ligand association and alkene dissociation. However, this would not change the fundamental argument—if accessible, the 7-coordinate species **15** should still preferentially undergo reductive elimination and cyclopropane formation. By analogy, that event would generate the 18-electron alkene complex iv by a pathway which should still be energetically favored (for both electronic and steric reasons) over the **14** → ii process. Moreover, metathesis from within **15** would be disfavored (relative to **14** → iii), since it would give rise to the 20-electron diene complex v. Finally, we note that if indeed $\eta^3$-allyl complexes like i are involved in the reactions described here, it is surprising that at no time have we observed the formation of a cyclopentene-containing product.




*I* *II* n = 0 *IV* n = 1 *III* n = 0 *V* n = 1

(14) (a) Casey, C. P., Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097. (b) Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, pp 218–220. (c) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 3966.

**Table II. Comparison of Normalized Ratios of Yields (% x/% a) of Cyclopropanes 10 Formed from Various Enynes 2 with the Chromium[2a] vs Molybdenum and Tungsten Carbene Complexes 1**

| carbene complex | % 10a/ % 10a | % 10d/ % 10a | % 10c/ % 10a | % 10e/ % 10a | % 10f/ % 10a | % 10g/ % 10a |
|---|---|---|---|---|---|---|
| | | increasing steric hindrance → | | | | |
| 1-Cr | 1.0 | 0.3 | 0.03 | $<10^{-2}$ | 0.9 | 0.03 |
| 1-Mo | 1.0 | 0.8 | 0.28 | $<10^{-2}$ | 0.9 | 0.65 |
| 1-W | 1.0 | 1.0 | 0.50 | 0.1 | 1.0 | 1.1 |

methoxy-1-phenylmethylidene)chromium—a case where higher CO pressure is known to influence the branching in favor of the reductive elimination event.[14c]

In the case of reaction of any of the three carbenes **1** with **2c**, metathesis is promoted relative to the case of **2a**, since the new electron-deficient carbene **16c**, formed by fragmentation, bears a stabilizing methyl group (i.e., $R^2$ = Me).[12] In addition, the reductive elimination to form cyclopropane **10c** is disfavored, since formation of the seven-coordinate species **15c** is inhibited by greater steric destabilization relative to that in **15a**. This inhibition could be either kinetic or thermodynamic in origin.

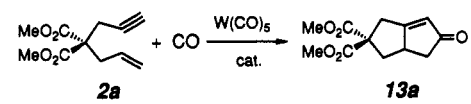
In the reaction of enyne **2d** with carbenes **1** the cyclopropanation pathway is only slightly curtailed (relative to **2a**), since the species **15d** does not suffer nearly the extent of steric destabilization between the methyl group ($R^1$) and the ligands on the metal as does **15c**.[15] On the other hand, the trisubstituted enyne **2e** would be expected to provide yet additional (relative to **2c**) steric hindrance in the 18-electron/7-coordinate metallacyclobutane **15e**, thereby further inhibiting the cyclopropanation event. Also, the additional alkyl substituent should further promote metathesis by increasing stabilization of the metathesis carbene **16e/16'e**. Such is the case. Carbene **1-W** is the only complex to provide even a trace of a trisubstituted cyclopropane (**10e** in which the $Me_2C$ moiety from the carrier carbene **16e/16'e** has been incorporated rather than the Me(MeO)C fragment from **1-W** itself), and all three of **1** gave relatively large proportions of metathesis dienes (**11c** and **12e**).

The inherent electronic factors present in enynes **2f** and **2g** seemingly also play a significant role in the competition between reductive elimination and retro 2 + 2 fragmentation from metallacyclobutanes **14/15**. Thus, retro 2 + 2 fragmentation of **14f/15f** or **14g/15g** would form the very unstable, electron-deficient, methoxycarbonyl-substituted Fischer carbene complexes **16f/16'f** or **16g/16'g**. These electronic factors apparently can override the steric elements within the 7-coordinate metallacycles **15f** (M = Cr, Mo, W) and **15g** (M = Mo, W), and the reductive elimination process now totally dominates the suppressed retro 2 + 2 fragmentation step.

It is also possible to rationalize some of the metal dependencies in these reactions of **1-Cr**, **1-Mo**, and **1-W** within this framework. Comparison (see Table II) of the relative yields of cyclopropane products **10** by normalization to the yield of **10a** derived from the simple vinyl-containing substrate **2a** across the series of progressively more sterically hindered substrates **2a**, **2d**, **2c**, and **2e** is very informative. Namely, cyclopropanation is most sensitive to steric effects in the chromium-mediated reactions and least sensitive with tungsten. This further supports the ideas and rationale represented in Scheme II, since the smallest, chromium atom analogue of **14/15** creates an environment in which added substitution more greatly destabilizes the 7-coordinate, chromium analogue of **15**. Molybdenum is intermediate in its behavior. Moreover and as previously mentioned, the electronic effect which suppresses the retro 2 + 2 fragmentation is sufficient to completely (for tungsten), mostly (for molybdenum), or partially (for chromium) override the steric constraints toward reductive elimination (cf. % **f**/% **a** with % **g**/% **a**).

Numerous reactions are known in which product distribution between structures not incorporating vs incorporating a carbon monoxide molecule is strongly coupled to the use of tungsten and molybdenum vs chromium carbenes, respectively.[2a,d,f,7,8] Authors have tended to rationalize the partitioning of vinyl carbene **8** to non-ketene- and ketene-derived products (**3** and **4** vs **5** and **6**, respectively) by focusing on the assumed large differences of rates of CO insertion within **8** (i.e., $k_i$, Scheme I). There is a second mechanistic extreme. Assume for a moment that carbon monoxide insertion within **8** is independent of the metal (i.e., constant $k_i$). Reductive elimination and metathesis within the **14/15** equilibrium are the processes which drain **7** from the **7/8/9** manifold. As suggested earlier, the equilibrium constant $K_{15/14}$ (=[15]/[14]) will be significantly greater for tungsten- relative to chromium-containing intermediates. At this end of the mechanistic spectrum it is the ease of reaction processes which are alternatives to CO insertion rather than the rate of CO insertion itself that dictates branching of **8** and subsequent product ratios. That is, the size around the metal center could again play an important role by favorably influencing the kinetic and/or thermodynamic preference for formation and/or reaction of metallacyclobutane **7**. We suggest that reality quite likely exists somewhere in between this pair of mechanistic extremes.

A final discussion about the origin of the unexpected Pauson–Khand (and reductive cyclization) products **13** is in order. We hypothesized that pentacarbonyltungsten, a byproduct of the reductive elimination leading to cyclopropanation, could mediate net CO insertion into an enyne like **2a** to give **13a** (eq 1). According to this picture,



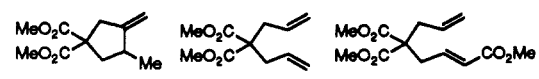

**2a** **13a** (1)

the overall transformation involves a $(CO)_5W$-catalyzed addition of carbon monoxide to, e.g., **2a** to give **13a**. To test this hypothesis, **2a** was treated with a solution of $(CO)_5W$·THF, generated by irradiation of a THF solution of the hexacarbonyl[16] prior to enyne addition. Although little reaction occurred until the mixture was warmed to ~55 °C, the cyclopentenone **13a** was then formed in 60% yield along with two reduction products.[17a] Electron-deficient alkenes are notoriously poor substrates for the typical, $Co_2(CO)_8$-mediated Pauson–Khand cyclization.[11c] Therefore, the ester-containing enyne **2f** was also subjected to $(CO)_5W$·THF. The cyclopentenone **21** was formed but in just 22% yield along with two other reduction products.[17b]

(15) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

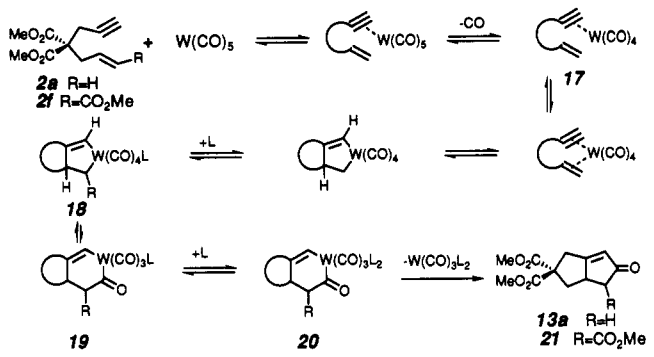
(16) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401.

(17) (a) Products from reductive cyclization (vi) and simple acetylene reduction (dimethyl diallylmalonate, vii) were isolated in 10 and 3% yield, respectively. (b) The diene viii (3%) and reductive cyclization product **13f** (11%) were also generated.




*vi* *vii* *viii*

**Scheme III**



A mechanism which accounts for these observations is shown in Scheme III. That we have never observed cyclopentenones like **13a** and **21** when using chromium-based carbene reagents is consistent with the suggestion that formation of the 7-coordinate species **18** and **20**, the Cr analogues of which would again be disfavored on steric grounds, is a necessary prerequisite to migratory insertion of carbon monoxide into the metal–alkyl bond to give **19** as well as for the reductive elimination within **20** to give **13a/21**. That the electron-withdrawing carbomethoxy substituent inhibits the overall process is consistent with the expected retardation of the migratory insertion of **18** to **19** in a substrate with a more electron-deficient alkyl ligand.[18] It is interesting to note in passing that the tungsten containing intermediates in this mechanism regularly oscillate between 16- and 18-electron species[19] but irregularly fluctuate among 5-, 6-, and 7-coordination.

Finally, we do not know the origin of the hydrogen atoms which are incorporated into the small amount of reduction products which accompanied several of the reactions described here.[17] These reductions are even more perplexing, since they were observed in reactions using both carbene 1-W as well as $(CO)_5W$·THF and in both of the solvents toluene and THF. We have not observed reduced byproducts from chromium or molybdenum carbene mediated reactions.[20]

In conclusion, comparison of the group 6 metal carbene complexes pentacarbonyl(1-methoxyethylidene)*molybdenum* and -*tungsten* with the *chromium* analogue reveals differences in reactivity patterns. Some are of synthetic advantage; in several instances both molybdenum and tungsten display higher selectivities for cyclopropane formation and exhibit a greater ability to access relatively hindered 7-coordinate intermediates as compared with the chromium analogue. The first *tri*substituted alkenes have participated in the cyclopropanation pathway. A new, Pauson–Khand-like process leading to cyclopentenones (i.e., **13a**, **13b**, and **21**) has been discovered. Dienes likely resulting from simple alkylidenemolybdenum and -tungsten "carrier" species (i.e., **12d**, **12e**, and ref 12) have been observed. Perhaps most importantly, significant mechanistic pictures (Schemes II and III) have emerged which allow for the effective rationalization of these differences. Both share the suggestion that pathways involving tungsten-containing intermediates differ, in part, from their chromium analogues because of the enhanced ability of this larger metal to access hindered, 7-coordinate species like **15**, **18**, and **20**.

## Experimental Section

**General Information.** All NMR and IR spectra were recorded in $CDCl_3$, and NMR chemical shifts are reported relative to residual $CHCl_3$ at δ 7.26 or $CDCl_3$ at δ 77.0. Capillary gas chromatography/mass spectrometry was performed with a Hewlett-Packard 5971-MSD instrument on an HP-5 (5% phenylmethylsilicone) column.

**General Procedure for the Reactions of Carbenes 1-Mo and 1-W with Enynes 2a–g.** In a screw-capped culture tube under a $N_2$ atmosphere were mixed the enyne (**2a–g**, ~0.50 mmol) and pentacarbonyl(1-methoxyethylidene)molybdenum or -tungsten (1.1 equiv) in ~10 mL of dry toluene. The reaction mixture was heated (120 °C external bath temperature) for 1–2 h for molybdenum or 16–24 h for tungsten, in which time the mixture assumed a dark, black-green appearance. Some of the reactions for tungsten were complete ($SiO_2$ TLC analysis in ~9:1 hex/EtOAc) in less than 16 h, but additional heating gave no appreciable difference in product yield. The crude mixture was cooled, opened to the air for ~30 min, passed through a plug of Florisil (2:1 hex/EtOAc elution; >95% crude mass recovery), and then purified by MPLC on $SiO_2$ (hexanes/EtOAc) to provide the products in the yields reported in Table I. Spectroscopic characterization data for previously unreported compounds follow.

**(±)-[1α,5α]-6,6-Dimethyl-1-(2-methyl-1-propenyl)bicyclo[3.1.0]hexane-3,3-dicarboxylic Acid Dimethyl Ester (10e).** IR: 2950 (m), 2880 (w), 1730 (vs), 1450 (m), 1435 (m), 1380 (w), 1260 (s), 1200 (s), 1180 (m), and 1070 (w) $cm^{-1}$. $^1H$ NMR (200 MHz): δ 5.26 (s, $CH$=$C(Me)_2$), 3.72 (s, $CO_2Me$), 3.67 (s, $CO_2Me$), 2.62 (dd, $J$ = 14.6 and 7.3 Hz, $CH_aH_bCH$), 2.40 (dd, $J$ = 14.5 and 8.5 Hz, $CH_mH_nCR_3$), 1.96 (dd, $J$ = 14.6 and 2.6 Hz, $CH_aH_bCH$), 1.65 [s, CH=C(Me)*Me*], 1.57 [s, CH=C(*Me*)Me], 1.11 [dd, $J$ = 7.3 and 2.6 Hz, $CH_aH_bCH$], 1.04 [s, CHC(Me)*Me*], and 0.90 [s, CHC(*Me*)Me]. $^{13}C$ NMR (50 MHz): δ 174.3, 172.2, 135.7, 127.1, 67.8, 52.7, 52.4, 41.3, 38.3, 37.1, 34.1, 29.4, 24.7 (2 C), 19.4, and 16.3. HRMS (CI, $NH_3$): calcd for $C_{16}H_{24}O_4^+$, $m/e$ 280.1668; found, $m/e$ 280.1674.

**(±)-[1α,5α,6α]-5-Methyl-1-(2-oxopropyl)bicyclo[3.1.0]hexane-3,3,6-tricarboxylic Acid Trimethyl Ester (10g).** IR: 3010 (w), 2950 (w), 1730 (vs), 1420 (s), 1430 (s), 1370 (m), 1250 (s), 1180 (s), 1100 (m), 1070 (m), and 880 (w) $cm^{-1}$. $^1H$ NMR (200 MHz): δ 3.73 (s, $CO_2Me$), 3.68 (s, $CO_2Me$), 3.57 (s, $CO_2Me$), 3.13 (d, $J$ = 18.3 Hz, $CH_aH_b$), 2.80 (d, $J$ = 14.25 Hz, $CH_cH_d$), 2.79 (d, $J$ = 14.28 Hz, $CH_eH_f$), 2.77 (d, $J$ = 18.3 Hz, $CH_aH_b$), 2.44 (d, $J$ = 14.28 Hz, $CH_eH_f$), 2.37 (d, $J$ = 14.25 Hz, $CH_cH_d$), 2.09 (s, C(O)*Me*), 1.52 (s, $CHCO_2Me$), and 1.22 (s, Me). $^{13}C$ NMR (50 MHz): δ 207, 173.0, 172.2, 171.7, 58.3, 53.3 (2 C), 51.5, 44.7, 43.3, 41.0, 37.3, 37.2, 30.6, 30.2, and 12.4. Anal. Calcd for $C_{16}H_{22}O_7$: C, 58.89; H, 6.80. Found: C, 58.79; H, 6.80.

**(*E*)-3-(2-Oxopropylidene)cyclopentane-, (*Z*)-3-(2-Oxopropylidene)cyclopentane-, 3-(2-Oxopropyl)-3-cyclopentene-, and 3-(2-Oxopropyl)-2-cyclopentene-1,1-dicarboxylic Acid Dimethyl Ester (*E*-11c‴, *Z*-11c‴, 11c′, 11c″).** MPLC resulted in an ~1:2 mixture of *E*-11c‴/*Z*-11c‴ to 11c′/11c″. Further fractionation of the latter mixture of regioisomers by $SiO_2$ HPLC (6:1 hex/EtOAc) gave, in order of elution, 11c′ and 11c″.

***E*-11c‴/*Z*-11c‴.** IR ($CDCl_3$): 3025 (w), 2950 (w), 2890 (w), 1730 (vs), 1680 (m), 1620 (s), 1430 (m), 1350 (m), 1280 (s), 1250 (m), 1200 (m), 1160 (m), 1060 (m), 960 (w), and 800 (m) $cm^{-1}$. $^1H$ NMR (200 MHz): δ 6.23 (m, $CH$=C), 3.72 [s, $(CO_2Me)_2$], 3.73 [s, $(CO_2Me)_2$], 3.42 (bs, $E_2CCH_2C$= in *Z*-isomer), 3.06 (bs, $E_2CCH_2C$= in *E*-isomer), 2.91 (bt, $J$ = 7.5 Hz, $CH_2CH_2C$= in *E*-isomer), 2.59 (bt, $J$ = 7.5 Hz, $CH_2CH_2C$= in *Z*-isomer), 2.35 (t, $J$ = 7.6 Hz), 2.26 (t, $J$ = 7.6 Hz), and 2.17 (s, COMe). $^{13}C$ NMR (50 MHz): δ 198.2, 172.0, 171.8, 162.1, 120.1, 60.4, 52.9, 52.8, 43.1, 40.9, 34.0, 33.9, 32.5, 31.6, and 30.9. GCMS (70 eV): first isomer, 240 (23), 209 (17), 181 (100), 180 (36), 165 (37), 149 (22), 148 (35), 138 (23), 121 (36), 120 (28), and 77 (23); second isomer, 240 (13), 181 (100), 180 (22), 165 (20), 149 (15), 148 (15), 138 (15), 121 (20), 120 (14), 107 (18), and 77 (19).

**11c′.** IR: 2950 (w), 2925 (w), 1730 (vs), 1705 (vs), 1440 (m), 1340 (s), 1280 (s), 1260 (m), 1220 (m), 1180 (m), 1160 (m), 1080

(18) E.g.: (a) Cotton, J. D.; Crisp, G. T.; Daly, V. A. *Inorg. Chim. Acta* **1981**, *47*, 165. (b) Alexander, J. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Ed.; Wiley: New York, 1985; Vol. 2, Chapter 5.

(19) The alkyne-$W(CO)_4$ complex **17** can be considered as either a 16- or 18-electron species at tungsten depending upon whether the alkyne is acting as a two- or four-electron donor, respectively.

(20) For an example of a reduction product arising from a Cr(0)-mediated reaction, see: Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334.

(m), 960 (w), and 800 (m) $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 5.42 (bs, C*H*=C), 3.72 [s, $(CO_2Me)_2$], 3.18 (bs, $CH_2$), 3.04 (bs, $CH_2$), 2.96 (bs, $CH_2$), and 2.16 (s, COMe). $^{13}C$ NMR (50 MHz): $\delta$ 206.0, 171.9 (2 C), 144.1, 127.2, 64.5, 52.8 (2 C), 46.4, 43.0, 41.3, and 31.6. GCMS (70 eV): 240 (16), 181 (5), 180 (16), 139 (42), 138 (100), 107 (13), 79 (34), 78 (15), 77 (25), and 43 (35).

**11c″**. IR: 3025 (w), 2975 (w), 2860 (w), 1735 (vs), 1700 (s), 1440 (m), 1360 (m), 1280 (s), 1260 (s), 1230 (m), 1160 (m), 1070 (m), 960 (w), and 800 (m) $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 5.65 (bs, C*H*=C), 3.73 [s, $(CO_2Me)_2$], 3.24 (bs, $CH_2CO$), 2.35–2.50 (m, $CH_2CH_2C$=), and 2.16 (s, COMe). $^{13}C$ NMR (50 MHz): $\delta$ 205, 171.8 (2 C), 142.8, 126.2, 66.3, 52.7 (2 C), 34.5, 32.0, 30.7, and 29.5. GCMS (70 eV): 240 (14), 181 (22), 180 (23), 139 (100), 138 (99), 107 (35), 79 (19), 78 (9), 77 (22), and 43 (23). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.80; H, 6.68.

**3-Ethenyl-4-methyl-3-cyclopentene-1,1-dicarboxylic Acid Dimethyl Ester (12d).** IR: 2950 (w), 2890 (w), 1730 (vs), 1440 (m), 1260 (s), 1180 (m), 1110 (w), and 1070 (w) $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 6.55 (dd, $J$ = 17.1 and 11.2 Hz, CH=C$H_a$C$H_b$), 5.04 (m, CH=C$H_a H_b$), 3.73 [s, $(CO_2Me)_2$], 3.14 [bs, C$H_2$C(Me)=C], 3.06 (bs, C$H_2$C=C), and 1.53 (bs, Me). $^{13}C$ NMR (50 MHz): $\delta$ 172.2 (2 C), 140.6, 135.5, 123.5, 117.4, 60.5, 52.7 (2 C), 43.3, and 40.3. HRMS (CI, $CH_4$): calcd for $C_{12}H_{16}O_4 + H^+$, $m/e$ 225.1126; found, $m/e$ 225.1130.

**3-(2-Methyl-1-propenyl)-3-cyclopentene-1,1-dicarboxylic Acid Dimethyl Ester (12e).** IR: 3020 (w), 2975 (w), 2950 (w), 1710 (vs), 1430 (m), 1420 (m), 1360 (s), 1220 (vs), and 1080 (w) $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 5.72 (bs, C$H_a$=C), 5.37 (bs, C$H_b$=C), 3.72 [s, $(CO_2Me)_2$], 3.19 (bs, $CH_2$), 3.03 (bs, $CH_2$), and 1.79 (d, C=C$Me_2$). $^{13}C$ NMR (50 MHz): $\delta$ 175.2 (2 C), 138.7, 135.5, 124.3, 120.6, 59.3, 52.7 (2 C), 43.2, 40.2, 27.2, and 19.7. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.62. Found: C, 65.69; H, 7.67.

**(±)-5,5-Dicarbomethoxy-3a,4,5,6-tetrahydro-2(3*H*)-pentalenone (13a).** IR: 3000 (w), 2950 (w), 1730 (vs), 1700 (vs), 1630 (s), 1430 (s), 1400 (w), 1280 (s), 1250 (vs), 1220 (s), 1190 (s), 1170 (m), 1160 (s), 1060 (m), 1030 (w), and 820 (w) $cm^{-1}$. $^1H$ NMR (300 MHz): $\delta$ 5.91 (bs C=CHC=O), 3.76 (s, $CO_2Me$), 3.73 (s, $CO_2Me$), 3.31 (bd, $J$ = 19.0 Hz, C$H_a H_b$C=CH), 3.26 (bd, $J$ = 19.0 Hz, C$H_a H_b$C=CH), 3.08 (vbs, $CH_2CHCH_2$), 2.79 (dd, $J$ = 12.8 and 7.6 Hz, C$H_a H_b$CHC$H_2$), 2.61 (dd, $J$ = 17.9 and 6.3 Hz, $CH_2$CHC$H_c H_d$), 2.1 (dd, $J$ = 17.9 and 3.3 Hz, $CH_2$CHC$H_c H_d$), 1.71 (t, $J$ = 12.7 Hz, C$H_a H_b$CHC$H_2$). $^{13}C$ NMR (50 MHz): $\delta$ 209.1, 184.9, 171.6, 170.9, 125.3, 60.4, 52.9, 52.8, 44.7, 41.8, 38.7, and 34.9. GCMS (70 eV): 238 (34), 207 (17), 206 (19), 178 (38), 151 (22), 150 (22), 119 (100), 91 (55). Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.69; H, 5.91.

**(±)-1(*H*)-2,4,5,6,7,7a-Hexahydro- and (±)-2(*H*)-3,3a,4,5,6,7-Hexahydro-2-oxoindene-5,5-dicarboxylic Acid Dimethyl Ester (13b, 13b′).** IR [data reported for an ~1:1 mixture (capillary GC) of the regioisomers]: 2960 (w), 2875 (w), 1730 (vs), 1705 (vs), 1620 (m), 1450 (w), 1435 (m), 1280 (w), 1250 (m), 1200 (m), 1080 (w), 1060 (w), 910 (vs), and 880 (s) $cm^{-1}$.

**13b.** $^1H$ NMR (300 MHz): $\delta$ 5.97 (bs, =C*H*), 3.76 and 3.72 (s, $CO_2Me$), 3.49 (bd, $J$ = 12.6, C$H_{eq}H_{ax}$C=CH), 2.67 (bd, $J$ = 12 Hz, $CH_{eq}H_{ax}$C=CH), ~2.65 (bm, $R_3CH$), 2.60 (dd, $J$ = ~18 and ~4 Hz, C$H_a H_b$CO), 2.55 (bd, $J$ = ~12 Hz, $E_2$CC$H_{eq}H_{ax}$CH), 2.2 (vbd, $J$ = ~12 Hz, $E_2CCH_2CH_{eq}H_{ax}$), 1.98 (d, $J$ = ~18 Hz, $CH_aH_b$CO), 1.93 (bt, $J$ = ~12 Hz, $E_2CCH_{eq}H_{ax}$CH), and 1.26 (bq, $J$ = ~12 Hz, $E_2CCH_2CH_{eq}H_{ax}$). GCMS (70 eV): 252 (50), 221 (14), 220 (13), 192 (100), 164 (34), 133 (60), and 105 (56).

**13b′.** $^1H$ NMR (300 MHz): $\delta$ 5.90 (bs, =C*H*), 3.82 and 3.73 (s, $CO_2Me$), 2.6–2.9 (m, 5 H), ~2.50 (btd, $J$ = ~12 and 3 Hz), 1.99 (bd, $J$ = ~18 Hz, $CH_aH_b$CO), 1.92 (btd, $J$ = ~12 and 3 Hz, 1 H), and ~1.6 (m). GCMS (70 eV): 252 (54), 221 (12), 220 (16), 192 (74), 145 (40), 133 (100), 113 (50), 108 (40), and 105 (46).

**(±)-3-(2-Methoxy-2-oxoethyl)-4-methylenecyclopentane-1,1-dicarboxylic Acid Dimethyl Ester (13f).** IR: 2910 (w), 2975 (m), 2860 (w), 1750 (vs), 1680 (w), 1440 (s), 1360 (w), 1340 (m), 1260 (vs), 1200 (s), 1175 (s), 1080 (m), 1020 (w), 910 (m), 880 (m), and 700 (m) $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ 4.96 (d, $J$ = 2.1 Hz; C=C$H_a H_b$), 4.80 (d, $J$ = 2.1 Hz; C=C$H_a H_b$), 3.72 (s, $CO_2Me$), 3.71 (s, $CO_2Me$), 3.67 (s, $CO_2Me$), 3.03 (bd, $J$ = 16.2 Hz, C$H_a H_b$-C=C$H_2$), ~2.95 (bm, $R_3CH$), 2.94 (bd, $J$ = 16.2 Hz, $CH_aH_b$C=C$H_2$), 2.66 (dd, $J$ = 13.2 and 8.2 Hz, $ECH_cH_dCHCH_eH_f$), 2.61 (dd, $J$ = 15.9 and 5.4 Hz, $EC H_cH_dCHCH_eH_f$), 2.33 (dd, $J$ = 15.7 and 7.7 Hz, $ECH_cH_dCHCH_eH_f$), 1.93 (dd, $J$ = 13.2 and 10.2 Hz, $ECH_cH_dCHCH_eH_f$). $^{13}C$ NMR (50 MHz): $\delta$ 173, 172.4 (2 C), 150.6, 106.6, 5.75, 52.5, 52.4, 51.2, 40.4, 39.5, 38.3, and 38.0. HRMS (CI, $NH_3$): calcd for $C_{13}H_{18}O_6 + H^+$, $m/e$ 271.1181; found, $m/e$ 271.1182.

**Reaction of Enynes 2a and 2f with $(CO)_5$W·THF To Produce the Pauson–Khand Products 13a and 21.** In a screw-capped culture tube under a $N_2$ atmosphere was placed tungsten hexacarbonyl (1.2 equiv) in ~15 mL of dry THF. The reaction mixture was irradiated (3500-Å light) for 2 h, in which time any undissolved hexacarbonyl dissolved and the solution became yellow. The enynes **2a,e** were added via syringe in ~2 mL of THF. The reaction mixture was heated (100 °C external bath temperature) for ~2 h, in which time the mixture assumed a deep red then black appearance. The crude mixture was cooled, opened to the air for ~30 min, passed through a plug of Florisil (2:1 hex/EtOAc elution; >95% crude mass recovery), and then purified by MPLC on $SiO_2$ (hexanes/EtOAc) to provide the products in the yields reported. Spectroscopic characterization data for previously unreported compounds follow.

**(±)-3,5,5-Tricarbomethoxy-3a,4,5,6-tetrahydro-2(3*H*)-pentalenone (21).** IR: 3000 (w), 2950 (w), 2850 (w), 1730 (vs), 1720 (vs), 1700 (vs), 1640 (s), 1430 (s), 1440 (w), 1435 (m), 1350 (w), 1320 (m), 1280 (s), 1250 (s), 1220 (s), 1200 (s), 1170 (m), 1160 (s), 1135 (m), 1060 (w), and 1020 (w) $cm^{-1}$. $^1H$ NMR (300 MHz): $\delta$ 5.92 (bs, C=CHC=O), 3.78 (s, $CO_2Me$), 3.76 (s, $CO_2Me$), 3.73 (s, $CO_2Me$), 3.51 (m; $CH_2CHCHCO_2Me$), 3.41 (d; $J$ = 19.1 Hz, C$H_a H_b$C=CH), 3.24 (d; $J$ = 19.1 Hz, C$H_a H_b$C=CH), 3.14 (d; $J$ = 3.85 Hz, $CHCO_2Me$), 2.85 (dd; $J$ = 12.7 and 7.8 Hz, C$H_c H_d$CHCHC$O_2$Me), 1.85 (t; $J$ = 12.7 Hz, $CH_cH_d$CHCHC$O_2$Me). $^{13}C$ NMR (50 MHz): $\delta$ 207.2, 184.4, 172.3, 170.5, 170.1, 123.4, 60.6, 59.1, 53.4, 53.2, 52.5, 48.4, 37.9, and 35.1. Anal. Calcd for $C_{14}H_{16}O_7$: C, 56.75; H, 5.44. Found: C, 56.66; H, 5.20.

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**Registry No.** **1-Cr**, 20540-69-6; **1-Mo**, 12365-46-7; **1-W**, 20540-70-9; **2a**, 107428-06-8; **2b**, 108561-17-7; **2c**, 113704-38-4; **2d**, 109468-75-9; **2e**, 107473-14-3; **2f**, 113704-39-5; **2g**, 140440-48-8; (*E*)-**5b**, 140440-56-8; (*Z*)-**5b**, 140656-74-2; (*E*)-**5e**, 140440-67-1; (*Z*)-**5e**, 140440-68-2; **6**, 141087-94-7; (*E*)-**10a** (enol ether), 140440-49-9; (*Z*)-**10a** (enol ether), 140440-50-2; **10a** (ketone), 140440-51-3; (*E*)-**10b** (enol ether), 140440-53-5; (*Z*)-**10b** (enol ether), 140440-54-6; **10b** (ketone), 140440-55-7; (*E*)-**10c** (enol ether), 140631-08-9; (*Z*)-**10c** (enol ether), 140631-09-0; **10c** (ketone), 121569-46-8; (*E*)-**10d** (enol ether), 140440-63-7; (*Z*)-**10d** (enol ether), 140440-64-8; **10d** (ketone), 140440-65-9; **10e**, 140440-69-3; (*E*)-**10f** (enol ether), 140631-10-3; (*Z*)-**10f** (enol ether), 140631-11-4; **10f** (ketone), 140631-12-5; (*E*)-**10g** (enol ether), 140440-71-7; (*Z*)-**10g** (enol ether), 140631-13-6; **10g** (ketone), 140464-10-4; (*E*)-**11c** (enol ether), 113704-49-7; (*Z*)-**11c** (enol ether), 113704-50-0; **11c′**, 140440-59-1; **11c″**, 140440-60-4; (*E*)-**11c‴**, 140440-61-5; (*Z*)-**11c‴**, 140440-62-6; **12d**, 109468-82-8; **12e**, 140440-66-0; **13a**, 140440-52-4; **13b**, 140440-57-9; **13b′**, 140440-58-0; **13f**, 140440-70-6; **21**, 140440-72-8; $(CO)_5$W·THF, 36477-75-5.

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