Intramolecular Reactions of Fischer Carbene Complexes with Alkynes and a Mechanistic Study of the Interception of Reactive Intermediates with Added Acetylenes

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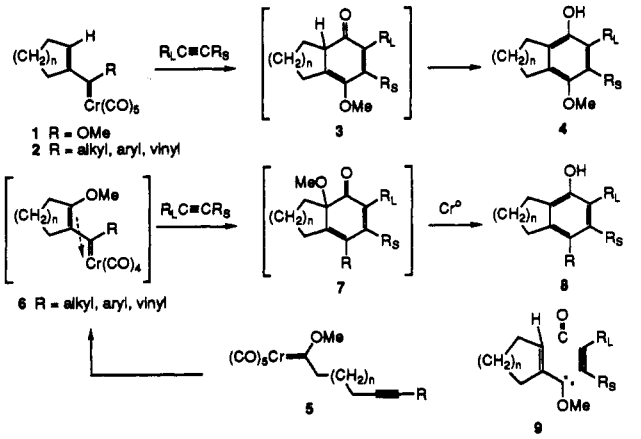
Received January 25, 1993[⊗]

Abstract: The reactions of 1-(4-hexynyl)methoxymethylenepentacarbonyl complexes **11** of the group 6 metals with alkynes lead to phenol and cyclopentenedione products, both of which are the result of cyclization with one molecule of the external alkyne and the internal alkyne in the carbene complex. All four of the possible phenol products of this reaction were independently synthesized, and the product distribution among the four isomers and the cyclopentenedione was investigated as a function of solvent, concentration, and the nature of the metal. The results of these experiments suggest that the phenol **13** arises from a vinyl carbene complexed intermediate and that the phenol **16** and cyclopentenedione **12** arise from a vinyl ketene complexed intermediate. This was confirmed by a series of methanol trapping experiments and by the isolation, characterization, and study of the chemistry of the proposed vinyl ketene complex.

The most widely utilized application of Fischer carbene complexes in organic synthesis is a one-step synthesis of benzene rings that can be carried out at near ambient temperatures and under neutral conditions.[2-4] This annulative process generally produces new benzene rings with 1,4-dioxygenated substitution patterns, as illustrated by the reaction of alkenyl complexes **1** in Scheme I. The phenol products **4** from these reactions are the result of the incorporation of the carbene carbon, the α,β-unsaturated substituent of the carbene carbon, the alkyne, and a carbon monoxide ligand, as illustrated diagrammatically in

Scheme I



structure **9**. The ultimate intermediate in these reactions has long been proposed to be the cyclohexadienone **3**, and recently an example of this intermediate has been characterized as a metal complex.[5] The phenol complexes **4** are normally produced as air-sensitive chromium tricarbonyl complexes, but the metal is usually lost during workup in air. The incorporation of the alkyne is regioselective, with the largest substituent appearing adjacent to the phenol function as indicated in **4**.[6] This is especially true for terminal acetylenes (≥100:1), which in combination with the typically good yields for this reaction (60–90%) constitutes an attractive methodology for aromatic systems that has been strategically deployed in the synthesis of a number of natural products.[3,4]

The benzannulation reaction is limited to the synthesis of 1,4-dioxygenated benzene derivatives of the type **4** since Fischer carbene complexes are stable and sufficiently easy to handle only if they have at least one heteroatom substituent such as the

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1993.

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(2) For reviews on the chemistry of Fischer carbene complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Casey, C. P. *React. Intermed. (Wiley)* **1985**, *3*. (d) Dötz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; tom Dieck, H., de Meijere, A., Eds; Springer: Berlin, 1988. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (f) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, 1989. (g) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (h) *Transition Metals in Total Synthesis*; Harrington, P. J.; John Wiley: New York, 1990, pp 346–399. (i) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991, Vol. 5, pp 1065–1113.

(3) For a list of citations to syntheses, see refs 2g and 4 and the following: Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293.

(4) For recent syntheses and model studies, see: (a) Gordon, D. M.; Danishefsky, S. H. *J. Org. Chem.* **1992**, *26*, 7052. (b) Chamberlin, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10667. (c) Parker, K. A.; Coburn, C. A. *J. Org. Chem.* **1991**, *56*, 1666. (d) Bos, M. E.; Wulff, W. D.; Brandvold, T. A.; Chamberlin, S.; Miller, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293. (e) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1991**, *56*, 2115. (f) King, J. S.; Quayle, P. *Tetrahedron Lett.* **1991**, *32*, 7759. (g) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1990**, *55*, 1919. (h) King, J.; Quayle, P.; Malone, J. F. *Tetrahedron Lett.* **1990**, *31*, 5221. (i) Dötz, K. H.; Popall, M.; Mueller, G.; Ackermann, K. *J. Organomet. Chem.* **1990**, *383*, 93. (j) Semmelhack, M. F.; Jeong, N. *Tetrahedron Lett.* **1990**, *31*, 605. (k) Semmelhack, M. F.; Jeong, N.; Lee, G. R. *Tetrahedron Lett.* **1990**, *31*, 609. (l) Boger, D. L.; Jacobson, I. C. *Tetrahedron Lett.* **1989**, *30*, 2037. (m) Flitsch, W.; Lauterwein, J.; Micke, W. *Tetrahedron Lett.* **1989**, *30*, 1633. (n) Yamashita, A.; Toy, A.; Scahill, T. A. *J. Org. Chem.* **1989**, *54*, 3625. (o) Yamashita, A.; Toy, A.; Ghazal, N. B.; Muchmore, C. R. *J. Org. Chem.* **1989**, *54*, 4581. (p) Bauta, W. E.; Wulff, W. D.; Pavkovic, S. F.; Saluzec, E. J. *J. Org. Chem.* **1989**, *54*, 3249.

(5) Wulff, W. D.; Brandvold, T. A.; Chan, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics*, in press.

(6) (a) Wulff, W. D.; Tang, P. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677. (b) Dötz, K. H.; Muhlemeier, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187. (c) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293. (d) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471.

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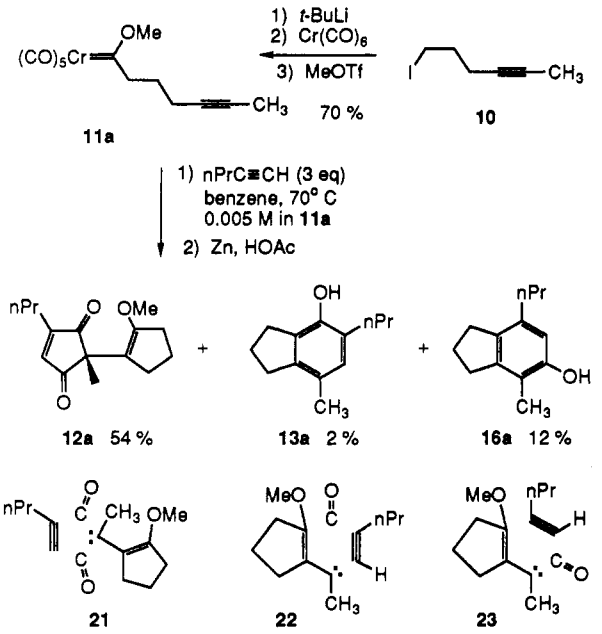
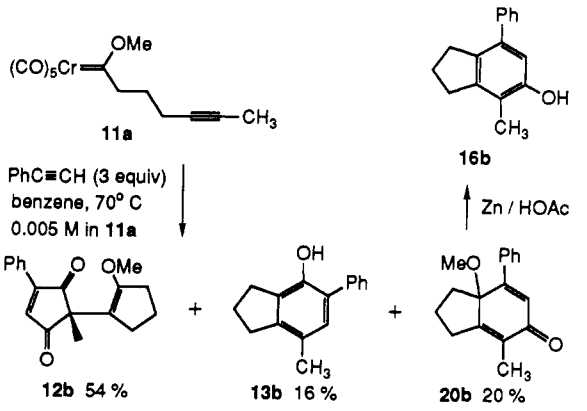
Scheme II



Scheme III



methoxyl in complex **1**.[7] That is to say that aryl products of the type **8** (R = alkyl, aryl, vinyl) are not possible from the classical form of the benzannulation reaction since the requisite carbene complexes of the type **2** cannot be prepared. The work described herein began with the idea to overcome this limitation of the benzannulation reaction by employing the intramolecular reaction of the alkynyl carbene complex **5**.[8,9] The intramolecular alkyne insertion in **5** should generate *in situ* the vinyl carbene complex **6**, which should serve as a surrogate for the carbene complex **2** in the benzannulation reaction since the anticipated 6-methoxy-substituted cyclohexadienone intermediate **7** would be expected to be easily reduced under the reaction conditions to give the phenol **8**.[10]

Initial Results

The actual outcome from the reaction of the alkynyl carbene complex **11a** with 1-pentyne in benzene as solvent is shown in Scheme II and radically contrasts to the anticipated outcome that was outlined in Scheme I on several counts. First, the anticipated product **13a** was formed in only 2% yield. The phenol **13a** can be thought of as being assembled from the pieces indicated by structure **22**, where the *in situ* carbene complex **6** is considered as the source of the carbene. In benzannulation reactions of carbene complexes of the type **1** the carbene carbon and the carbon monoxide ligands are always incorporated into para positions, and it is for this reason that the actual predominate phenol product **16a** was unexpected since the carbene carbon and the carbon monoxide ligands are incorporated in ortho positions, as indicated by structure **23**, and the annulations of an α,β-unsaturated carbene complex have never produced this substitution pattern.[11] The regiochemistry of the incorporation of 1-pentyne in phenol **16a** was also completely unexpected since the benzannulations of α,β-unsaturated carbene complexes always produce as the major regioisomer that which has the phenol function and the largest group of the alkyne in adjacent positions on the arene ring.[6] Finally, the major product of the reaction was the yellow cyclopentenedione **12a**, which represented a completely unprecedented transformation in the reactions of carbene complexes with alkynes. It was the first product found from these reactions that incorporates two alkynes and two carbon monoxide ligands.[13] Clearly, our inability to even come close in predicting the products from the reaction of **11a** and 1-pentyne indicates a significant lack of understanding of the mechanisms of the reaction of carbene complexes and acetylenes, and the goal of the present work is to shed more light on these mechanisms by studying the specific reactions of alkynyl carbene complexes of the type **5**.

The isolation of phenol **13a** from the reaction of complex **11a** with 1-pentyne strongly implies that the 6-methoxy-substituted cyclohexadienone **7** (Scheme I) was indeed an intermediate in this reaction and that it was reduced *in situ* by chromium(0). Cyclohexadienones can also be isolated from the general reaction indicated in Scheme I, and these products were first observed in the reaction of complex **11a** with phenylacetylene. In this case the nonreduced cyclohexadienone product **20b** could be isolated in 20% yield from the reaction in benzene at 0.005 M. It was established that the cyclohexadienone **20b** was not the precursor to phenol **13b** when it was observed that the reduction of **20b** with zinc and acetic acid gave a phenol which was different from **13b**. As indicated in Scheme IV, there are four possible phenol and cyclohexadienone products, and the structures of **13b** and **20b** are assigned on the basis of the unambiguous assignments made for the products from the reaction of **11a** with 1-pentyne. The cyclopentenedione **12b** was obtained as a red crystalline solid, and its structure has been confirmed by X-ray diffraction.[8b]

Assignment of the Regiochemistry of the Phenol Products 13a and 16a

The assignment of the structures of the phenols **13a** and **16a** from the reaction of complex **11** and 1-pentyne was unambiguously made on the basis of the independent syntheses and labeling experiments illustrated in Schemes V–VII. These experiments were designed to distinguish between the four possible phenols **13–16** indicated in Scheme IV that could theoretically be produced from these reactions. This set of four phenols can be generated

(7) Six-membered-ring products can also be obtained from the reaction of thio-substituted and properly substituted amino-substituted carbene complexes: (a) Reference 2g, p 238. (b) Yamashita, A.; Toy, A.; Ghazal, N. B.; Muchmore, C. R. *J. Org. Chem.* **1989**, *54*, 4481. (c) Dötz, K. H.; Leue, V. *J. Organomet. Chem.* **1991**, *407*, 337. (d) Aumann, R.; Schröder, J. *Chem. Ber.* **1990**, *123*, 2053. (e) Dötz, K. H.; Grotjahn, D.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1384.

(8) Preliminary accounts of different facets of the present work have been published in preliminary form: (a) Wulff, W. D.; Xu, Y. C. *Tetrahedron Lett.* **1988**, *29*, 415. (b) Xu, Y. C.; Challener, C. A.; Dragisich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269. (c) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615.

(9) Various aspects of the present work have been presented at the 195th ACS National Meeting, June 5–10, 1988, Toronto, Canada, ORG 154, and at the 199th ACS National Meeting, April 22–27, 1990, Boston, MA, INORG 215.

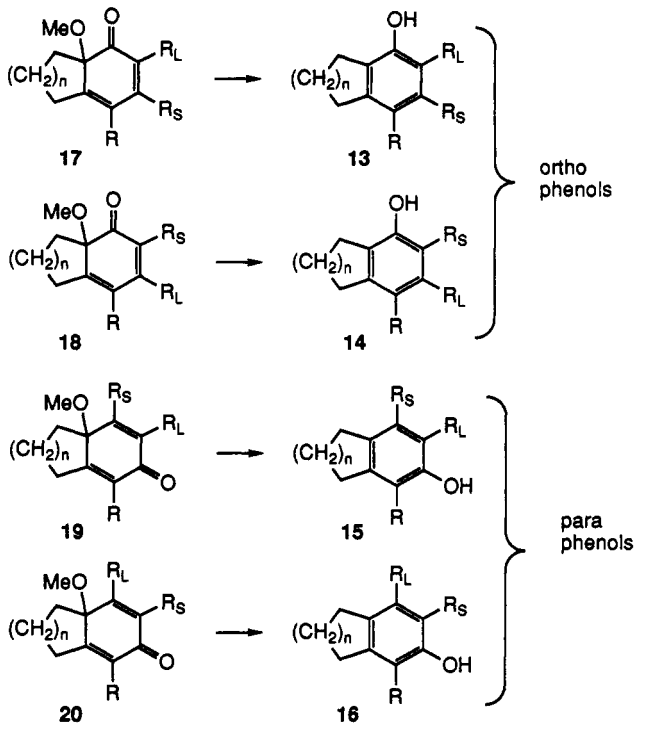
(10) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

(11) The only exceptions to this observation are found in photochemical reactions[12] and related reactions that incorporate two alkynes.[10]

(12) (a) Reference 2f, p 336. (b) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418.

(13) A second example has been reported: Bao, J.; Dragisich, V.; Wenglowsky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873.

Scheme IV



as the only possible phenol products that could be produced from this reaction if the reasonable assumption is made that the carbon–carbon bonds in the two acetylene functions are not broken in the process. The structures of these four phenols and their cyclohexadienone precursors are indicated in Scheme IV.

The series of reactions outlined in Scheme V was carried out since it has the advantage of producing both of the regioisomers of **13a** and **14a** in a single pot. Isomers **13** and **14** have in common the incorporation of the carbon monoxide ligand into a position adjacent to that of the carbon bearing the methoxyl group, as illustrated by structure **22** in Scheme II, and differ only by the regiochemistry of alkyne incorporation into **22**. The isomers **13** and **14** are to be contrasted to the pair of isomers **15** and **16**, which are both derived from incorporation of the carbon monoxide ligand para to the methoxyl-bearing carbon, as illustrated by structure **23** in Scheme II. The synthesis of **13a** and **14a** begins with the known reaction of the cyclopentenyl carbene complex **24** with 1-pentyne.[6c] The phenol product **26** had been previously reported from the reaction of **24** in THF,[6c] but unlike the reaction in hexane indicated in Scheme V, the cyclopentenedione product **25** was not previously reported for this reaction but has been observed from the reaction of aryl and alkyl carbene complexes.[8b,14] This is the only example of a vinylcyclopentenedione product from the reaction of an alkenyl carbene complex. The addition of methyllithium to the quinone **27** was not regioselective as might have been anticipated[15] and gave both of the cyclohexadienones **28** and **29** (1.6:1.0 mixture), which were reduced with zinc and acetic acid to a separable mixture of **13a** and **14a**.

The synthesis strategy outlined in Scheme V was designed to provide authentic samples of **13a** and **14a**, but it cannot distinguish between them. Nonetheless, an analysis of the spectral data of the two phenols produced in the synthesis outlined in Scheme V reveals that the phenol produced from the major methyllithium adduct **28** is identical to the phenol which is produced as a minor product from the reaction of the carbene complex **11** with 1-pentyne (Scheme II). The major phenol product from the carbene complex **11** is nonidentical with either of the phenols produced from the reactions indicated in Scheme V. Therefore, the minor phenol product from the reaction of **11** with 1-pentyne must belong to the isomeric pair **13** and **14**, whereas the major phenol product must belong to the isomeric pair **15** and **16**. The labeling experiment outlined in Scheme VI was carried out to simultaneously assign the regiochemistry for both products. The ^{13}C NMR spectra of the two phenol products from the reaction of the labeled complex **33** with 1-pentyne reveal that the minor phenol has the labeled carbon coupled to two quaternary carbons and thus is **13a** and not **14a**, whereas the major phenol was the labeled carbon coupled to one quaternary carbon and one tertiary carbon and thus is **16a** and not **15a**.

Determination of the Degree of Regioselectivity of the Reaction of the Chromium, Molybdenum, and Tungsten Complexes 11a–c with 1-Pentyne and an Independent Synthesis of 15a

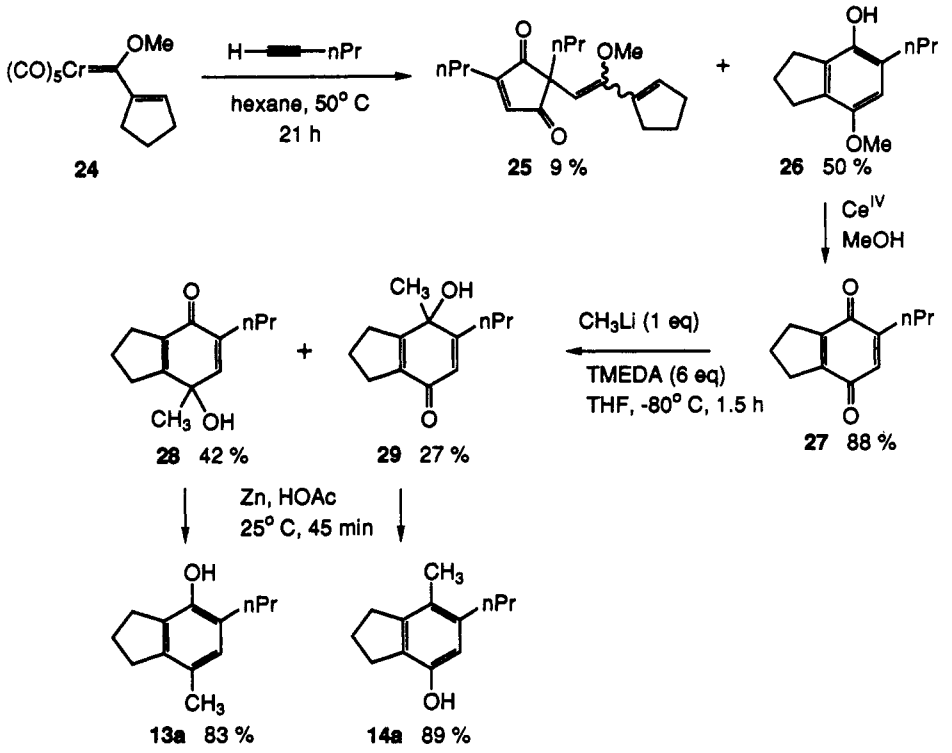
The regiochemistry of the incorporation of the alkyne into the phenol product with the CO adjacent to the methoxyl-bearing carbon occurs with the preferential formation of the phenol **13a** over **14a**, where the larger group on the alkyne becomes incorporated adjacent to the phenol hydroxyl. This is the same regioselectivity that has been observed previously for the benzannulations of complexes of the type **1** with alkynes (Scheme I). The regiochemistry of the incorporation of the alkyne into the phenol product with the CO para to the methoxyl-bearing carbon is reversed and occurs with the selective formation of **16a**, where the larger group on the alkyne is meta to the phenol hydroxyl, and this regioselectivity is unprecedented in the benzannulation of carbene complexes. It is for this reason that a careful analysis was made for the presence of all four of the regioisomeric phenols **13–16** in the reaction of the chromium complex **11a** with 1-pentyne. The reactions indicated in Schemes II and V provided authentic samples of phenols **13a**, **14a**, and **16a**. The fourth regioisomer, **15a**, was synthesized by the reaction of the *n*-propyl carbene complex **34** with the 1,6-heptadiyne **35** and obtained as a single regioisomer.[10] On the basis of the previous demonstration of the regioselectivity of the reactions of carbene complexes with diynes, it was anticipated that the reaction of **34** with **35** would produce the desired phenol **15a** (rather than **36**), which is formed by the selective insertion of the less substituted triple bond of the diyne before the more substituted triple bond. That this regioselectivity was observed for the reaction of **34** with **35** was suggested by the NOE experiments (Experimental Section) and confirmed by the fact that the phenol **15a** was observed in the reactions of the amino complexes **62** (Table V), where the formation of **36** would not be possible.

With authentic samples of all of the regioisomers **13a–16a** in hand, the crude mixtures from the reaction of the chromium complex **11a** with 1-pentyne under a variety of conditions were examined by capillary GC, and the amounts present or the upper limits possible for each of the four regioisomers were determined and are presented in Table I. To ensure that the quantitation of the four phenols was not adversely affected by the incomplete reduction of any or all of the four isomeric cyclohexadienones **17–20** (Scheme IV), the crude reaction mixtures were reduced prior to analysis either by zinc and acetic acid or by a mixture of titanium trichloride and lithium aluminum hydride. The four phenols were then quantified on this reduced mixture by capillary GC; however, the cyclopentenedione product **12** does not survive this reduction, and this product was quantified by isolation from a separate reaction which was not subjected to the reductive workup. As indicated by entries 3–5 for the reactions in benzene solvent, the yields of the cyclopentenedione **12a** and the phenol **16a** increase with decreasing concentration, whereas the yield of the phenol **13a** decreases with decreasing concentration. The product distribution in hexane is similar to that in benzene, and in THF the mass balance is reduced. Interestingly, in acetonitrile

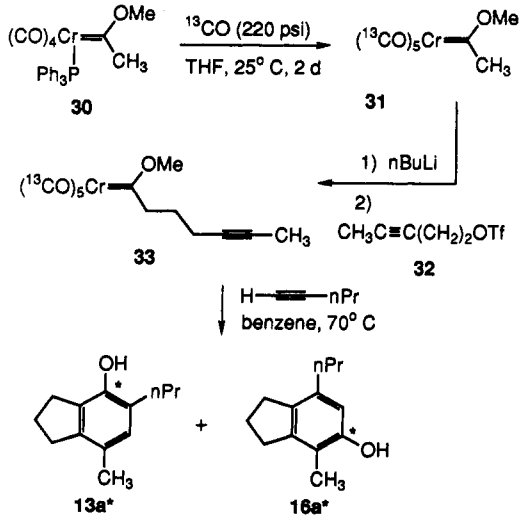
(14) Challener, C. A.; Wulff, W. D.; Anderson, B. A.; Chamberlin, S.; Faron, K. L.; Kim, O. K.; Murray, C. K.; Xu, Y. C.; Yang, D. C.; Darling, S. D. *J. Am. Chem. Soc.* **1993**, *115*, 1359.

(15) Liotta, D.; Saindame, M.; Barnum, C. *J. Org. Chem.* **1981**, *46*, 3369.

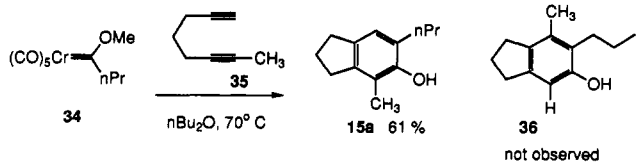
Scheme V



Scheme VI



Scheme VII



only the phenol **13a** is produced and the formation of all of the other products is suppressed. With regard to regioselectivity, it can be seen that the reaction of **11a** with 1-pentyne is completely selective for the formation of **13a** over **14a**, and for the formation of **16a** over **15a**.

Studies of the effect of the metal on the distribution of products from the intramolecular two-alkyne annulation of complexes **11a**, **11b**, and **11c** with 1-pentyne were carried out, and the results are summarized in Table II. At the same concentrations, the chromium complex **11a** has the greatest propensity to generate the cyclopentenedione product **12a**, the molybdenum complex **11b** shifts the distribution in favor of the two-alkyne phenol **13a**, and the tungsten complex **11c** gives the phenol **13a** as the exclusive product at all concentrations, albeit in low yields. The concentration dependence of the yield of **12a** is the same for molybdenum as it is for chromium; the yield of **12a** increases as the concentration decreases. It is also interesting to note that the chromium complex produces mixtures of the phenols **13a** and **16a**, while both the molybdenum and tungsten complexes are selective for the production of phenol **13a**, since the presence of the phenol **16a** cannot be detected in their reactions at any concentration.

Mechanistic Possibilities

The mechanistic possibilities outlined in Scheme IX include reasonable pathways to the three major products **12**, **13**, and **16** that are produced in the intramolecular two-alkyne annulation of carbene complexes of the type **5**. The central issue is whether the products are derived from pathways that include the vinyl carbene complexed intermediate **38**,[16] from the vinyl ketene complexes **47**,[8c] or from some combination of both pathways. For instance, the cyclopentenedione **12** could be generated by reaction of the second alkyne with intermediate **38** to give the metallacyclobutenone **43**, which could undergo CO insertion to give the maloyl carbene complex **44**, which could lead to the product **12** by an insertion and reductive elimination. Alternatively, **12** could be formed from the vinyl ketene complex **47** by a reductive coupling of the second alkyne and the carbon–carbon bond of the coordinated ketene to give the metallacyclopentenone **46**, which upon CO insertion ties into the previous mechanism at intermediate **45**. The former mechanism is attractive since evidence has been presented for a related process in the coupling of a maloyl and vinylidene ligand of a cobalt complex to give a methylene cyclopentenedione.[17] Two quite reasonable mechanisms can also be proposed for formation of the phenol **16**. These involve either the [4 + 2] cycloaddition of an alkyne and the vinyl carbene complex **38** to give the metallacyclohexadiene **42** or the

(16) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908.

(17) Hufmann, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 8617.

Scheme VIII

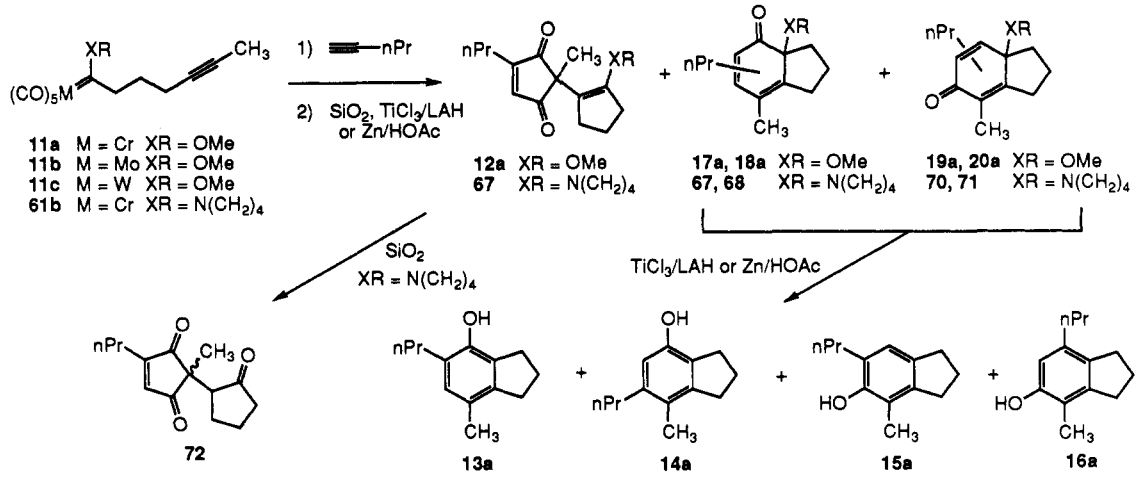


Table I. Solvent and Concentration Effects on the Reaction of **11a** with 1-Pentyne

entry	solvent	[11a]	equiv alkyne	temp (°C)	time (h)	workup method	% yield 12a[a]	13a[a]	14a[b]	15a[b]	16a[a]
1	benzene	0.005	3	70	22	silica gel	55	3			15
2	benzene	0.005	3	70	18	Zn/HOAc	54	2			12
3	benzene	0.5	3	85	20	$TiCl_3$/LAH	14[c]	7	≤0.8	≤1.2	5[d]
4	benzene	0.05	3	85	20	$TiCl_3$/LAH	38[c]	5	≤0.1	≤0.6	11[d]
5	benzene	0.005	3	85	20	$TiCl_3$/LAH	53	2	≤0.3	≤1.0	13
6	THF	0.05	10	80	4	$TiCl_3$/LAH	23	7[b]	≤0.1	≤1	≤0.3[b]
7	benzene	0.05	10	80	4	$TiCl_3$/LAH	41	8[b]	≤0.2	≤0.6	2[b]
8	CH_3CN	0.05	10	80	4	$TiCl_3$/LAH	≤1	15[b]	≤0.5	≤0.5	≤0.5[b]
9	CH_3CN	0.08	3	70	15	silica gel		41			
10	CH_3CN	0.005	2.5	70	15	silica gel		17			
11	hexane	0.08	2	60	24	silica gel	43	4			4
12	hexane	0.01	2	60	24	silica gel	56	10			9
13	hexane	0.005	2	60	24	silica gel	57	10			10
14	hexane[e,f]	0.004	1.2	60	24	silica gel	24	2			2

[a] For those experiments with a reductive workup, the yield of **12a** was determined in a separate experiment by isolation. [b] Determination by a combination of ^1H NMR and capillary GC with triphenylmethane as internal standard in each case. [c] Determined by ^1H NMR with triphenylmethane as internal standard. [d] Determined by capillary GC with triphenylmethane as internal standard. [e] Carried out under a carbon monoxide atmosphere (~3 atm). [f] A 22% yield of **52** and an 18% yield of **53** also obtained in this reaction.

Table II. Effect of the Metal on the Reactions of the Group 6 Complexes **11** with 1-Pentyne[a]

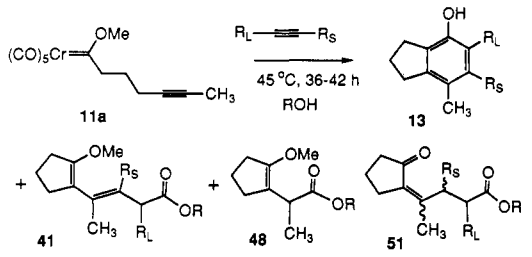
complex		[11]	% yield 12a[b]	13a	14a	15a[c]	16a
11a	Cr	0.5	14[d]	7[e]	≤0.8[e]	≤1.2	5[e]
11a	Cr	0.05	38[d]	5[e]	≤0.1[e]	≤0.6	11[e]
11a	Cr	0.005	53[c]	2[e]	≤0.3[e]	≤1.0	13[c]
11b	Mo	0.5	1[d]	36[d]	≤0.4[d]	≤0.4	≤0.4[d]
11b	Mo	0.05	5[d]	43[d]	≤0.5[d]	≤0.4	≤0.5[d]
11b	Mo	0.005	20[d]	48[c]	≤0.5[d]	≤1.0	≤0.5[d]
11c	W	0.5	≤0.5[d]	17[e]	≤0.5[d]	≤0.5	≤0.5[d]
11c	W	0.05	≤0.5[d]	27[e]	≤0.5[d]	≤0.5	≤3.0[e]
11c	W	0.005	≤0.2[d]	29[c]	≤1.0[d]	≤2.0	≤1.0[d]

[a] All reactions were carried out in benzene at 85 °C for 20 h with 3 equiv of alkyne and workup with $TiCl_3$/LAH prior to analysis. [b] The yields of **12a** were determined in a separate experiment where a reductive workup was not employed. [c] Isolated yield. [d] Yield by ^1H NMR with Ph_3CH as internal standard. [e] Yield by capillary GC with Ph_3CH as internal standard.

[4 + 2] cycloaddition of an alkyne and the vinyl ketene complex **47** to give the cyclohexadienone **20**. The conversion of **47** to **20** could be either a direct [4 + 2] cycloaddition or a reductive coupling to give **46** followed by a 1,3 shift of the metal. The phenol **13** could be formed by insertion of the second alkyne into the vinyl carbene complexed intermediate **38** to give the homologated vinyl carbene complexed intermediate **39-Z**, which upon CO insertion to the vinyl ketene complex **40-Z** could lead directly to **13** by electrocyclic ring-closure and tautomerization. An alternate mechanism for the formation of **13** from the vinyl ketene complex **47** can be envisioned but is considered less likely since it would involve a ring-contraction from the intermediate **46** to **43** and then a ring-expansion to the vinyl ketene complex **40-Z**. It would be anticipated that the ring-contraction of a metallacyclopentenone to a metallacyclobutenone would be endothermic. With regard to the regiochemistry of the phenols, the phenol **13** has the same regiochemistry as that observed for the normal benzannulation (complex **1**, Scheme I), and this correlates with the fact that the regioselectivity is determined in the same step in each case: an insertion of an alkyne into a metal carbene bond.[6] The regiochemistry of the phenol **16** is opposite to that for the normal benzannulation, and this is perhaps just a reflection of the likelihood that the step in which the regiochemistry is determined is quite different in this case: the [4 + 2] cycloaddition of an alkyne to either **38** or **47** with the incorporation of the large group on the alkyne adjacent to the methoxyl group. The regiochemistry for the reaction of the alkyne with intermediates **38** and **47** to give **43** and **46** cannot be determined due to the symmetry of the cyclopentenedione product.

The effect of concentration on the product distribution was most securely determined in benzene (entries 3–5, Table I). The mass balance of these reactions is not constant, thus making interpretation of these results tenuous, but the trends that are evident suggest that the relative yields of cyclopentendione **12** and the phenol **16** increase with decreasing concentration, whereas for phenol **13** they decrease. This trend is also seen for the methanol trapping experiments in Table III. These results are consistent with a partition point at the vinyl carbene complexed intermediate **38**, in which phenol **13** arises from a bimolecular

Table III. Reactions of Complex **11a** with Alkynes in Alcohol Solvents[a]



				% yield		
R_L	R_S	[**11a**]	ROH	**13**	**41**[b]	**48**
Ph	H	0.07	MeOH	36 **13b**	40 **41b**	12 **48a**
Ph	H	0.07	*i*-PrOH	37 **13b**	14 **41c**	≤1 **48b**
Ph	Ph[c]	0.07	MeOH	5 **13d**	≤1 **41d**	41 **48a**
n-Bu	H	0.07	MeOH	21 **13e**	27 **41e**	13 **48a**
n-Pr	H	0.005	MeOH	9 **13a**	12 **41a**	45 **48a**
n-Pr	H	0.21	MeOH	18 **13a**	18 **41a**	11 **48a**

[a] Unless otherwise specified, all reactions were carried out under argon with 3 equiv of alkyne in neat alcohol at 45 °C for 36–42 h. [b] All of the dienyl ketones **41** were isolated as a single isomer, which is assigned as *E* on the basis of NOE experiments on **41b**. Compounds **41** were sensitive to hydrolysis to the diketone **51**. [c] 2.1 equiv of alkyne.

reaction of **38** with the alkyne, and the phenol **16** and cyclopentenedione **12** arise from a CO insertion in **38** to give the vinyl ketene intermediate **47** followed by subsequent reactions with the alkyne (Scheme IX). The concentration effects seen here are quite different and have different origins than those seen for the benzannulation reaction where the partition between two intramolecular processes (one CO insertion) is affected by the concentration of alkyne.[4d] It appears that more coordinating solvents such as THF and especially acetonitrile disfavor the CO insertion in intermediate **38** relative to insertion of alkyne. The reasons for this are not clear at this point but may be due to the displacement of the double bond in **38** by a molecule of solvent. This has been suggested to result in a lower proportion of CO-inserted products in related reactions.[4d,5,47] The study of the effect of the metal on these reactions (Table II) reveals that the tungsten complex gives only the phenol **13**, and this is consistent with previous observations that the vinyl carbene intermediates of tungsten have a much lower propensity than chromium for CO insertion in the benzannulation reaction.[2g,i,5,48] The molybdenum complex did produce the cyclopentenedione **12**, suggesting that CO insertion does occur in the vinyl carbene complexed intermediate **38** but not to the same extent as chromium and interestingly does not produce the phenol **16**. That the molybdenum complex gives less CO insertion products than chromium is consistent with observations made in the benzannulation[2g,i,5,49] and cyclopropanation[50] reactions, but the observation that it gives more CO insertion products than tungsten is not consistent with observations made in the benzannulation reaction.[5] The order of the relative ease of CO insertion in **38** to give **47** relative to alkyne insertion to give **39** is chromium > molybdenum > tungsten. This trend correlates with the metal–CO bond strengths in the metal hexacarbonyls (ΔH_{Cr-CO} = 36.8 kcal/mol, ΔH_{Mo-CO} = 40.5 kcal/mol, ΔH_{W-CO} = 46.0 kcal/mol).[51]

Alcohol Trapping Experiments

With the mechanistic possibilities in Scheme IX in mind, we have carried out a number of experiments to determine which products are formed from which intermediates. The experiments summarized in Tables III and IV involve the trapping of ketene intermediates with alcohols. The reactions of complex **11a** with the four different alkynes and the two different alcohol solvents indicated in Table III all occur with the complete shutdown of the formation of the phenol **16** and the cyclopentenedione **12**. The formation of the phenol **13** is apparently not affected by the alcohol solvent and suggests that the vinyl ketene intermediate **40-Z** undergoes electrocyclic ring-closure faster than it can be trapped with either methanol or 2-propanol. This is supported by data in the literature where it has been shown that electrocyclic ring-closures are faster than alcohol trapping for both free and metal-complexes *Z*-unsaturated ketenes.[18,19] The other two products from the reactions in Table III, in addition to the phenol **13**, are **41** and **48**, which are the alcohol trapping products of the vinyl ketene complexes **40-E** and **47**, respectively. The dienyl esters **41** were all isolated as a single diastereomer, which was assigned as *E* in all cases on the basis of NOE experiments on **41b**, which are described in the Experimental Section. All of the dienyl esters **41** could be isolated in pure form as a single diastereomer, but most were sensitive to hydrolysis to give a mixture of diastereomers of the keto esters **51**, and many were more completely characterized after hydrolysis.

The first entry in Table III has a relative high mass balance, which indicates that most of the vinyl ketene complexes are being largely intercepted. Since the phenol **13b** and ketene-trapping product **41b** are formed in nearly a 1:1 ratio, this means that, although the insertion of the alkyne into the vinyl carbene intermediate **38** occurs with high regioselectivity, it is also essentially stereorandom, producing approximately equal amounts of the (*Z*)- and (*E*)-vinyl carbene complexes intermediates **39**. The reaction of **11a** with 1-pentyne in methanol (entries 5 and 6) gives less of the trapping product **48a** at high concentration (0.21 M) than at a lower concentration (0.005 M). This is consistent with the mechanism proposed in Scheme IX since the reaction of **38** with alkyne to give **39** is a bimolecular reaction and the CO insertion to the vinyl ketene complex **47** is unimolecular. The results with diphenylacetylene are interesting and different in two respects compared to the reactions with terminal acetylenes. Diphenylacetylene gives significantly more **48** relative to **13** and **41** than does either phenylacetylene or 1-pentyne, and this can be rationalized by the reasonable proposition that disubstituted acetylenes are less effective at intercepting vinyl carbene intermediate **38** than are terminal acetylenes. In addition, the partition between **13** and **41** is more in favor of **13** for diphenylacetylene than for either phenylacetylene or 1-pentyne, indicating that diphenylacetylene is more selective for the formation of **39-Z** over **39-E**. A related enhanced selectivity of disubstituted alkynes has been made previously for the normal benzannulation reaction and has been linked to the steric differential of the second substituent on the disubstituted alkyne to the hydrogen of the terminal alkyne.[18]

The experiments summarized in Table IV were designed to examine the effect of the concentration of the alcohol trapping reagent on the product distribution. The reactions were carried out by adding increasing amounts of methanol to the reaction of the chromium complex **11a** with 1-pentyne in benzene solvent. The product partition in pure benzene is given in entry 1 of Table IV, and as can be seen from the rest of the data in Table IV, the yields of both the cyclopentenedione **12a** and the phenol **16a** both decrease with increasing amounts of added methanol, while the yield of the methanol trapping product **48a** undergoes concomitant increases. This is consistent with a mechanism in which both of these products are formed via the pathways that involve the vinyl ketene intermediate **47** and not via pathways that involve the vinyl carbene intermediate **38**, as outlined in Scheme VIII. The yield of the phenol **13a**, on the other hand, is constant throughout the range of experiments with various amounts of added methanol, suggesting that it is formed from the vinyl carbene complex **38** and not via the vinyl ketene intermediate **47**, as illustrated in Scheme IX.

(18) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.
(19) Huisgan, R.; Mayr, H. *J. Chem. Soc., Chem. Commun.* **1976**, 55.

Scheme IX

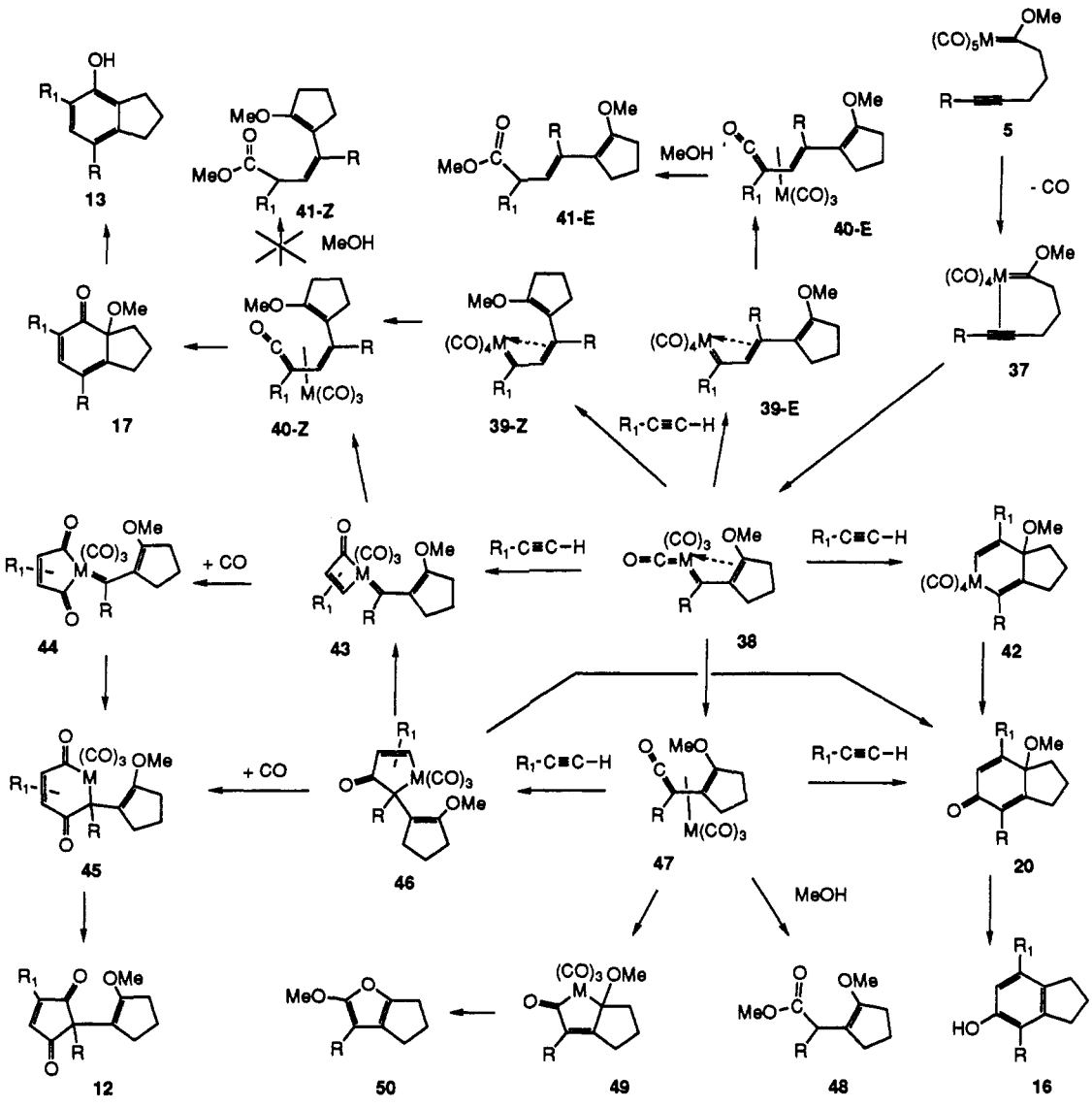


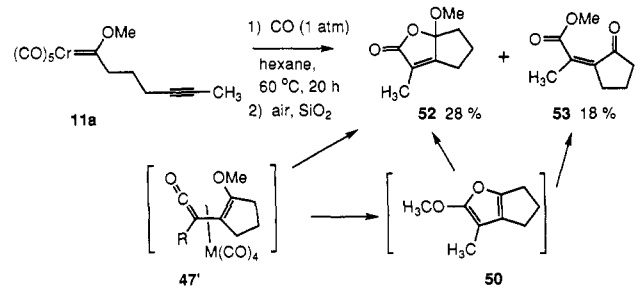
Table IV. Reaction of Complex **11a** with 1-Pentyne in the Presence of Added Methanol[a]

entry	equiv of MeOH	% yield[b] 12a	13a	16a	48a
1	0	54	2	12	0
2	5	41	*c*	*c*	1
3	10	42	*c*	*c*	4
4	20	35	4	9	8
5	50	34	2	4	9
6	100	11	1	3	49
7	200	12	3	3	49
8	500	4	3	1	74

[a] All reactions were carried out under argon with 3 equiv of 1-pentyne at 0.005 M in **11a** in benzene at 60–80 °C for 12–24 h. [b] Yields determined by ^{1}H NMR with Ph_3CH as internal standard. [c] Yields not determined.

The reaction of **11a** with 1-pentyne under an atmosphere of CO results in a reduced yield of **12a**, **13a**, and **16a** and the appearance of the lactone **52** and the keto ester **53** (entry 14, Table I). These same two products can also be obtained by the thermolysis of **11a** under carbon monoxide (Scheme X). One interpretation of this result is that the keto ester is formed from the furan **50** since it is known that furan products of the type **50** are formed in related reactions and that they are normally sensitive to air oxidation to give unsaturated keto esters.[18] The lactone **52** could result from air oxidation of either the vinyl ketene intermediate **47** or the furan **50**. A possible explanation why **52** and **53** are only observed under a CO atmosphere is that the tricarbonyl intermediate **47** may be intercepted by CO to give the tetracarbonyl intermediate **47′**, which is saturated and is thus incapable of coordinating to an alkyne to give either **12** or **16**. It is also possible that the metal in **47** is saturated by virtue of coordination to the methoxyl group (*vide infra*), in which case the reaction with alkynes to produce **46** and with CO to produce **47′** may be associative processes.

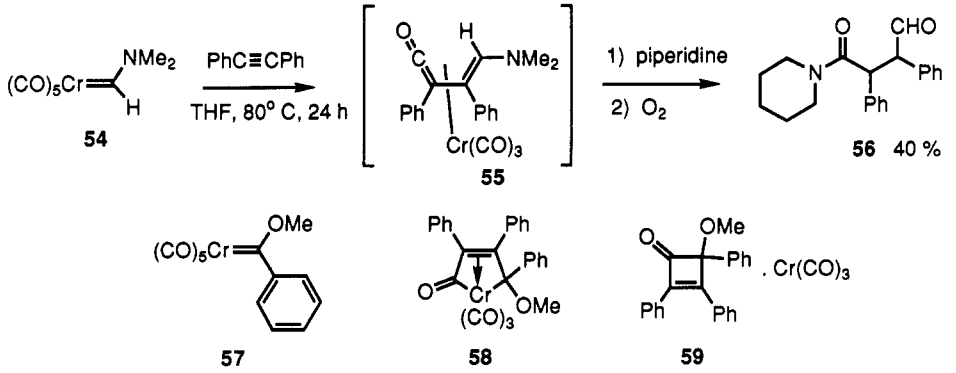
Scheme X



Isolation and Reactions of a Vinyl Ketene Intermediate of the Type 47

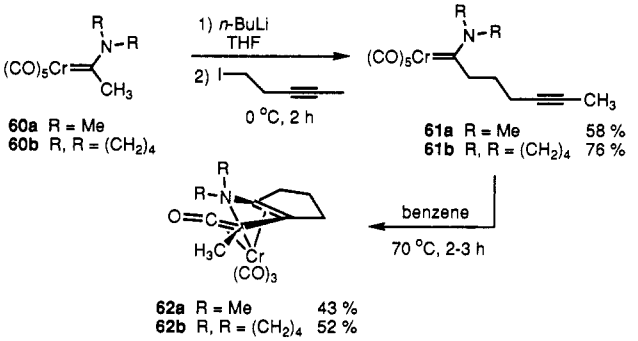
The methanol trapping experiments for the reaction of complex **11a** with 1-pentyne provided evidence that the η^4-vinyl ketene

Scheme XI



intermediate **47** in Scheme IX is involved in the formation of all of the products of this reaction except the phenol **13**. Although a number of η^4-vinyl ketene complexes were known for various metals, there were no examples for chromium, and no examples for d^6-complexes of the group 6 metals.[20-24] More important in regard to the benzannulation reaction, there were no examples of η^4-vinyl ketene complexes isolated from the reaction of a group 6 carbene complex with an alkyne.[20,25] There are reports of examples of η^4-vinyl ketene complexes that have been obtained and structurally characterized from the reactions of a cobalt carbene complex and an alkyne[25] and an iron carbene complex and an alkyne;[26] however, these reactions do not give phenol products but rather furans and pyrones, respectively. There are two reports of reactions which gave products suggested to be η^4-vinyl ketene complexes from the reactions of chromium carbene complexes and alkynes (Scheme XI). The first report was of a material that was obtained from the reaction of the complex **57** with diphenylacetylene as a minor product which was speculated to be the complex **58** on the basis of limited characterization.[27] We have repeated the reaction of complex **57** with diphenylacetylene to determine if the product suggested to be **58** was, in fact, a vinyl ketene complex. As was reported, we found that the most polar product (~5%) was a red oil and had an IR stretch at 1759 cm^{-1}; however, the rest of the spectral data for this compound clearly indicated that it was the cyclobutenone **59** with a chromiumtricarbonyl group coordinated to one of the aryl rings. We screened all of the rest of the fractions from this reaction

Scheme XII



and found that the only other compound with an IR stretch in the 1700–1800-cm^{-1} range was the free cyclobutenone derived from **59**, and thus we were unable to identify any product from the reaction of complex **57** and diphenylacetylene whose spectral data could be interpreted as that expected from the structure **58**. The second report is from the recent work of Hegedus, who observed that the reaction of the amino complex **54** with diphenylacetylene produced a product that was quite polar and did not elute from SiO_2 with nonpolar solvents.[28] This product could not be purified and was not characterized but was suggested to be the vinyl ketene complex **55** on the basis that it could be trapped with piperidine and the trapping product oxidized upon purification to the amide aldehyde **56**.

It was anticipated that replacing the methoxyl group in the complex **5** with an amino group would lead to reactions with alkynes in which the many possible reaction intermediates outlined in Scheme IX would be stabilized and possibly to the point of permitting isolation. The requisite amino complexes **61a** and **61b** were prepared by alkylation of the corresponding methyl complexes with 5-iodo-2-pentyne (Scheme XII). The alkylation of amino complexes is a more useful reaction[29] than those of alkoxy complexes where triflates are required (Scheme VI)[30] due to the increased reactivity of the anions of amino complexes (pK_a of **60a** = 20.4)[31] compared to that of the anions of alkoxy complexes (pK_a of **31** = 8).[32] With amino alkynyl complexes in hand, it was found that the thermolysis of each of these complexes in benzene at 70 °C produced a relatively clean reaction mixture that was composed of essentially a single product that was mobile on silica gel. These compounds were air-stable and quite polar but could be chromatographed on silica gel with a 1:1 mixture of ethyl acetate and hexanes as eluent (R_f = 0.40). The red-brown solids obtained from the thermolysis of **61a** and **61b** in 43% and 52% yields, respectively, were identified as the η^4-vinyl ketene complexes **62a** and **62b**.[24]

(20) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1–83.

(21) For recent citations, see ref 25 and the following: (a) Alcock, N. W.; Danks, T. N.; Richards, C. J.; Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1989**, 21. (b) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368. (c) Valeri, T.; Meier, F.; Weiss, E. *Chem. Ber.* **1988**, *121*, 1093. (d) Mayr, A.; Asaro, M. F.; Glines, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2215. (e) Richards, C. J.; Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1990**, 307.

(22) (a) Templeton, J. L.; Herrick, R. S.; Rusik, C. A.; McKenna, C. E.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 1383. (b) Jens, K. J.; Weiss, E. *Chem. Ber.* **1984**, *117*, 2469. (c) Franck-Neumann, M.; Dietrich-Buchecker, C.; Khemiss, A. B. *J. Organomet. Chem.* **1982**, *224*, 133. (d) Newton, M. G.; Pantaleo, N. S.; King, R. B.; Chu, C. K. *J. Chem. Soc., Chem. Commun.* **1979**, 10. (e) Binger, P.; Cetinkaya, B.; Kruger, C. *J. Organomet. Chem.* **1978**, *159*, 63.

(23) Uncomplexed silyl-substituted vinyl ketenes have been isolated from reactions of chromium carbene complexes: (a) Dötz, K. H.; Fugen-Koster, B. *Chem. Ber.* **1980**, *113*, 1449. (b) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132. (c) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.

(24) Since our initial report,[8c] another example of an η^4-vinyl ketene complex has been reported from a closely related reaction: Chelain, E.; Goumont, R.; Hamon, L.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Am. Chem. Soc.* **1992**, *114*, 8088.

(25) An η^4-vinyl ketene complex from a cobalt carbene complex has been isolated: Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520.

(26) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Park, J.; Steigerwald, M.; Ho, S. *New Aspects of Organic Chemistry, Proceedings of the Third International Kyoto Conference on Organic Chemistry*; Kyoto, Japan, March, 1986; Kodansha Ltd.: Tokyo, Japan.

(27) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177.

(28) Hegedus, L. S.; Miller, D. B., Jr. *J. Org. Chem.* **1989**, *54*, 1241.

(29) Wulff, W. D.; Anderson, B. A.; Isaacs, L. D. *Tetrahedron Lett.* **1989**, *30*, 4061.

(30) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.

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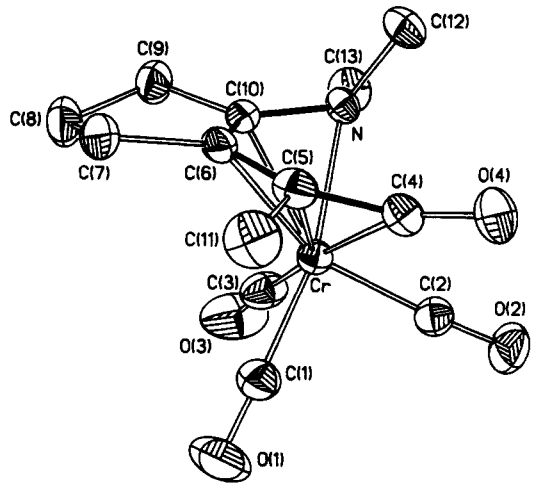

Figure 1.

The IR spectral data of **62a** and **62b** are similar to those of known η^4-vinyl ketene complexes[17,20-22,25] with the carbonyl stretch of the coordinated ketene at 1726 and 1732 cm^{-1}, respectively. The ^{13}C NMR spectral data of the complexes **62** are also consistent with those that have been observed for known η^4-vinyl ketene complexes,[17,20-22,25] where the four bound carbons of the vinyl ketene ligand are spread over a characteristically large chemical shift range. The four quaternary carbons in **62a** are at δ = 253.40, 111.24, 106.71, and 23.75 ppm, and those for **62b** are at δ = 252.6, 112.2, 105.5, and 23.6 ppm. The vinyl ketene complex **62a** provided suitable crystals for structural analysis. The X-ray structure of **62a** revealed that the sixth coordination site on chromium is occupied by nitrogen, as indicated in Figure 1, and that these complexes are actually η^5-enaminyl ketene complexes. The O–C–C bond angle of the coordinated ketene is 136° and is typical of vinyl ketene complexes that have been structurally characterized.[20-24] The short metal–carbon bond to the ketene carbon (2.024 Å) is also typical; however, unusual is the fact that the metal–carbon bond distance to C(10) is not the longest of the metal–carbon bonds to the four vinyl ketene carbons, and this may be due in this case to the coordination of the nitrogen substituent at C(10) (see Table VI in Experimental Section).

The reaction of the η^4-vinyl ketene complex **62a** with diethylpropynylamine was found to give the [2 + 2] cycloaddition product **64**,[33] where the alkyne has added to the carbon–carbon double bond of the ketene function. In addition, this reaction produces two isomers of a product tentatively identified as **65**.[34] The vinyl ketene complex **62a** will also undergo 1,2 additions with pyrrolidine and with sodium methoxide in methanol to give the products indicated in Scheme XIII, where the enamine has hydrolyzed during the workup. It is thus considered very likely that the product Hegedus and Miller isolated from the reaction of complex **54** and diphenylacetylene is the η^4-vinyl ketene complex **55** (Scheme XI).[28] The CO insertion step leading to vinyl ketene complex formation is reversible in some systems;[21,25] however, we could find no evidence for the reversibility of the CO insertion for complex **62b**. Exposure of a benzene solution of **62b** to an atmosphere of ^{13}C-labeled carbon monoxide (balloon) at 80 °C for 20 min led to a 14% recovery of **62b** in which no label had been incorporated into the ketene carbon (C(4)) or into the CO ligands.

Scheme XIII

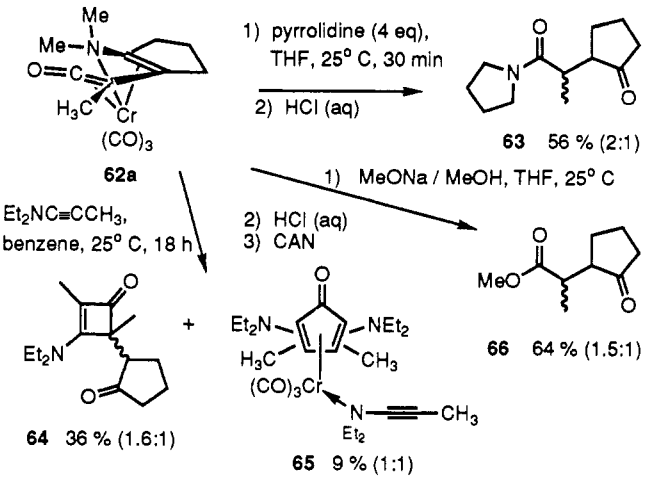

Table V. Comparison of the Reactions of Alkoxy and Amino Carbene Complexes **11a** and **61b** and the Vinyl Ketene Complex **62b** with 1-Pentyne[a]

				% yield[b,c]				
entry	complex	[complex]	solvent	**12a**	**13a**	**14a**	**15a**	**16a**
1	**11a**	0.05	THF	23	7	≤0.1	≤1	0.3
2	**11a**	0.05	benzene	41	8	≤0.2	≤0.6	2
3	**11a**	0.05	CH_3CN	≤1	15	≤0.5	≤0.5	≤0.5
4	**61b**	0.05	THF	16	2	≤1.0	7	16
5	**61b**	0.05	benzene	17	2.4	≤0.2	3	14
6	**61b**	0.5	benzene	11	3	≤1.0	5	11
7	**61b**	0.05	CH_3CN	≤1	≤0.3	≤0.2	≤0.3	≤0.2
8	**62b**	0.05	THF	19[d]	≤1	≤0.2	11	26
9	**62b**	0.05	benzene	26[d]	≤0.7	≤0.3	3	11

[a] Unless otherwise specified, all reactions run with 10 equiv of alkyne at 80–85 °C for 2–4 h and subjected to a reductive workup with $TiCl_3$/LAH. [b] Yields of **12a** and **72** determined by isolation by silica gel chromatography from a separate reaction in which a reductive workup was not employed. [c] Yields of phenols **13a–16a** determined by GC and ^1H NMR with triphenylmethane as internal standard. [d] Isolated as the hydrolyzed product **72**.

The methanol trapping experiments on the reaction of the methoxyl complex **11a** with 1-pentyne described above provide evidence that the η^4-vinyl ketene species **47** in Scheme IX is an intermediate in the formation of the cyclopentenedione product **12** and the phenol **16** but not in the formation of the phenol **13**. With the finding that the η^4-vinyl ketene complexes **62** could be isolated, we were in a position to test mechanistic conclusions of the methanol trapping experiments. The reactions of the η^4-vinyl ketene complex **62b** with 1-pentyne were carried out in both THF and benzene under the conditions described in Table V. Indeed, both of these reactions produced the cyclopentenedione **12a** and the phenol **16a**, but no detectable amounts of the phenol **13a**. In this case the product **12a** was isolated as the hydrolyzed triketone **72** as a result of the greater sensitivity of the amino derivative **67** to hydrolysis than the methoxy derivative **12a** (Scheme VIII). The proper control experiment for the reaction of the vinyl ketene complex **62b** with 1-pentyne is the reaction of the amino complex **61b** with 1-pentyne since it may simply be the case that amino-substituted vinyl ketene complexes do not give the phenols **13** but alkoxy complexes do. As indicated by the data in Table V, the amino carbene complex **61b** does give the phenol **13a** just as does the alkoxy complex **11a**. From these data we can conclude that for both amino and alkoxy carbene complexes **11a** and **61b** the vinyl carbene complexed intermediates (of the type **38** in Scheme IX) give rise to the phenol **13a** and that the vinyl ketene complexed intermediates (of the type **47** in

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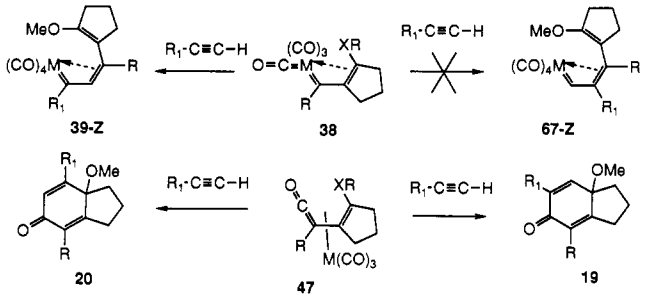
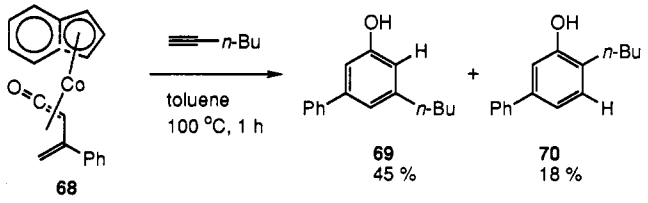
Scheme XIV



Scheme XV



Scheme IX) give rise to the cyclopentenedione product **12a** and the phenol **16**. The isolation and characterization of the amino vinyl ketene intermediates **62** suggest that the structure of the alkoxy complexes **47** actually should be considered as saturated η^5-alkoxyvinyl ketene complexes. The reactions of alkynes and the saturated complexes **47** could thus occur via either associative or dissociative processes, but we have no data at this point to determine the molecularity of these reactions.

One interesting observation that is revealed by the data in Table V (and also Tables I and II) is that there is a difference in the regioselectivity in the formation of the ortho and para phenols (Scheme IV). Of the two possible ortho phenols **13a** and **14a**, only the isomer **13a** was detected in all of the reactions reported here for both alkoxy and amino carbene complexes. This indicates that the vinyl carbene complexed intermediate **38** will undergo insertion of a terminal alkyne to give only the new vinyl carbene complexed intermediate **39-Z** and not the isomeric intermediate **67-Z** (Scheme XIV). This is consistent with previous observations of the reactions of terminal alkynes with carbene complexes.[6]

The formation of the para phenols **15** and **16** is regioselective for the reactions of alkoxy complexes, but not for the reactions of the amino complexes. For example, in the reaction of the methoxyl complex **11a** with 1-pentyne, a 13% yield of **16a** is observed under the conditions described for entry 5 in Table I, while the isomeric phenol **15a**, if formed, yields less than the detection limit of 1%. In contrast, while the reaction of the amino complex **61b** (and the ketene complex **62b**) does produce phenol **16a** as the major isomer, substantial amounts of the regioisomer **15a** are formed in these reactions (Table V). If in fact the formation of the para phenols involves a [4 + 2] cycloaddition as indicated in Scheme IX, then the addition of alkyne to intermediate **47** (Scheme XIV) is highly regioselective for the formation of **19** over **20** when XR = OMe but only moderately regioselective when XR = $N(C_4H_8)$ with ~2:1 selectivity for **19** over **20** and thus for phenol **16a** over **15a**. A similar selectivity has been recently reported for the [4 + 2] cycloaddition of 1-hexyne with the insolable η^4-vinyl ketene complex **68** (Scheme XV), where the regiochemistry of the major product **69** corresponds to the regiochemistry of the major product **16a** from the reaction of the isolable η^4-vinyl ketene complex **62b** (Table V, entry 8).

The effects of the concentration, the solvent, and the nature of the metal on the reactions of the carbene complexes **11** with alkynes are consistent with the mechanism shown in Scheme IX, where the phenol **13** is formed from the vinyl carbene complexed intermediate **38** and the phenol **16** and the cyclopentenedione **12** are formed from the vinyl ketene intermediate **47**. This is supported by the methanol trapping experiments and by the isolation of the vinyl ketene complexes **62** and their reactions with alkynes. The formation of the cyclopentenedione products **12** is quite remarkable, and with the proper choice of solvent and concentration these products can be made in moderate yield, which may in fact be synthetically attractive since six carbon–carbon bonds are made in a single transformation. Finally, the isolation of the first η^4-vinyl ketene complex **62a** from the reaction of a chromium carbene complex and an alkyne should serve to stimulate attempts at the isolation of these intermediates from other reactions of carbene complexes with alkynes where they are thought to be key reaction intermediates.

Experimental Section

Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial suppliers without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Di-*n*-butyl ether was freshly distilled over calcium hydride after refluxing over calcium hydride for 24 h and storage over sodium hydroxide for 24 h. Routine ^{1}H NMR spectra were recorded on either a General Electric QE-300 MHz or a DS 1000 (Chicago built) 500-MHz spectrometer in $CDCl_3$. The ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer at 100 MHz or a General Electric QE-300 spectrometer at 75 MHz. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer. Low-resolution mass spectra were recorded on a Finnigan 1015 instrument, and high-resolution mass spectra were recorded on a VG 70-250 mass spectrometer, or by the Midwest Center for Mass Spectrometry, Lincoln, NE. Elemental analyses were carried out by Galbraith Labs, Inc., Knoxville, TN, or Desert Analytics, Tucson, AZ.

Preparation of 1-Iodo-4-hexyne (10). 4-Hexyn-1-ol was prepared from the commercially available 4-pentyn-1-ol by a procedure reported in the literature.[40] 4-Hexyn-1-ol (6.87 g, 0.070 mol) was converted to 1-iodo-4-hexyne (**10**)[45] (9.90 g, 0.0476 mol) in 68% overall yield via the tosylate, utilizing the procedure that has been reported for 1-iodo-3-pentyne.[41] Spectral data for **10**: ^{1}H NMR ($CDCl_3$) δ 1.78 (t, 3 H, J = 2.5 Hz), 1.96 (pentet, 2 H, J = 6.7 Hz), 2.24–2.29 (m, 2 H), 3.30 (t, 2 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 3.36, 5.73, 19.70, 32.42, 76.68, 76.87; IR (neat) 2958 s, 2917 s, 2840 m, 2735, w, 1430 s, 1347 m, 1265 m, 1221 s, 1167 s, 1155 m, 951 w, 847 w cm^{-1}; mass spectrum *m/z* (relative intensity) 208 M^+ (43), 149 (14), 123 (16), 111 (26), 97 (46), 81 (100), 71 (78).

Preparation of the 5-Hexynyl Chromium Carbene Complex 11a. Procedure A. To a solution of 1-iodo-4-hexyne (0.97 g, 4.66 mmol) in 50 mL of freshly distilled ether cooled to –78 °C under an argon atmosphere was added a 1.7 M solution of *tert*-butyllithium (6.6 mL, 11.2 mmol) in pentane.[35] After 10 min the solution of 1-lithio-4-hexyne was transferred to a flask containing a solution of chromium hexacarbonyl (1.13 g, 5.14 mmol) in 50 mL of ether at –78 °C. The resulting mixture was stirred

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from −78 to 0 °C for 2.5 h followed by addition of methyl fluorosulfonate (1.45 mL, 2.06 g, 18.1 mmol) to the mixture at 0 °C. After 25 min the reaction mixture was quenched and washed three times with saturated aqueous $NaHCO_3$. The organic layer was dried with anhydrous $MgSO_4$, and after removal of the solvent the product was purified from the residue by chromatography on silica gel with a 1:1:30 mixture of CH_2Cl_2/ether/hexane as eluent to give a 70% yield (1.034 g, mmol) of **11a** as a dark yellow oil. Spectral data for **11a**: ^{1}H NMR ($CDCl_3$) δ 1.60 (pentet, 2 H, J = 7.4 Hz), 1.77 (t, 3 H, J = 2.4 Hz), 2.11–2.18 (m, 2 H), 3.43 (t, 2 H, J = 7.4 Hz), 4.77 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 4.11, 19.09, 26.05, 62.65, 68.16, 77.35, 78.29, 216.25, 222.99, 361.95; IR (neat) 2963 m, 2924 m, 2857 m, 2063 s, 1977–1919 s, 1454 s, 1291 m, 1250 s, 1157 m, 1072 m, 1039 m, 953 m, 667 s cm^{-1}; mass spectrum m/z (% relative intensity) 316 M^+ (17), 232 (23), 204 (72), 176 (71), 161 (72), 146 (58), 144 (75), 133 (17), 118 (28), 105 (100), 91 (14), 80 (42); calcd for $C_{13}H_{12}O_6Cr$ m/z 316.0039, measd m/z 316.0060.

Procedure B. To a solution of (methylmethoxymethylene)pentacarbonylchromium(0)[36] (0.243 g, 0.97 mmol) in 12 mL of diethyl ether at −78 °C and under an argon atmosphere was added a 1.6 M solution of *n*-butyllithium in hexanes (0.61 mL, 0.97 mmol). The mixture was stirred at −78 °C for 10 min, and then 3-pentynyl triflate (420.0 mg, 1.94 mmol) was introduced by syringe. This triflate was prepared from the commercially available 3-pentyn-1-ol and trifilic anhydride by the procedure of Hannack and used immediately.[37] After addition of the triflate, the mixture was warmed to 0 °C and stirred for 1 h. The reaction was quenched by the addition of 10 mL of water and 20 mL of ether. The organic layer was washed with water and brine and dried over anhydrous $MgSO_4$. The product was purified by silica gel chromatography as described in procedure A to give **11a** in 62% yield (189.2 mg, 0.60 mmol) as a yellow oil.

The ^{13}C-labeled carbene complex **33** was prepared by procedure B from (methylmethoxymethylene)pentacarbonylchromium(0) (**31**) which was labeled with ^{13}C in the carbon monoxide ligands. Introduction of the label in **31** could not be efficiently accomplished by heating the unlabeled complex with labeled carbon monoxide since this resulted in ≥80–90% decomposition of the carbene complex. This could be accomplished in 70% yield by exposing a THF solution of the triphenylphosphine derivative **30**[23c,38] to 220 psi of ^{13}C-labeled carbon monoxide (Isotec, Inc., 99% ^{13}C) at 25 °C for 2 days.

Preparation of the 5-Hexynyl Molybdenum Carbene Complex (11b). According to procedure A for complex **11a**, the molybdenum complex **11b** was prepared from 1-iodo-4-hexyne in 70% yield and obtained as a yellow oil. Spectral data for **11b**: ^{1}H NMR ($CDCl_3$) δ 1.67 (m, 2 H), 1.78 (t, 3 H, J = 2.5 Hz), 2.12–2.17 (m, 2 H), 3.39 (t, 2 H, J = 7.6 Hz), 4.69 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 3.42, 18.38, 25.06, 62.22, 69.53, 76.95, 77.90, 205.65, 213.12, 354.51; IR (neat) 2957 w, 2923 w, 2070 s, 1922 s, 1451 m, 1254 m, 1158 w, 1072 w, 1038 w, 961 w, 930 w cm^{-1}; mass spectrum m/z (relative intensity) 362 M^+ (15, ^{98}Mo), 278 (62, ^{98}Mo), 248 (50), 222 (65, ^{98}Mo), 216 (90), 79 (100). Complex **11b** could only be prepared in 12% yield utilizing a method analogous to that in procedure B described for **11a**.

Preparation of the 5-Hexynyl Tungsten Carbene Complex (11c). According to procedure A for complex **11a**, the tungsten complex **11c** was prepared from 1-iodo-4-hexyne in 71% yield and obtained as a yellow oil. Spectral data for **11c**: ^{1}H NMR ($CDCl_3$) δ 1.68 (pentet, 2 H, J = 7.4 Hz), 1.77 (t, 3 H, J = 2.4 Hz), 2.16 (m, 2 H), 3.32 (t, 2 H, J = 7.6 Hz), 4.60 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 3.4, 18.3, 25.5, 64.1, 65.8, 70.5, 77.9, 197.2, 203.3, 336.4; IR (neat) 2957 s, 2923 s, 2852 m, 2353 w, 2017 s, 1985–1891 s, 1451 s, 1295 s, 1260 s, 1073 s, 1039 s cm^{-1}; mass spectrum m/z (relative intensity) 448 M^+ (36, ^{184}W), 364 (100, ^{184}W), 336 (16, ^{184}W), 308 (77, ^{184}W), 306 (96, ^{184}W), 291 (53, ^{184}W), 278 (35), 263 (46), 249 (51), 238 (25), 212 (20), 181 (18), 119 (24), 84 (20); calcd for $C_{13}H_{12}O_6{}^{184}W$ m/z 448.0143, measd m/z 448.0142.

The tungsten complex **11c** can also be prepared according to procedure B that is described for the chromium complex **11a**. Following this procedure with the exception that alkylation with 3-pentynyl triflate is effected for 30 min at −78 °C and then for 5 min at 0 °C before quenching gives **11c** in 42% yield, and 8% recovery of (methylmethoxymethylene)-pentacarbonyltungsten(0), and a 15% yield of the dialkylated product.

Reactions of the Carbene Complexes 11 with 1-Pentyne with and without Added Methanol. Procedure A. To a 0.08 M solution of the carbene complex **11a** (269.4 mg, 0.85 mmol) in hexane (10 mL) in a one-necked flask equipped with a threaded stopcock was added 1-pentyne (0.18 mL, 124.4 mg, 1.83 mmol). The resulting mixture was deoxygenated by the freeze–thaw method (−196 °C → 0 °C, three cycles), and on the last cycle the flask was backfilled with argon. The threaded stopcock was sealed at 1 atm of argon at 25 °C, and then the flask was heated at 60 °C for 24 h. The reaction mixture was opened to air and stirred for 20 min to facilitate oxidative removal of the metal by air. After filtration through Celite and removal of the solvent, the crude residue was loaded onto a silica gel column, and upon elution with a 1:1:4 mixture of ether, CH_2Cl_2, and hexanes, three fractions were collected. In order of elution these compounds were identified as the phenol **13a** (R_f = 0.64, 4% yield, 7.1 mg, 0.037 mmol), phenol **16a** (R_f = 0.44, 4% yield, 6.9 mg, 0.036 mmol), and the cyclopentenedione **12a** (R_f = 0.39, 42.5% yield, 89.6 mg, 0.36 mmol). Spectral data for **13a**: white solid, mp 65–76 °C; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 7.3 Hz), 1.61 (sextet, 2 H, J = 7.4 Hz), 2.11 (t, 2 H, J = 7.5 Hz), 2.16 (s, 3 H), 2.52 (t, 2 H, J = 7.6 Hz), 2.76–2.84 (m, 4 H), 4.27 (s, 1 H, OH), 6.71 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.14 (q, J = 124.9 Hz), 18.36 (q, J = 126.3 Hz), 23.48 (t, J = 128.6 Hz), 24.91 (t, J = 130.3 Hz), 29.02 (t, J = 129.1 Hz), 31.77 (t, J = 129.1 Hz, 2 carbons), 125.38 (s), 125.85 (s), 128.66 (s), 129.28 (d, J = 152.6 Hz), 142.28 (s), 147.79 (s); IR (neat) 3462 br s, 2958 s, 2931 s, 2871 s, 1626 w, 1486 s, 1278 m, 1204 s, 1081 m cm^{-1}; mass spectrum m/z (relative intensity) 190 M^+ (35), 161 (100), 147 (10), 135 (4), 128 (4), 115 (5), 105 (6), 91 (10), 86 (27), 84 (43), 77 (5), 69 (5); calcd for $C_{13}H_{18}O$ m/z 190.1358, measd m/e 190.1365. In an NOE experiment, a 4.5% enhancement of the aryl singlet at δ = 6.71 was observed upon irradiation at the aryl methyl (δ = 2.16). Spectral data for **16a**: ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7.4 Hz), 1.57 (m, 2 H), 2.05 (pentet, 2 H, J = 7.4 Hz), 2.12 (s, 3 H), 2.45 (t, 2 H, J = 7.6 Hz), 2.76–2.85 (m, 4 H), 4.41 (s, 1 H, OH), 6.42 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.99 (q, J = 126.8 Hz), 14.09 (q, J = 124.7 Hz), 23.32 (t, J = 127.5 Hz), 24.89 (t, J = 129.8 Hz), 30.88 (t, J = 129.3 Hz), 31.95 (t, J = 129.5 Hz), 35.42 (t, J = 123.8 Hz), 113.08 (d, J = 153.3 Hz), 116.78 (s), 134.37 (s), 136.31 (s), 144.65 (s), 152.28 (s); IR (neat) 3400 br s, 2956 s, 2928 s, 2870 s, 1612 m, 1596 m, 1462 s, 1414 m, 1346 m, 1286 m, 1075 m, 846 m cm^{-1}; mass spectrum m/z (relative intensity) 190 M^+ (15), 181 (13), 169 (14), 161 (31), 147 (14), 131 (33), 119 (23), 100 (13), 84 (24), 83 (47), 69 (100); calcd for $C_{13}H_{18}O$ m/z 190.1358, measd m/z 190.1369. Spectral data for cyclopentenedione **12**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7.4 Hz), 1.24 (s, 3 H), 1.57–1.71 (m, 2 H), 1.83 (pentet, 2 H, J = 7.4 Hz), 2.32–2.47 (m, 6 H), 3.35 (s, 3 H), 6.78 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.73, 16.64, 19.08, 20.19, 27.49, 28.63, 28.95, 51.05, 56.02, 111.44, 141.05, 153.04, 163.45, 204.53, 206.12; IR (neat) 2962 s, 2935 s, 2873 m, 2851 m, 1745 m, 1701 s, 1671 m, 1613 m, 1455 m, 1340 m, 1305 m, 1274 m, 1253 m, 1029 m cm^{-1}; mass spectrum m/z (relative intensity) 248 M^+ (100), 233 (24), 219 (10), 205 (12), 191 (10), 189 (17), 187 (12), 177 (22), 161 (10), 159 (21), 147 (11), 145 (10), 131 (9), 109 (19), 97 (10), 96 (12), 91 (14), 79 (13), 67 (13); calcd for $C_{15}H_{20}O_3$ m/z 248.1412, measd m/z 248.1444. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.74; H, 8.28.

This reaction was carried out with procedure A in a number of solvents and at several different concentrations, and the results are listed in Table I. The reaction of ^{13}C-labeled carbene complex **33** was carried out on 0.5 g of the complex with procedure A, and the two phenols **13a** and **16a** were isolated as described above. The labeled carbon for phenol **13a*** was δ = 147.79 ppm (25.6-fold enhancement). This carbon was coupled to the carbon at δ = 125.85 ppm (J = 62.7 Hz) and to the carbon at δ = 128.66 ppm (J = 62.7 Hz). The labeled carbon for phenol **16a*** was δ = 152.28 ppm (12.8-fold enhancement). This carbon was coupled to the carbon at δ = 116.78 ppm (J = 65.2 Hz) and to the carbon at δ = 113.08 ppm (J = 68 Hz).

Procedure B (Reductive Workup). This procedure is the same as A except a reductive workup is employed to facilitate the quantitative analysis of the phenols **13–16** by ^{1}H NMR and capillary GC. To a 0.005 M solution of the carbene complex **11a** (198 mg, 0.63 mmol) in benzene (125 mL) was added 1-pentyne (0.185 mL, 127 mg, 1.87 mmol), and the resulting mixture was deoxygenated and then heated at 85 °C for 20 h under an argon atmosphere. The solution was filtered through Celite if particulate matter settled out during the reaction and then divided into two equal parts by volume. The first part was concentrated and the chromatographed on silica gel as described in procedure A to determine the isolated yield of the cyclopentenedione **12a** (0.0415 g, 0.67 mmol, 53%) since it does not survive the reductive workup. In this particular reaction the phenol **16a** was also isolated in 13% yield (0.0076 g, 0.04 mmol). The second part of the reaction mixture was stripped of solvent and redissolved in 20 mL of THF with a second filtration through Celite if necessary. To this solution was added an ether suspension of a 4:1 mixture of $TiCl_3/LiAlH_4$ (0.32 g, Aldrich) all in one portion. After being stirred for 1 h at 25 °C, the reaction mixture was quenched with pH 7 buffer, extracted with ether and CH_2Cl_2, dried over $MgSO_4$, and

concentrated. The yields of the phenol products **16a** (11%), **15a** (≤1.0%), **13a** (2%), and **14a** (≤0.3%) were determined by GC and/or ^{1}H NMR using triphenylmethane as an internal standard. The GC analysis was carried out using a 0.2 mm × 25 m Carbowax column with split injection and a temperature program of 110 °C for 3 min, ramping to 155 °C for 2 min at 10 °C/min and then 200 °C for 30 min. The retention times (t_R, min) and calculated response factors (R_f, vs triphenylmethane) were **15a**, t_R = 31.36, R_f = 0.57; **16a**, t_R = 35.72, R_f = 0.39; **13a**, t_R = 32.04, R_f = 0.47; **14a**, t_R = 36.02, R_f = 0.50. Quantitation by ^{1}H NMR was by integration of the methine proton of triphenylmethane versus the aromatic singlet for each phenol (**13a** δ = 6.71 ppm, **14a** δ = 6.47 ppm, **15a** δ = 6.81 ppm, **16a** δ = 6.42 ppm).

This reaction was carried out in various solvents, at various concentrations and with all three of the group 6 metals in the carbene complex **11**, and the results, with the reductive workup with McMurry's reagent are indicated in Tables I and II. Note that in entry 2 of Table I zinc and acetic acid (25 °C, 2 h) can be substituted for McMurry's reagent in the reduction step (this is not true for the amino complexes (Table V), which require the stronger reducing agent). In the reactions with the chromium complex **11a** with 1-pentyne in the presence of added amounts of methanol (Table IV), the reduction step was carried out with zinc and acetic acid and the phenols were quantified by ^{1}H NMR with triphenylmethane as an internal standard. In these reactions the methanol trapping product **48a** is also formed, which is the major product when the reaction is run in methanol as solvent (*vide infra*).

Reaction of Complex 11a with 1-Pentyne in the Process of 1 atm of CO. The reaction was carried out according to procedure A, and after deoxygenation the reaction mixture was heated at 60 °C for 24 h under a balloon filled with carbon monoxide. The five products produced from this reaction were separated by chromatography on silica gel with a 1:1:4 mixture of ether, methylene chloride, and hexane as eluent and were identified as indanol **13a** (2%), indanol **16a** (2%), cyclopentenedione **12a** (24%), lactone **52** (22%), and γ-keto ester **53** (18%). Spectral data for **52**: ^{1}H NMR ($CDCl_3$) δ 1.58–1.66 (m, 1 H), 1.89 (s, 3 H), 2.01–2.09 (m, 1 H), 2.18–2.29 (m, 2 H), 2.38–2.50 (m, 2 H), 3.17 (s, 3 H); IR (neat) 2959 s, 2942 m, 1770 s, 1707 m, 1437 m, 1304 m, 1291 m, 1179 m, 1159 m, 1089 m, 1067 m, 1021 m, 956 s, 935 m cm^{-1}; mass spectrum, m/z (relative intensity) 168 M^+ (5), 163 (3), 153 (4), 141 (9), 140 (100), 137 (22), 125 (6). Spectral data for **53**: ^{1}H NMR ($CDCl_3$) δ 1.96 (pentet, 2 H, J = 7.6 Hz), 1.97 (s, 3 H), 2.34 (t, 2 H, J = 8.0 Hz), 2.62 (t, 2 H, J = 7.4 Hz), 3.82 (s, 3 H); IR (neat) 2952 s, 1734 s, 1722 s, 1648 s, 1433 s, 1298 s, 1288 s, 1231 s, 1215 s, 1147 s, 1092 s, 1004 m, 957 m, 769 m cm^{-1}; mass spectrum m/z (relative intensity) 168 M^+ (25), 153 (14), 140 (100), 125 (7).

Reaction of the Carbene Complex 11a with Phenylacetylene. To a 0.005 M solution of the carbene complex **11a** (52.1 mg, 0.16 mmol) in benzene (32 mL) in a one-necked flask equipped with a threaded stopcock was added phenylacetylene (0.055 mL, 51.2 mg, 0.50 mmol). The resulting mixture was deoxygenated by the freeze–thaw method (–196 °C → 0 °C, three cycles), and on the last cycle the flask was backfilled with argon. The threaded stopcock was sealed at 1 atm of argon at 25 °C, and then the flask was heated at 70 °C for 15 h. The reaction mixture was opened to air and stirred for 20 min to facilitate oxidative removal of the metal by air. After filtration through Celite and removal of the solvent, the crude residue was loaded onto a silica gel column, and upon elution with a 1:1:10 mixture of ether, CH_2Cl_2, and hexanes, three fractions were collected. In order of elution these compounds were identified as the phenol **13b** (R_f = 0.32, 16% yield, 5.7 mg, 0.025 mmol), cyclohexadienone **20b** (R_f = 0.17, 20% yield, 8.5 mg, 0.033 mmol), and the cyclopentenedione **12b** (R_f = 0.14, 54.3% yield, 24.5 mg, 0.087 mmol). Spectral data for **13b**: white solid, mp 58–59 °C; ^{1}H NMR ($CDCl_3$) δ 2.15 (t, 2 H, J = 7.5 Hz), 2.22 (s, 3 H), 2.87 (t, 2 H, J = 7.5 Hz), 2.94 (t, 2 H, J = 7.5 Hz), 4.95 (s, 1 H), 6.85 (s, 1 H), 7.32–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.34 (q, J = 122.8 Hz), 24.88 (t, J = 130.4 Hz), 29.52 (t, J = 129.4 Hz), 31.89 (t, J = 129.4 Hz), 125.71, 125.88, 127.42 (d, J = 163.5 Hz), 129.14 (d, J = 159.0 Hz), 129.72, 137.59, 144.83, 146.59 (1 C not located); IR (neat) 3555–3417 br s, 3057–3025 br m, 2950–2846 br s, 1620 w, 1600 m, 1499 m, 1470 s, 1437 s, 1406 m, 1307 s, 1277 s, 1221 s, 770 s, 703 s cm^{-1}; mass spectrum m/z (relative intensity) 224 M^+ (100), 209 (28), 195 (7), 178 (7), 165 (12), 152 (5), 147 (8), 128 (4), 115 (8), 103 (4), 91 (5), 77 (7); calcd for $C_{16}H_{16}O$ m/z 224.1201, measd m/z 224.1169. Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.20. Found: C, 85.85; H, 7.70. The regiochemistry was confirmed by an NOE experiment. Irradiation of the methyl peak at δ = 2.22 ppm resulted in a 6% enhancement for the aryl singlet at δ = 6.85 ppm. Spectral data for **20b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.85–1.95 (m, 2 H), 1.90 (s, 3 H), 2.16–2.26 (m, 2 H), 2.55–2.65 (m, 2 H), 3.08 (s, 3 H), 6.50 (s, 1 H), 7.34–7.40 (m, 3 H), 7.65–7.70 (m, 2 H); IR (neat) 2955 m, 2929 m, 1675 m, 1642 s, 1445 m, 1361 m, 1329 m, 1303 m, 1062 s, 771 m, 698 m cm^{-1}; mass spectrum m/z (relative intensity) 254 M^+ (100), 239 (33), 224 (46) 223 (81), 221 (27), 195 (26), 178 (21), 165 (28), 152 (17), 115 (20), 91 (18), 77 (14); calcd for $C_{17}H_{18}O_2$ m/z 254.1307, measd m/e 254.1320. Spectral data for **12b**: red solid, mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3 H), 1.86 (pentet, 2 H, J = 7.4 Hz), 2.34–2.44 (m, 4 H), 3.32 (s, 3 H), 7.21 (s, 1 H), 7.44–7.46 (m, 3 H), 7.90–7.92 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.5, 19.1, 28.6, 28.8, 52.5, 56.3, 111.6, 128.8, 129.1, 129.6, 131.2, 138.6, 153.2, 156.0, 203.5, 204.8; IR (neat) 3057 w, 2958–2906 br s, 2870–2850 br s, 1740 s, 1699 s, 1669 s, 1600 m, 1571 m, 1491 m, 1448 m, 1339 m, 1305 m, 1260 s, 1054 m, 693 m cm^{-1}; mass spectrum m/z (relative intensity) 282 M^+ (100), 268 (17), 267 (17), 253 (6), 239 (14), 223 (53), 221 (25), 211 (17), 197 (15), 195 (29), 186 (22), 184 (13), 179 (13), 165 (13), 152 (12), 141 (12), 129 (12), 115 (17), 109 (41), 103 (17), 102 (58), 97 (18), 91 (18), 81 (25), 67 (26); calcd for $C_{18}H_{18}O_3$ m/z 282.1256, measd m/z 282.1234. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.56; H, 6.43. Found: C, 76.71; H, 6.65.

The assignment of the structure of cyclopentenedione **12b** was made on the basis of an X-ray structure that has been previously reported.[8b] It was demonstrated that the isolated cyclohexadienone product **20b** was not related to the isolated phenol **13b** since reduction of **20b** with zinc and acetic acid produced a phenol that was nonidentical with **13b** and is assigned the structure **16b**. The assignment of the structures **13b** and **16b** was made on the basis that it was proven that the reaction of **11a** with 1-pentyne produces the phenols **13a** and **16a** by independent syntheses and that phenol **13b** (but not phenol **16b**) would be expected to exhibit an NOE between the methyl group and the aromatic singlet. Spectral data for **16b**: ^{1}H NMR ($CDCl_3$) δ 2.04 (pentet, 2 H, J = 7.4 Hz), 2.20 (s, 3 H), 2.88 (t, 2 H, J = 7.4 Hz), 2.91 (t, 2 H, J = 7.4 Hz), 4.57 (s, 1 H), 6.65 (s, 1 H), 7.23–7.40 (m, 5 H), irradiation at δ = 2.20 ppm produced no NOE at δ = 6.65 ppm; IR (neat) 3345–3460 br s, 3030 w, 2948 s, 2885–2844 br s, 1694 w, 1600 m, 1486 s, 1398 s, 1344 s, 1285 m, 1257 s, 1151 s, 1064 s, 767 s, 700 s cm^{-1}; mass spectrum m/z (relative intensity) 224 M^+ (65), 223 (25), 209 (23), 195 (7), 178 (8), 165 (15), 152 (6), 147 (12), 115 (7), 87 (23), 85 (97), 83 (100); exact mass calcd for $C_{16}H_{20}O$ m/e 224.1201, measd m/z 224.1171.

Reaction of the Pentacarbonylchromium Cyclopentylmethoxy Carbene Complex (24) with 1-Pentyne. To a 0.1 M solution of the carbene complex **24**[5,39] (0.959 g, 3.17 mmol) in hexane (32 mL) in a one-necked flask equipped with a threaded stopcock was added 1-pentyne (0.324 g, 4.76 mmol). The resulting mixture was deoxygenated by the freeze–thaw method (–196 °C → 0 °C, three cycles), and on the last cycle the flask was backfilled with argon. The threaded stopcock was sealed at 1 atm of argon at 25 °C, and then the flask was heated at 50 °C for 21 h, after which time TLC indicated that complex **24** had been consumed. The reaction mixture was opened to air and stirred for 20 min to facilitate oxidative removal of the metal by air. After filtration through Celite and removal of the solvent, the crude residue was loaded onto a silica gel column, and elution first with a 1:1:10 mixture of ether, CH_2Cl_2, and hexanes and then with a 1:1:4 solvent mixture gave the cyclopentenedione **25** (0.087 g, 9.1%) and the phenol **26** (0.361 g, 50.6%). Spectral data for **25**: ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3 H, J = 7.1 Hz), 0.89–1.01 (m, 1 H), 1.00 (t, 3 H, J = 7.4 Hz), 1.02–1.16 (m, 1 H), 1.57–1.68 (m, 2 H), 1.74 (t, 2 H, J = 8.3 Hz), 1.86 (t, 2 H, J = 7.4 Hz), 2.27–2.41 (m, 4 H), 2.41–2.48 (m, 2 H), 3.26 (s, 3 H), 4.74 (s, 1 H), 5.76 (s, 1 H), 6.86 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.26, 14.76, 18.18, 20.77, 23.60, 27.99, 33.19, 33.53, 37.54, 55.29, 58.73, 113.01, 130.36, 137.13, 142.41, 154.5, 164.93, 205.65, 206.36; IR (CCl_4) 2963 s, 2935 m, 2874 m, 1744 w, 1701 vs, 1642 w, 1617 w, 1458 w, 1446 w, 1381 w, 1352 w, 1322 w, 1299 w, 1174 w, 1150 w, 1126 w, 1085 w, 1054 w, 909 w cm^{-1}; mass spectrum m/z (relative intensity) 302 M^+ (100), 273 (68), 259 (80), 241 (38), 225 (46), 215 (36), 201 (25), 187 (28), 177 (42), 171 (10), 164 (73), 159 (9), 151 (77), 145 (30), 135 (12), 129 (26), 121 (20), 115 (18), 110 (8), 105 (17), 95 (44), 91 (48), 77 (26), 67 (42). Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.09; H, 8.62. Spectral data for **26**: white needles, mp 92–93 °C; ^{1}H NMR ($CDCl_3$) δ 1.01 (br t, 3 H, J = 6.8 Hz), 1.56–1.72 (m, 2 H), 2.13 (br t, 2 H, J = 7.0 Hz), 2.58 (br t, 2 H, J = 7.3 Hz), 2.84 (br t, 2 H, J = 6.6 Hz), 2.89 (br t, 2 H, J = 6.7 Hz), 3.79 (s, 3 H), 4.26 (s, 1 H), 6.48 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 23.5, 25.1, 29.3, 32.2, 55.8, 110.8, 126.7, 130.8, 131.2, 143.7, 149.6; IR ($CHCl_3$) 3600 s, 1485 s, 1460 s, 1280 s, 720 s; mass spectrum m/z (relative intensity) 206 M^+ (70), 178 (100), 117 (15), 91 (20), 65 (11); calcd for $C_{13}H_{18}O_2$ m/z 206.1307, measd m/z 206.1298.

The yield of the phenol **26** from this reaction is not improved over the same reaction in THF.[6c] The yield of the phenol **26** can be dramatically improved (80%) if the molybdenum carbene complex analogous to **24** is employed.[5]

Oxidation of Phenol 26 to the Quinone 27. A solution of 0.180 g (0.87 mmol) of phenol **26**, 1.150 g (2.10 mmol) of ceric ammonium nitrate, and 0.120 g (0.87 mmol) of anhydrous potassium carbonate in 25 mL of dry methanol was stirred for 5 min, after which time TLC indicated that phenol **26** had been completely consumed. The reaction mixture was diluted with water and extracted three times with hexane. The organic layers were combined, washed with saturated aqueous $NaHCO_3$, water, and brine, and then dried over anhydrous $MgSO_4$. After filtration through Celite and removal of solvents, the quinone **27** was obtained in 87.6% yield (0.145 g), which was utilized in the conversion to **28** and **29** without further purification. Spectral data for **27**: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H, J = 7.4 Hz), 1.53 (sextet, 2 H, J = 7.5 Hz), 2.03 (pentet, 2 H, J = 7.8 Hz), 2.38 (t, 2 H, J = 7.6 Hz), 2.78 (t, 4 H, J = 7.6 Hz), 6.41 (s, 1 H). The oxidation in methanol was expected to give a dimethylquinone monoacetal,[6c] which in this case was not detected and must have been extremely sensitive to the aqueous workup.

Addition of Methyllithium to Quinone 27. To a solution of 0.145 g (0.76 mmol) of quinone **27** and 0.531 g (4.57 mmol) of TMEDA in 30 mL of THF at −80 to −90 °C under argon was added dropwise 0.54 mL (0.76 mmol) of a 1.4 M solution of methyllithium in diethyl ether.[15] After the reaction solution had been stirred for 1.5 h, it was diluted with hexane, washed with dilute aqueous HCl, saturated aqueous $NaHCO_3$, and brine, and then dried over anhydrous $MgSO_4$. After filtration through Celite and removal of the solvent, the crude residue was loaded onto a silica gel column, and elution first with a 1:1:4 mixture of ether, CH_2Cl_2, and hexanes and then with a 1:1:1 solvent mixture gave the hydroxycyclohexadienones **28** (0.042 g, 27%) and **29** (0.066 g, 42%). Spectral data for **28**: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.4 Hz), 1.34 (s, 3 H), 1.48–1.50 (m, 2 H), 1.86–2.00 (m, 2 H), 2.11–2.88 (m, 2 H), 2.54 (s, 1 H), 2.56 (t, 2 H, J = 7. Hz), 2.56–2.68 (m, 1 H), 2.74–2.84 (m, 1 H), 6.51 (s, 1 H). Spectral data for **29**: ^{1}H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7.3 Hz), 1.40 (s, 3 H), 1.58 (sextet, 2 H, J = 7.6 Hz), 1.84–1.96 (m, 1 H), 1.91–2.02 (m, 1 H), 2.31 (pentet, 1 H, J = 7.9 Hz), 2.46 (pentet, 1 H, J = 8.4 Hz), 2.57 (t, 2 H, J = 7.8 Hz), 2.63 (s, 1 H), 2.62–2.73 (m, 1 H), 2.78–2.88 (m, 1 H), 5.89 (s, 1 H).

Reduction of Hydroxycyclohexadienones 28 and 29 to Phenols 13a and 14a. A solution of 0.066 g (0.32 mmol) of hydroxycyclohexadienone **28** in ~2 mL of Et_2O and 7 mL of HOAc was stirred with a spatula-tip full of zinc dust for 45 min at room temperature. The solution was then filtered through Celite, diluted with ether, and washed several times with H_2O and then with saturated aqueous $NaHCO_3$ until a neutral pH was obtained. The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated to give phenol **13a** in 83% yield (61 mg). The ^{1}H NMR and ^{13}C NMR spectra of this phenol were found to be identical with those of the phenol that was obtained as the minor product from the reaction of complex **11a** with 1-pentyne. This result was further confirmed by a ^{1}H NMR spectrum of a mixture of the phenols which was identical with the ^{1}H NMR spectra of the individual phenols.

The hydroxycyclohexadienone **29** was reduced with the same procedure to give the phenol **14a** in 89% yield. Spectral data for **14a**: white solid, mp 78 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.3 Hz), 1.58 (sextet, 2 H, J = 7.7 Hz), 2.12 (pentet, 2 H, J = 7.6 Hz), 2.15 (s, 3 H), 2.53 (t, 2 H, J = 7.9 Hz, CH_2Et), 2.86 (t, 2 H, J = 7.2 Hz), 2.87 (t, 2 H, J = 7.1 Hz), 4.51 (s, 1 H), 6.47 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.68, 15.67, 24.29, 25.20, 29.44, 32.95, 35.86, 114.19, 124.21, 126.78, 140.96, 146.06, 149.97; IR (CCl_4) 3612 s, 2959 s, 2932 s, 2872 m, 2844 m, 1620 w, 1478 m, 1456 m, 1445 m, 1423 m, 1378 w, 1343 w, 1320 m, 1298 m, 1289 m, 1170 m, 1154 s, 1082 m, 1044 w cm^{-1}; mass spectrum m/z (relative intensity) 190 M^+ (3), 161 (10), 99 (3), 84 (38), 71 (19), 57 (100); calcd for $C_{13}H_{18}O$, m/z 190.1358, measd m/z 190.1348.

Preparation of 1,6-Octadiyne 35. To a solution of 1,6-heptadiyne (8.16 g, 88.7 mmol) in 120 mL of THF was added a 1.6 M solution of n-butyllithium (55.46 mL, 88.7 mmol) in hexanes at −78 °C under argon. This solution was transferred via cannula to a solution of iodomethane (13.2 g, 90.4 mmol) in 120 mL of THF at 0 °C. The solution was warmed to 23 °C for 40 min, and then the reaction was quenched by the addition of saturated aqueous $NaHCO_3$. The organic layer was washed with water and brine, then dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. The residue was distilled under reduced pressure to give the monoalkylated product **35** (1.0 g, 9.4 mmol) in 11% yield. Dialkylation was a serious competing reaction. Spectral data for **35**: ^{1}H NMR ($CDCl_3$) δ 1.70 (pentet 2 H, J = 7 Hz, CH_2), 1.78 (t, 3 H, J = 2.5 Hz, CH_3), 1.95 (t, 1 H, J = 2.6 Hz, CH), 2.23–2.32 (m, 4 H, 2 CCH_2); ^{13}C NMR ($CDCl_3$) δ 3.35, 17.43, 17.71, 27.82, 68.59, 76.13, 77.90, 83.66; mass spectrum m/z (relative intensity) 106 M^+ (4), 105 (22), 91 (100), 79 (17), 78 (24), 77 (20), 66 (22), 65 (13), 51 (20).

Preparation of the *n*-Propyl Carbene Complex 34. To a solution of 1-iodopropane (0.87 g, 5.1 mmol) in 30 mL of ether at −78 °C was added a solution of 1.7 M t-BuLi (11.27 mmol) in pentane. After 10 min this solution was transferred to a suspension of $Cr(CO)_6$ (1.24 g, 5.6 mmol) in 30 mL of ether at −78 °C. The resulting mixture was stirred at −78 °C for 10 min and then allowed to warm to 0 °C over a period of 2.5 h. Methyl triflate was added and allowed to react at 0 °C for 30 min. The solution was poured into saturated aqueous $NaHCO_3$. The organic layer was washed with water and brine and dried over anhydrous $MgSO_4$. After removal of solvents, the residue was chromatographed on silica gel with hexane as eluent to give a 60% yield (0.853 g, 0.31 mmol) of complex **34** as a yellow oil. Spectral data for **34**: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3 H, J = 7.4 Hz), 1.51 (sextet, 2 H, J = 7.5 Hz), 3.27 (t, 2 H, J = 7.6 Hz), 4.75 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 13.66, 19.81, 64.94, 67.59, 216.38, 223.18, 363.67; IR (neat) 2063 m, 1993 m, 1920 s, 1455 m, 1251 m cm^{-1}; mass spectrum m/z (relative intensity) 278 M^+ (98), 250 (99), 222 (100), 194 (90), 166 (26), 138 (54), 118 (16); calcd for $C_{10}H_{10}CrO_6$ m/z 277.9882, measd m/z 277.9877. This complex was also made in 50% yield by alkylation of (methylmethoxymethylene)pentacarbonylchromium(0) with ethyl triflate according to procedure B described for complex **11a**.

Preparation of Phenol 15a from the Carbene Complex 34 and Octadiyne 35. To a 0.006 M solution of the carbene complex **34** (0.347 g, 1.25 mmol) in freshly distilled n-butyl ether (200 mL) in a one-necked flask equipped with a threaded stopcock was added 1,6-octadiyne (**35**) (0.150 g, 1.42 mmol). The resulting mixture was deoxygenated by the freeze–thaw method (−196 °C → 0 °C, three cycles), and on the last cycle the flask was backfilled with argon. The threaded stopcock was sealed at 1 atm of argon at 25 °C, and then the flask was heated at 70 °C for 6 h. The solvent was removed by rotary evaporation (bath temperature, 45 °C), and the residue was dissolved in a hexane/ether solution and filtered through a plug of Celite. A GC trace of this crude reaction mixture (fused silica Carbowax coated capillary column) gave a single major peak which accounted for 98.9% of the integrated peak areas. The product was purified by silica gel chromatography with a 1:1:10 mixture of ether/CH_2Cl_2/hexane as eluent to give **15a** (0.144 g, 0.76 mmol) as a white solid in 61% yield. Spectral data for **15a**: mp 57–58 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 7.3 Hz, CH_3), 1.62 (sextet, 2 H, J = 7.6 Hz, CH_2), 2.04 (pentet, 2 H, J = 7.4 Hz, CH_2), 2.15 (s, 3 H, CH_3), 2.54 (t, 2 H, CH_2), 2.80 (t, 2 H, J = 7.3 Hz, CH_2), 2.83 (t, 2 H, J = 7.2 Hz, CH_2), 4.43 (br s, 1 H, OH), 6.81 (s, 1 H, ArH). The regiochemistry was verified by the following NOE data. Irradiation of the singlet at 6.81 ppm resulted in a 0.5% enhancement of protons at 2.80 and 2.54 ppm. Irradiation of the triplet at 2.54 ppm gave a 1.6% enhancement of the protons at 6.81 ppm and 3.3% at 1.62 ppm. No NOE was observed upon irradiation of the singlet at 2.15 ppm. ^{13}C NMR ($CDCl_3$): δ 12.48 (q, J = 126 Hz), 14.16 (q, J = 126 Hz), 23.22 (t, J = 127 Hz), 25.25 (t, J = 132 Hz), 31.79 (t, J = 129 Hz), 32.56 (t, J = 128 Hz), 32.60 (t, J = 128 Hz), 119.03 (s), 122.65 (d, J = 155 Hz), 125.58 (s), 135.23 (s), 142.03 (s), 149.97 (s). IR (thin film): 3430 br s, 2960 s, 2930 m, 2872 w, 2863 w, 1407 m, 1338 m, 1210 m cm^{-1}. Mass spectrum: m/z (relative intensity) 191 M^+ + 1 (4), 190 M^+ (25), 162 (14), 161 (100), 147 (7), 133 (5). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.73; H, 9.55.

General Procedure for the Reactions of the Complex 11a with Alkynes in Alcohol Solvents Illustrated for the Reaction of Phenylacetylene in Methanol. To a 0.08 M solution of the carbene complex **11a** (143.0 mg, 0.45 mmol) in methanol (6 mL) in a one-necked flask equipped with a threaded stopcock was added phenylacetylene (0.16 mL, 148.8 mg, 1.46 mmol). The resulting mixture was deoxygenated by the freeze–thaw method (−196 °C → 0 °C, three cycles), and on the last cycle the flask was backfilled with argon. The threaded stopcock was sealed at 1 atm of argon at 25 °C, and then the flask was heated at 42 °C for 48 h. The reaction mixture was opened to air and stirred for 20 min to facilitate oxidative removal of the metal by air. After filtration through Celite to remove chromium hexacarbonyl solid, the crude residue was loaded onto a silica gel column, and upon elution with a 1:1:20 mixture of ether, CH_2Cl_2, and hexanes, three fractions were collected. In reverse order of elution these compounds were identified as the methyl ester **48a** obtained in 12% yield (R_f = 0.11, 9.8 mg, 0.053 mmol) as a colorless oil, the alkyne-inserted methyl ester **41b** obtained in 40% yield as a colorless oil (R_f = 0.14, 52.0 mg, 0.18 mmol), and 4-indanol **13b** obtained in 36%

yield (R_f = 0.18, 35.5 mg, 0.16 mmol), which was identical with the indanol **13b** obtained from the same reaction in benzene. Spectral data for **48a**: ^{1}H NMR ($CDCl_3$) δ 1.19 (d, 3 H, J = 7.1 Hz), 1.80–1.86 (m, 2 H), 2.17–2.21 (m, 1 H), 2.25–2.32 (m, 1 H), 2.42–2.47 (m, 2 H), 3.58 (q, 1 H, J = 7.1 Hz), 3.58 (s, 3 H), 3.65 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 15.29, 19.40, 28.23, 28.75, 36.37, 51.66, 56.68, 113.04, 152.48, 175.29; IR (neat) 2952–2939 br s, 2849 m, 1737 s, 1683 m, 1458 m, 1344 s, 1310 m, 1249 m, 1225 m, 1199 m, 1163 m, 1049 s cm^{-1}; mass spectrum m/z (relative intensity) 184 M$^+$ (51), 170 (16), 153 (8), 139 (17), 125 (93), 111 (27), 101 (19), 97 (100), 88 (35), 86 (70), 84 (97), 83 (24), 77 (75), 67 (35); calcd for $C_{10}H_{16}O_3$ m/z 184.1099, measd m/z 184.1098. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.17; H, 8.76. Found: C, 65.46; H, 8.64. Spectral data for **41b**: ^{1}H NMR ($CDCl_3$) δ 1.77–1.86 (m, 2 H), 1.96 (s, 3 H), 2.44–2.50 (m, 2 H), 2.55–2.60 (m, 2 H), 3.60 (s, 3 H), 3.66 (s, 3 H), 4.62 (d, 1 H, J = 9.3 Hz), 5.68 (d, 1 H, J = 9.2 Hz), 7.20–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.54, 18.99, 30.57, 31.64, 50.07, 52.06, 56.47, 114.86, 121.89, 126.88, 127.85, 128.52, 134.46, 139.61, 154.80, 173.77; IR (neat) 3027 m, 2950 s, 2846 s, 1737 s, 1631 s, 1591 m, 1452 m, 1435 m, 1307 m, 1240 s, 1158 s cm^{-1}; mass spectrum m/z (relative intensity) 286 M$^+$ (20), 240 (13), 224 (11), 215 (5), 195 (4), 137 (80), 105 (6), 91 (13), 88 (7), 86 (70), 84 (100), 77 (7), 69 (6). A single diastereomer of **41b** was observed and assigned the trans stereochemistry by NOE experiments. No enhancement for the proton at δ = 5.68 ppm (olefinic proton) and a 10.2% enhancement for the proton at δ = 4.62 ppm (benzylic proton) were observed upon irradiation of the protons of the methyl group at δ = 1.96 ppm.

The compound **41b** could not be characterized by combustion analysis since it is quite sensitive to hydrolysis of the enol ether functionality to give the corresponding keto ester **51b**, which is formed as a 1:1 mixture of diastereomers. Spectral data for **51b** collected on a 1:1 mixture of isomers: ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 3 H), 2.14 (t, 3 H, J = 1.9 Hz), 1.82–1.86 (m, 2 H), 2.21–2.32 (m, 6 H), 2.52 (t, 2 H, J = 7.2 Hz), 2.57–2.61 (m, 2 H), 2.85–2.90 (m, 2 H), 3.22–3.25 (m, 2 H), 3.64 (s, 3 H), 3.65 (s, 3 H), 3.78–3.85 (m, 2 H), 7.20–7.32 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 18.19 (q, J = 128 Hz), 19.29 (t, J = 132 Hz), 19.48 (t, J = 132 Hz), 23.32 (q, J = 126 Hz), 29.26 (t, J = 132 Hz), 29.50 (t, J = 131 Hz), 37.61 (t, J = 133 Hz), 40.35 (t, J = 132 Hz), 40.45 (t, J = 131 Hz), 42.05 (t, J = 130 Hz), 49.06 (d, J = 134 Hz), 50.88 (d, J = 133 Hz), 51.95 (q, J = 147 Hz), 52.15 (q, J = 147 Hz), 127.15 (d, J = 160 Hz), 127.56 (d, J = 160 Hz), 127.75 (d, J = 158 Hz), 128.04 (d, J = 159 Hz), 128.43 (d, J = 160 Hz), 128.65 (d, J = 160 Hz), 132.87, 133.07, 138.21, 138.78, 145.75, 147.95, 173.65, 174.10, 206.84, 207.89; IR (neat) 3024 m, 2952 s, 2881 m, 1735 s, 1704 s, 1625 s, 1454 m, 1436 s, 1269 s, 1198 s, 1165 s, 700 s cm^{-1}; mass spectrum m/z (relative intensity) 272 M$^+$ (12), 241 (28), 240 (100), 213 (32), 212 (40), 211 (29), 197 (21), 184 (31), 155 (16), 141 (20), 135 (26), 129 (25), 121 (37), 91 (80), 77 (37), 67 (15); calcd for $C_{17}H_{20}O_3$ m/z 272.1412, measd m/z 272.1406. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.96; H, 7.41. Found: C, 75.05; H, 7.56.

Utilizing the same procedure, the reaction of **11a** (192.0 mg, 0.608 mmol) with phenylacetylene (0.20 mL, 186.0 mg, 1.82 mmol) in 2-propanol (6 mL) gave the indanol **13b** in 37% yield (50.8 mg, 0.227 mmol) and the alcohol trapping product **41c** in 14% yield (26.4 mg, 0.084 mmol). Spectral data for **41c**: ^{1}H NMR ($CDCl_3$) δ 1.16 (d, 3 H, J = 6.2 Hz), 1.21 (d, 3 H, J = 6.7 Hz), 1.80–1.85 (m, 2 H), 1.96 (s, 3 H), 2.45–2.50 (m, 2 H), 2.55–2.60 (m, 2 H), 3.60 (s, 3 H), 4.55 (d, 1 H, J = 9.3 Hz), 4.95–5.00 (m, 1 H), 5.67 (d, 1 H, J = 9.3 Hz), 7.20–7.33 (m, 5 H); IR (neat) 3030 w, 2979–2936 br s, 2879 m, 1729 s, 1626 s, 1495 m, 1454 m, 1374 m, 1171 s, 1107 s, 699 cm^{-1}. The enol ether **41c** was hydrolyzed quantitatively to a 1:1 mixture of the cis and trans isomers of the keto ester **51c**: ^{1}H NMR ($CDCl_3$) δ 1.12 (d, 6 H, J = 6.2 Hz), 1.20 (d, 6 H, J = 6.3 Hz), 1.67 (s, 3 H), 1.82–1.86 (m, 2 H), 2.16 (s, 3 H), 2.22–2.31 (m, 6 H), 2.50–2.64 (m, 4 H), 2.86–2.90 (m, 2 H), 3.22–3.26 (m, 2 H), 3.74–3.80 (m, 2 H), 4.94–5.00 (m, 2 H), 7.20–7.34 (m, 10 H); IR (neat) 3024 w, 2979 s, 2938 m, 2879 m, 1727 s, 1706 s, 1626 s, 1454 m, 1373 m, 1270 m, 1196 m, 1173 s, 1107 s, 816 m, 700 m cm^{-1}; mass spectrum m/z (relative intensity) 300 M$^+$ (15), 241 (33), 240 (100), 213 (42), 212 (48), 211 (56), 196 (18), 184 (25), 169 (7), 155 (12), 136 (17), 135 (22), 118 (8), 104 (10), 91 (77), 79 (17), 77 (14); calcd for $C_{19}H_{24}O_3$ m/z 300.1725, measd m/z 300.1746.

Reaction of the Complex 11a with Diphenylacetylene in Methanol. The reaction of **11a** (170 mg, 0.538 mmol) with diphenylacetylene (200 mg, 1.12 mmol) in methanol (7 mL) gave after chromatography on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexane the indanol **13d** in 5% yield (R_f = 0.35, 7.8 mg, 0.026 mmol) and the methyl ester **48a** in 41% yield (R_f = 0.27, 40.5 mg, 0.22 mmol), which was identical with the methyl ester obtained from the reaction of **11a** with phenylacetylene. Spectral data for **13d**: white solid, mp 174–175 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 3 H), 2.19 (pentet, 2 H, J = 7.5 Hz), 2.95 (t, 2 H, J = 7.5 Hz), 3.01 (t, 2 H, J = 7.5 Hz), 4.75 (s, 1 H), 6.93–7.20 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 16.99, 24.59, 29.80, 32.63, 123.72, 125.79, 125.96, 127.15, 127.41, 128.32, 128.56, 130.31, 131.02, 135.79, 140.11, 140.44, 144.91, 146.70; IR (neat) 3500 br s, 3049 m, 3013 m, 2950–2951 br s, 2838 s, 1668 m, 1583 m, 1422 s, 1323 s, 1266 s, 1210 s, 1175 s, 1060 m, 780 m, 696 s cm^{-1}; mass spectrum m/z (relative intensity) 300 M$^+$ (50), 285 (7), 265 (4), 251 (4) 239 (4), 223 (6), 207 (5), 179 (7), 164 (4), 149 (10), 126 (4), 105 (100), 91 (6), 77 (36), 69 (8), 57 (8); calcd for $C_{22}H_{20}O$ m/z 300.1514, measd m/z 300.1511.

Reaction of the Complex 11a with 1-Hexyne in Methanol. The reaction of **11a** (74.6 mg, 0.236 mmol) with 1-hexyne (0.08 mL, 57.2 mg, 0.70 mmol) in methanol (4 mL) gave after chromatography on silica gel with a 1:1:20 mixture of ether/CH_2Cl_2/hexane the methyl ester **48a** in 13% yield (R_f = 0.10, 5.5 mg, 0.03 mmol), the indanol **13e** in 21% yield (R_f = 0.14, 10.0 mg, 0.049 mmol), and the alkyne-inserted methyl ester **41e** in 27% yield (R_f = 0.19, 17.0 mg, 0.064 mmol). Spectral data for indanol **13e**: mp 61–62 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7.3 Hz), 1.39 (h, 2 H, J = 7.5 Hz), 1.57 (pentet, 2 H, J = 7.7 Hz), 2.11 (pentet, 2 H, J = 7.5 Hz), 2.16 (s, 3 H), 2.55 (t, 2 H, J = 7.7 Hz), 2.81 (t, 2 H, J = 7.5 Hz), 2.82 (t, 2 H, J = 7.5 Hz), 4.27 (s, 1 H), 6.72 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.01, 18.38, 22.72, 24.90, 29.00, 29.39, 31.73, 32.59, 125.41, 126.03, 128.65, 129.20, 142.26, 147.72; IR (neat) 3300 br s, 3002 w, 2960–2932 br s, 2856 s, 1612 w, 1465 s, 1374 m, 1274, 1199 s, 1067 m, 860 m, 725 w cm^{-1}; mass spectrum m/z (relative intensity) 204 M$^+$ (28, 161 (100), 147 (5), 133 (4), 128 (3), 115 (5), 105 (6), 91 (7), 77 (4), 65 (4); calcd for $C_{14}H_{20}O$ m/z 204.1514, measd m/z 204.1517. Spectral data for **41e**: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, J = 7.2 Hz), 1.25–1.35 (m, 4 H), 1.45–1.52 (m, 2 H), 1.80 (pentet, 2 H, J = 7.4 Hz), 1.97 (s, 3 H), 2.39–2.45 (m, 2 H), 2.56 (t, 2 H, J = 7.4 Hz), 3.33 (dt, 1 H, J = 9.5, 7.2 Hz), 3.61 (s, 3 H), 3.64 (s, 3 H), 5.16 (d, 1 H, J = 9.5 Hz); IR (neat) 2957 s, 2934 s, 2857 m, 1737 s, 1634 m, 1458 m, 1433 m, 1328 w, 1260 m, 1239 m, 1161 m, 1035 m cm^{-1}. The enol ether **41e** was further characterized by hydrolysis to a 1:1 mixture of the cis and trans isomers of the keto ester **51e**. Spectral data for **51e**: ^{1}H NMR ($CDCl_3$) δ 0.85–0.90 (m, 6 H), 1.22–1.32 (m, 12 H), 1.61–1.67 (m, 2 H), 1.80 (s, 3 H), 1.82–1.88 (m, 2 H), 2.18 (s, 3 H), 2.25–2.32 (m, 4 H), 2.45–2.70 (m, 8 H), 3.15–3.20 (m, 2 H), 3.63 (s, 6 H); IR (neat) 2956–2930 br s, 2873–2859 br s, 1736 s, 1707 s, 1626 s, 1435 m, 1375 m, 1268 s, 1292 s, 1168 s, 1004 m, 826 m cm^{-1}; mass spectrum m/z (relative intensity) 252 M$^+$ (27), 220 (30), 192 (30), 177 (16), 164 (18), 149 (9), 135 (100), 123 (14), 109 (10), 93 (8), 81 (12), 79 (12), 67 (10); calcd for $C_{15}H_{24}O_3$ m/z 252.1725, measd m/z 252.1719.

Reaction of the Complex 11a with 1-Pentyne in Methanol. To a 0.005 M solution of the carbene complex **11a** (186 mg, 0.59 mmol) in methanol (60 mL) was added 1-pentyne (121 mg, 1.77 mmol), and the reaction was carried out with the general procedure described above (77 °C, 24 h). Triphenylmethane (0.0781 g) was added to the crude reaction mixture, which was concentrated by a rotary evaporator. After complete removal of the solvent by high vacuum (0.01 mmHg), the yields of the three products were determined by integration against triphenylmethane to be 45% for the methyl ester **48a**, 9% for the indanol **13a**, and 12% for the alkyne-inserted methyl ester **41a**. Spectral data for **41a**: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 7.3 Hz, Pr-CH_3), 1.20–1.41 (m, 2 H, Pr-CH_2CH$_3$), 1.43–1.54 (m, 1 H, C(H)CH(H)Et), 1.68–1.78 (m, 1 H, C(H)-CH(H)Et), 1.80 (pentet 2 H), J = 7.4 Hz, cyclopentenyl 4-CH_2), 1.98 (s, 3 H, CH_3), 2.42 (br s, 2 H, cyclopentenyl 3- or 5-CH_2), 2.57 (br t, 2 H, J = 7.3 Hz, cyclopentenyl 3- or 5-CH_2), 3.35 (q, 1 H, J = 9.2 Hz, C(H)Pr), 3.61 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 5.15 (d, 1 H, J = 9.5 Hz, 3-CH); ^{13}C NMR ($CDCl_3$) δ 14.64 q, 16.32, 19.70, 21.11, 31.30, 32.39, 36.10, 44.90 d, 52.31 q, 57.22 q, 115.74 s, 123.78 d, 134.76, 155.03 s, 176.28 s; IR (CCl_4) 2990 m, 2957 s, 2937 s, 2873 m, 2846 m, 1737 vs, 1635 s, 1459 m, 1447 m, 1434 m, 1390 m, 1372 m, 1333 m, 1305 m, 1291 w, 1189 w, 1160 s, 1131 m, 1100 w, 1052 w, 1037 m cm^{-1}; mass spectrum m/e (relative intensity) 252 M$^+$ (43), 209 (36), 193 (100), 169 (14), 149 (14), 137 (21), 118 (36), 105 (14), 91 (21).

When the reaction was repeated and the crude reaction mixture was reduced with zinc and acetic acid, the phenol was obtained in the same yield of 9%. When the reaction was run at 0.21 M in the carbene complex, the yields were determined to be 11% for **48a**, 18% for indanol **13a**, and 18% for the alkyne-inserted methyl ester **41a**.

Search for the Vinyl Ketene Complex 58. The reaction of (phenylmethoxymethylene)pentacarbonylchromium(0) (**57**) (1.870 g, 5.994 mmol) and diphenylacetylene (1.18 g, 6.63 mmol) was carried out in 24

mL of degassed heptane at 80 °C for 45 min as was described.[27] The mixture was concentrated and purified by silica gel chromatography with a 1:1:10 mixture of ether/CH_2Cl_2/hexane as eluent. Seven fractions were isolated in which the slowest moving fraction was R_f = 0.17. Two fractions (R_f = 0.67 and 0.17) contained products with IR bands at ~1750 cm^{-1}. The more rapidly eluting fraction (R_f = 0.67) was a mixture of the metal-free cyclobutenone and 2,3-diphenyl-4-methoxy-1-naphthol. The slower fraction (R_f = 0.17) eluted as a yellow solution, but was isolated as a red oil upon concentration to give 120 mg (4%, 0.260 mmol) of a material that was identified as the chromium tricarbonyl complexed cyclobutenone **59** on the basis of the following spectral data: ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 3 H, OCH_3), 5.10 (t, 1 H, J = 6.4 Hz, *m*-ArH·Cr-$(CO)_3$), 5.16 (t, 1 H, J = 6.4 Hz, *m*-ArH·$Cr(CO)_3$), 5.56 (t, 1 H, J = 6.2 Hz), 5.78 (d, 1 H, J = 6.5 Hz *o*-ArH·$Cr(CO)_3$), 5.91 (d, 1 H, J = 6.4 Hz, *o*-ArH·$Cr(CO)_3$), 7.27–7.77 (m, 10 H, ArH); ^{13}C NMR ($CDCl_3$) δ 53.44, 88.86, 91.30, 94.56, 94.69, 100.84, 125.85, 128.42, 128.44, 128.71, 129.16, 130.11, 136.3, 134.13, 156.81, 190.06, 230.66 (1 C not located); IR (thin film) 1967 vs, 1898 br s, 1751 s; (CS_2) 1981 vs, 1921 br s, 1759 s cm^{-1}; mass spectrum m/z (relative intensity) 462 M^+ (17), 378 (97), 326 (68), 267 (100), 233 (2); calcd for $C_{26}H_{18}O_5Cr$ m/z 462.0559, measd m/z 462.0565.

Preparation of 1-Iodo-3-pentyne 53. The preparation of 1-iodo-3-pentyne **53** from the commercially available 3-pentyn-1-ol via the tosylate was accomplished in 76% overall yield by the procedure previously described.[41] Spectral data for **53**: ^{1}H NMR ($CDCl_3$) δ 1.75 (br s, 3 H, CH_3), 2.68 (m, 2 H, CH_2), 3.17 (t, 2H, J = 7.3 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 2.60, 3.53, 24.05, 77.69, 77.86; IR (thin film) 2965 m, 2907 m, 2844 w, 1428 m, 1243 s, 1168 s cm^{-1}.

Preparation of the Dimethylamino 4-Hexynyl Carbene Complex 61a. To a solution of the carbene complex **60a**[42] (0.602 g, 2.29 mmol) in 10 mL of THF was added a 1.6 M solution of *n*-butyllithium (1.44 mL, 2.31 mmol) in hexanes at –78 °C under an argon atmosphere. After 15 min, 1-iodo-3-pentyne (0.56 g, 2.86 mmol) was injected. The solution was warmed and stirred at 0 °C for 2 h and was then quenched with saturated aqueous $NaHCO_3$ solution. The mixture was diluted with ether, washed with brine, dried over $MgSO_4$, filtered through Celite, and concentrated. The product was separated from the residue by silica gel chromatography to give the carbene complex **61a** (0.440 g, 1.33 mmol) as a very light yellow oil in 58% yield. Spectral data for **61a**: R_f = 0.74; ^{1}H NMR ($CDCl_3$) δ 1.53–1.59 (m, 2 H), 1.77 (t, 3 H, J = 2.3 Hz, CH_3), 2.24–2.27 (m, 2 H, CH_2), 3.14–3.20 (m, 2 H, CH_{2a}), 3.34 (s, 3 H, NCH_3), 3.82 (s, 3 H, NCH_3); ^{13}C NMR (d_6-acetone) δ 3.06, 18.97, 24.64, 42.70, 52.21, 53.74, 77.02, 78.30, 218.74, 224.07, 271.90; IR (thin film) 2946 w, 2917 w, 2871 w, 2052 m, 1967 shoulder, 1902 vs, 1534 m, 1438 w, 1397 w cm^{-1}; mass spectrum m/z (relative intensity) 329 M^+ (4), 273 (5), 245 (18), 235 (22), 217 (32), 189 (100), 174 (72), 136 (83), 122 (95), 99 (44). Anal. Calcd for $C_{14}H_{15}O_5CrN$: C, 51.07; H, 4.59; N, 4.25. Found: C, 50.97; H, 4.68; N, 4.86.

Preparation of the Pyrrolidino 4-Hexynyl Carbene Complex 61b.[29] A solution of the carbene complex **60b**[43] (0.990 g, 3.426 mmol) in 8 mL of THF was cooled to –78 °C under an argon atmosphere, and a 1.6 M *n*-butyllithium solution (2.14 mL, 3.43 mmol) in hexane was injected. The resulting solution was stirred for 20 min, after which period 1-iodo-3-pentyne (0.780 g, 3.98 mmol) was injected. The dry ice/acetone bath was replaced with an ice/water bath, and the solution was stirred for 1 h. The reaction was quenched by addition of 5% aqueous $NaHCO_3$. The mixture was diluted with ether, and the organic layer was washed with water and then brine. The organic solution was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. Silica gel chromatography (1:5 benzene/hexanes, then 1:1 benzene/hexanes) led to the isolation of **61b** (0.925 g, 2.61 mmol) in 76% yield as a viscous oil, which turned to a light tan solid upon standing in the freezer. Spectral data for **61b**: mp 57–58 °C; ^{1}H NMR ($CDCl_3$) δ 1.62–1.68 (m, 2 H, $CH_2CH_2CH_2$), 1.78 (t, 3 H, J = 2.5 Hz, CH_3) 2.07–2.14 (m, 4 H, CH_2-CH_2), 2.25–2.30 (m, 2 H, CH_2CH_2C), 3.05–3.11 (m, 2 H, CH_{2a}), 3.61–3.73 (m, 2 H, NCH_2), 4.09–4.14 (m, 2 H, NCH_2); ^{13}C NMR ($CDCl_3$) δ 3.38, 18.93, 24.38, 24.88, 25.53, 51.73, 52.67, 61.09, 76.81, 77.80, 218.27, 223.15, 272.12; IR (thin film) 2957 w, 2915 w, 2873 w, 2050 m, 1964 shoulder, 1899 s, 1492 m, 1443 m, 675 m, 660 m cm^{-1}; mass spectrum m/z (relative intensity) 355 M^+ (8), 327 (5) 299 (6), 271 (12), 243 (14), 215 (40), 173 (100), 163 (46), 121 (33), 80 (38). Anal. Calcd for $C_{16}H_{17}O_5CrN$: C, 54.08; H. 4.82; N, 3.94. Found: C, 53.55; H, 4.82; N, 3.89.

Utilizing the same procedure, the anion of **60b** could also be alkylated with the tosylate of 3-pentyn-1-ol with the reaction temperature at 0 °C for 2 h and then 25 °C for 3 h to give **61b** in 36% yield in addition to a 21% recovery of the starting carbene complex **60b**.

Table VI. Bond Lengths for η^5-Vinyl Ketene Complex 62a

Cr–C(1)	1.851(5)	Cr–C(2)	1.867(4)
Cr–C(3)	1.888(4)	Cr–N	2.194(3)
Cr–C(4)	2.024(4)	Cr–C(5)	2.219(4)
Cr–C(6)	2.200(4)	Cr–C(10)	2.130(4)
C(1)–O(1)	1.154(6)	C(2)–O(2)	1.151(5)
C(3)–O(3)	1.142(6)	O(4)–C(4)	1.215(4)
N–C(10)	1.421(4)	N–C(12)	1.486(5)
N–C(13)	1.487(5)	C(4)–C(5)	1.430(5)
C(5)–C(6)	1.424(6)	C(5)–C(11)	1.529(6)
C(6)–C(7)	1.510(6)	C(6)–C(10)	1.404(5)
C(7)–C(8)	1.535(7)	C(8)–C(9)	1.545(7)
C(9)–C(10)	1.503(5)		

Isolation of the (Dimethylamino)-η^5-vinyl Ketene Complex 62a. A round-bottom flask with a high-vacuum threaded stopcock was charged with the carbene complex **61a** (0.730 g, 2.42 mmol) which was dissolved in 100 mL of benzene to give a 0.02 M solution. This was deoxygenated by the freeze–thaw method (–196 °C → 0 °C, three cycles), and on the last cycle the flask was backfilled with argon. The threaded stopcock was sealed at 1 atm of argon at 25 °C, and then the flask was heated at 70 °C for 3.5 h. The resulting solution was concentrated by rotary evaporation and loaded onto a silica gel column, and upon elution with a 1:1 mixture of hexane and ethyl acetate, and the carbene complex **62a** (0.393 mg, 1.30 mmol) was obtained as a red-brown solid in 54% yield. The average yield of **62a** was 43% for several runs. Spectral data for **62a**: R_f = 0.39 (1:1 hexane/ethyl acetate); mp 110–115 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3 H, NCH_3), 1.83 (s, 3 H, CCH_3), 2.13–2.19 (m, 1 H, HC*H*), 2.34–2.40 (m, 1 H, HC*H*), 2.52–2.56 (m, 1 H, HC*H*), 2.63 (s, 3 H, NCH_3), 2.89–2.96 (m, 1 H, HC*H*), 3.13–3.17 (m, 1 H, HC*H*), 3.36–3.43 (m, 1 H, HC*H*); ^{13}C NMR ($CDCl_3$) δ 15.8 (q, J = 130 Hz), 22.0 (t, J = 133 Hz), 23.7 (s), 30.2 (t, J = 132 Hz), 31.1 (t, J = 132 Hz), 42.6 (q, J = 140 Hz), 52.0 (q, J = 139 Hz), 106.7 (s), 111.2 (s), 230 (br s), 253.5 (s). The broad, unresolved resonance observed at 230 ppm sharpens to three resolved resonances at 226.9, 230.1, and 233.4 ppm upon cooling from +23 to –50 °C. An APT experiment confirmed carbons resonating at 23.7, 106.7, 111.2, and 253.5 ppm to be quaternary. IR (thin film): 1981 s, 1917 s, 1872 s, 1726 m cm^{-1}; mass spectrum m/z (relative intensity) 301 M^+ (6), 273 (13), 245 (19), 217 (17), 189 (100), 192 (79), 146 (23), 136 (27), 122 (35), 96 (37). Anal. Calcd for $C_{13}H_{15}O_4CrN$: C, 51.83; H, 5.02; N, 4.65. Found: C, 52.03; H, 5.38; N, 4.40. This complex was also characterized by X-ray crystallography; see below.

Crystal Structure Determination for the η^5-Vinyl Ketene Complex 62a. Crystal data for **62a**: monoclinic, $P2_1/n$, a = 7.688(2) Å, b = 16.339(3) Å, c = 11.239(2) Å, β = 97.42(2)°, V = 1400.0(5) $Å^3$, Z = 4, μ (Mo Kα) 8.6 cm^{-1}, D (calcd) = 1.43 g/cm^3. Data collection (Nicolet R3m, 2θ = 50°) yielded 1740 independent, observed $F_o > 5\sigma(F_o)$ reflections. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in idealized positions. $R(F)$ = 0.0427; $R(wF)$ = 0.0466; GOF = 1.24; $\Delta(\rho)$ = 0.416 e A^{-3}; Δ/σ = 0.040; and N_o/N_v = 10.12. SHELXTL (5.1) software was used for all computations (G. Sheldrick, Nicolet XRD, Madison, WI). The results of the structure determination are summarized in Tables VI–IX.

Isolation of the Pyrrolidino-η^5-vinyl Ketene Complex 62b. With the procedure for **61a**, complex **61b** (0.177 g, 0.50 mmol) gave **62b** in 52% yield (85.2 mg, 0.26 mmol). Spectral data for **62b**: red-brown crystalline solid; mp 114–117 °C; R_f = 0.41 (1:1 hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 1.40–1.76 (m, 6 H, 1.79 (s, 3 H, CH_3), 2.10–2.21 (m, 1 H), 2.31–2.40 (m, 1 H), 2.47–2.55 (m, 1 H), 2.65–2.74 (m, 1 H), 2.85–2.96 (m, 1 H), 3.12–3.31 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 15.7, 22.3, 22.7, 22.8, 23.6, 31.0, 31.1, 53.0, 59.4, 105.4, 112.1, 120 (br) 252.6. The broad, unresolved resonance observed at 230 ppm sharpens to three resolved resonances at 227.1, 229.9, and 233.4 ppm upon cooling from +23 to –50 °C. APT experiments indicate carbons resonating at 23.6, 105.4, 112.1, and 252.6 ppm to be quaternary and the 15.7 ppm resonance to be the methyl carbon. IR (thin film) 1966 s, 1912 s, 1870 s, 1732 m cm^{-1}; mass spectrum m/z (relative intensity) 327 M^+ (4), 299 (10), 271 (19), 243 (16), 220 (88), 215 (48), 191 (26), 173 (98), 163 (46), 148 (66), 134 (35), 108 (100), 80 (95); calcd for $C_{15}H_{17}O_4CrN$ m/z 327.0569, measd m/z 327.0596.

Several attempts were made to observe labeled-^{13}CO incorporation into the ketene complex; however, none met with success. In one

Table VII. Bond Angles for η^5-Vinyl Ketene Complex 62a

C(1)–Cr–C(2)	92.9(2)	C(1)–Cr–C(3)	85.2(2)
C(2)–Cr–C(3)	89.7(2)	C(1)–Cr–N	166.0(2)
C(2)–Cr–N	101.1(2)	C(3)–Cr–N	94.1(2)
C(1)–Cr–C(4)	100.3(2)	C(2)–Cr–C(4)	81.5(2)
C(3)–Cr–C(4)	169.8(2)	N–Cr–C(4)	82.7(1)
C(1)–Cr–C(5)	89.4(2)	C(2)–Cr–C(5)	119.6(2)
C(3)–Cr–C(5)	150.5(2)	N–Cr–C(5)	84.4(1)
C(4)–Cr–C(5)	39.1(1)	C(1)–Cr–C(6)	100.0(2)
C(2)–Cr–C(6)	152.7(1)	C(3)–Cr–C(6)	115.1(2)
N–Cr–C(6)	67.7(1)	C(4)–Cr–C(6)	72.6(1)
C(5)–Cr–C(6)	37.6(1)	C(1)–Cr–C(10)	127.6(2)
C(2)–Cr–C(10)	139.3(2)	C(3)–Cr–C(10)	89.8(2)
N–Cr–C(10)	38.3(1)	C(4)–Cr–C(10)	93.5(1)
C(5)–Cr–C(10)	70.8(2)	C(6)–Cr–C(10)	37.8(1)
Cr–C(1)–O(1)	178.4(4)	Cr–C(2)–O(2)	175.1(3)
Cr–C(3)–O(3)	173.9(4)	Cr–N–C(10)	68.4(2)
Cr–N–C(12)	125.4(2)	C(10)–N–C(12)	115.5(3)
Cr–N–C(13)	119.2(2)	C(10)–N–C(13)	114.4(3)
C(12)–N–C(13)	108.2(3)	Cr–C(4)–O(4)	145.7(3)
Cr–C(4)–C(5)	77.8(2)	O(4)–C(4)–C(5)	136.0(4)
Cr–C(5)–C(4)	63.1(2)	Cr–C(5)–C(6)	70.5(2)
C(4)–C(5)–C(6)	122.7(3)	Cr–C(5)–C(11)	131.2(3)
C(4)–C(5)–C(11)	116.4(4)	C(6)–C(5)–C(11)	119.1(3)
Cr–C(6)–C(5)	71.9(2)	Cr–C(6)–C(7)	131.9(3)
C(5)–C(6)–C(7)	125.2(3)	Cr–C(6)–C(10)	68.4(2)
C(5)–C(6)–C(10)	126.0(3)	C(7)–C(6)–C(10)	108.6(3)
C(6)–C(7)–C(8)	104.5(3)	C(7)–C(8)–C(9)	106.5(4)
C(8)–C(9)–C(10)	101.8(3)	Cr–C(10)–N	73.3(2)
Cr–C(10)–C(6)	73.8(2)	N–C(10)–C(6)	119.9(3)
Cr–C(10)–C(9)	135.1(3)	N–C(10)–C(9)	126.2(3)
C(6)–C(10)–C(9)	112.7(3)		

Table VIII. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for η^5-Vinyl Ketene Complex 62a

	x	y	z	U[a]
Cr	5965.4(8)	4001.7(3)	2948.2(5)	38.6(2)
C(1)	4841(6)	3543(3)	4148(4)	59(2)
C(2)	4449(5)	4898(3)	2773(3)	49(1)
C(3)	7358(6)	4547(3)	4213(4)	64(2)
O(1)	4172(5)	3244(3)	4900(3)	98(2)
O(2)	3481(5)	5434(2)	2582(3)	79(1)
O(3)	8092(5)	4855(3)	5041(3)	110(2)
O(4)	3143(4)	3795(2)	730(3)	61(1)
N	7729(4)	4289(2)	1619(3)	39(1)
C(4)	4371(5)	3619(2)	1478(3)	45(1)
C(5)	5332(6)	2892(2)	1838(3)	46(1)
C(6)	7156(5)	2899(2)	2274(3)	42(1)
C(7)	8156(6)	2196(3)	2913(4)	67(2)
C(8)	9852(7)	2586(3)	3532(5)	79(2)
C(9)	10 120(5)	3385(3)	2844(4)	63(2)
C(10)	8281(5)	3577(2)	2290(3)	41(1)
C(11)	4245(6)	2135(3)	2051(4)	69(2)
C(12)	7319(6)	4168(2)	302(3)	53(1)
C(13)	8946(6)	4997(3)	1832(4)	62(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

experiment, a solution of ketene complex **62b** (0.123 g, 0.376 mmol) in 10 mL of benzene was deoxygenated by the freeze–thaw method and backfilled with ^{13}CO (balloon). The solution was stirred at 80 °C for 20 min and then concentrated. The residue was purified by silica gel chromatography (1:1 hexane/ethyl acetate) to give the ketene complex **62b** (16.8 mg, 0.051 mmol) in 14% recovery. The ^{13}C NMR indicated that no label had been incorporated into any of the carbons of the ketene ligand, and a low-temperature (–50 °C) spectrum indicated that no label had been incorporated into the CO ligands.

Reactions of the Pyrrolidino 4-Hexynyl Carbene Complex 61b with 1-Pentyne. The reactions were performed with variations of procedure B for the reaction of **11a** with 1-pentyne. A deoxygenated solution of carbene complex **61b** (0.2646 g, 0.745 mmol) and 1-pentyne (0.50 g, 7.4 mmol) in 15 mL of THF was heated to 84 °C for 7 h under argon. The solution cooled to 23 °C, and a solution of $[Fe(DMF)_3Cl_2][FeCl_4]$ (0.7 g in ~7 mL of water) was added in two portions.[44] After oxidation for 10 min, the solution was diluted with ether and then washed with water and brine. The ethereal extract was allowed to air oxidize overnight, and the resulting cloudy solution was filtered through Celite and purified by

Table IX. H-Atom Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å \times 10^3$) for η^5-Vinyl Ketene Complex 62a

	x	y	z	U
H(7A)	7499	1951	3491	76
H(7B)	8412	1790	2344	76
H(8A)	9739	2700	4356	93
H(8B)	10 828	2225	3492	93
H(9A)	10 887	3308	2243	72
H(9B)	10 579	3810	3386	72
H(11A)	5010	1683	2287	81
H(11B)	3511	2001	1320	81
H(11C)	3526	2245	2670	81
H(12A)	6540	3710	147	64
H(12B)	8380	4065	–40	64
H(12C)	6765	4652	–51	64
H(13A)	9238	5085	2679	72
H(13B)	8382	5476	1470	72
H(13C)	9997	4889	1481	72

preparatory thin-layer chromatography on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexane to give several fractions that were tentatively identified as metal complexes of dienone of the type **67–71** (Scheme VIII) but which were not further characterized. Some of the fractions contained phenols, but these were not quantified since complete reduction of the dienones was not observed. The cyclopentenedione **72** was obtained in pure form in 16% yield (27.1 mg, 0.116 mmol) as a 1.0:0.9 mixture of diastereomers which could not be separated on silica gel. Spectral data for **72** was collected on the isomeric mixture: clear yellow oil; R_f = 0.3 (1:1:4); ^1H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7.4, minor CH_3), 1.03 (t, 3 H, J = 7.4, major CH_3), 1.21 (s, 3 H, major CH_3), 1.22 (s, 3 H, minor CH_3), 1.51–1.77 (m, 6 H, mixture), 2.00–2.09 (m, 4 H, mixture), 2.17–2.28 (m, 6 H, mixture), 2.39–2.53 (m, 4 H, mixture), 2.72–2.74 (m, 2 H, mixture), 6.80 (s, 1 H, major CH), and 6.94 (s, 1 H, minor CH); IR (thin film) 2966 m, 2933 w, 2875 w, 1736 s, 1699 vs, 1614 w, 1458 w, 1292 w cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.95; H, 7.60. The remaining spectral data could be extracted from the 1.1:1.0 mixture and is reported first for the major diastereomer. ^{13}C NMR ($CDCl_3$) δ 13.65, 19.11, 20.17, 20.77, 24.95, 27.53, 37.35, 49.12, 53.83, 142.30, 164.04, 205.12, 206.44, 217.3; mass spectrum (GC/MS) t_R = 8.913 min, m/z (relative intensity) 235 M^+ + 1 (16), 234 (100, M^+), 205 (15), 191 (17), 179 (47), 178 (53), 163 (20), 152 (19), 150 (24), 121 (34), 106 (36). Minor isomer: ^{13}C NMR ($CDCl_3$) δ 13.58, 19.30, 20.25, 20.68, 25.06, 27.20, 37.35, 49.39, 53.16, 142.33, 163.62, 205.75, 206.96, 217.3; mass spectrum (GC/MS), t_R = 9.048 min, m/z (relative intensity) 235 (16, M^+ + 1) 234 (100, M^+), 205 (16), 191 (17), 179 (51), 178 (53), 163 (21), 152 (17), 151 (20), 150 (24), 124 (24), 121 (43), 107 (51). These compounds were identical to the mixture of diastereomers resulting from hydrolysis of the cyclopentenedione **12a**.

The phenol products were quantified in a second experiment run under identical conditions but with a reductive workup with $TiCl_3/LiAlH_4$ since all of the dienone products were reduced under these conditions. The crude mixture from the reaction of the carbene complex **61b** (0.155 g, 0.438 mmol) and 1-pentyne (0.290 g, 4.26 mmol) in 9 mL of THF (84 °C for 4 h) was cooled to 0 °C and treated with an ether suspension of a 4:1 mixture of $TiCl_3$/LAH (0.3 g) added in one portion. The reaction was quenched by the addition of a pH 7 buffer, and the mixture was extracted with ether/dichloromethane. The organic layer was dried over magnesium sulfate, filtered through Celite, and concentrated. The yields of the phenol products **16a** (16%), **15a** (7%), and **13a** (2%) were determined by GC and ^1H NMR using triphenylmethane as an internal standard as described for the reaction of **11a** with 1-pentyne.

The reactions of **61b** and 1-pentyne in benzene and acetonitrile that are indicated in Table V were performed with the same procedure except that the yield of the cyclopentenedione **72** was determined on a portion of the reaction mixture that was not treated with any oxidizing agents other than air.

Reactions of the Pyrrolidino-η^4-vinyl Ketene Complex 62b with 1-Pentyne. According to procedure B for the reaction of **11a** with 1-pentyne, a solution of the vinyl ketene complex **62b** (0.1504 g, 0.560 mmol) and 1-pentyne (0.381 g, 5.6 mmol) in 9 mL of THF was heated to 80 °C for 3.5 h. The solution was filtered through Celite and concentrated. The residue was taken up in 1:1 hexane/ether and once again filtered through Celite. The solution was concentrated and dissolved in 10 mL of THF and cooled to 0 °C under nitrogen, and 4:1 $TiCl_3$/LAH (0.2 g, Aldrich) was added in one portion. After 5 min, the mixture was

warmed to 23 °C for 30 min and pH 7 buffer was added. The solution was extracted with 2:1 ether/dichloromethane, which was then dried over magnesium sulfate, filtered, and concentrated. The ^{1}H NMR and a GC trace of this mixture were recorded. Silica gel chromatography led to the isolation of phenol **16a** (22.6 mg, 0.119 mmol) in 26% yield and a small amount of the enedione **72** (<9.5 mg, 0.041 mmol) in <9% yield. From the isolated yield of **16a**, and the ^{1}H NMR and GC trace of the mixture, the yields of **15a** (11%) and **13a** (≤1%) were determined. The appropriate adjustments were made for the GC response factors of each component. The yields for the same reaction in benzene are given in Table V.

The yield of the enedione product **72** was determined by conducting a separate reaction which was not exposed to the reducing agent. A solution of the ketene complex **62b** (0.0916 g, 0.280 mmol) and 1-pentyne (0.19 g, 2.8 mmol) in 5.5 mL of THF was heated to 80 °C for 3 h. The solution was filtered and concentrated. The enedione was separated from the residue by preparatory thin-layer chromatography with a 1:1:4 mixture of ether/CH_2Cl_2/hexane to give the enedione **72**, which was further purified by column chromatography on silica gel (1:1:10) to give **72** (12.3 mg, 0.053 mmol) in 19% yield as a 1:1 diastereomeric mixture.

Reactions of the Pyrrolidino-η^4-vinyl Ketene Complex 62b with 1-(*N*,*N*-Diethylamino)-1-propyne. To a solution of **62a** (0.1502 g, 0.5023 mmol) in 20 mL of benzene was added 1-(*N*,*N*-diethylamino)-1-propyne (0.180 g, 1.64 mmol). The solution was deoxygenated by the freeze–thaw method and stirred under an atmosphere of argon for 18 h at 25 °C. The mixture was concentrated and purified by preparatory thin-layer silica gel chromatography (1:1 hexane/ethyl acetate), which resulted in the sequential elution of two isomeric organometallic complexes, some organic compounds which had not incorporated any ketene features and which were not identified, and finally a 1.6:1 mixture of the very polar (R_f = 0.14) diastereomeric cyclobutenones **64** (45.4 mg, 0.182 mmol) as a clear pale yellow oil in 36% yield. The diastereomers could be enriched, but not completely separated. The following spectral data for the major and minor products were extracted from the spectrum of the mixture. Spectral data for **64** (major): ^{1}H NMR ($CDCl_3$) δ 1.19–1.31 (m, 10 H, $(CH_2)_2$, $2CH_3$), 1.56 (s, 3 H CH_3), 1.69 (s, 3 H CH_3), 1.85–2.45 (m, 3 H, CH, CH_2), 3.22–3.47 (m, 4 H, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 7.2, 13.8, 14.0, 19.4, 20.6, 26.6, 38.6, 42.9, 44.6, 50.4, 63.1, 108.0, 170.3, 187.8, 218.2. Spectral data for **64** (minor): ^{1}H NMR ($CDCl_3$) δ 1.19–1.31 (m, 10 H, $(CH_2)_2$, $2CH_3$), 1.42 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 1.85–2.24 (m, 3 H, CH, CH_2), 3.22–3.47 (m, 4 H, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 7.1, 13.5, 13.8, 19.8, 20.7, 27.0, 39.7, 42.8, 44.9, 52.3, 61.5, 106.9, 171.7, 187.7, 219.0. Spectral data for **64** (mixture): IR (thin film) 2970 m, 2935 m, 1741 s, 1631 shoulder, 1585 vs, 1444 s, 1381 m, 1293 m cm^{-1}; mass spectrum m/z (relative intensity) 250 M^+ + 1 (9), 249 M^+ (48), 206 (16), 192 (33), 179 (17), 178 (41), 165 (33), 164 (88), 151 (15), 150 (54), 136 (40), 122 (44), 100 (64), 72 (100); calcd for $C_{15}H_{23}O_2N$ m/z 249.1728, measd m/z 249.1735.

The diastereomeric organometallic complexes **65** were quantified in a separate reaction carried out under identical conditions between complex **62a** (0.074 g, 0.245 mmol) and 1-(*N*,*N*-diethylamino)-1-propyne (0.118 g, 1.06 mmol). The products were isolated by preparatory thin-layer silica gel chromatography (1:1 hexane ethyl acetate), which gave 7.7 mg (0.015 mmol) of the major isomer (R_f = 0.86) and 5.3 mg (0.011 mmol) of the minor isomer (R_f = 0.83) for a combined yield of 10%. The products have been tentatively identified as the complexed cyclopentenones **65**. Spectral data for **65** (major): R_f = 0.86; yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 6 H, J = 7.1 Hz, 2 CH_2CH_3), 1.08 (t, 6 H, J = 7.1 Hz, 2 CH_2CH_3), 1.20 (t, 3 H, J = 7.3 Hz, CH_2CH_3), 1.39 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.56 (s, 3 H, CH_3), 1.87 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.61–2.68 (m, 2 H, 2 NC*H*), 2.72–2.79 (m, 2 H, 2 NC*H*), 2.97–3.04 (m, 2 H, 2 NC*H*), 3.06–3.31 (m, 2 H, 2 NC*H*), 3.57–3.63 (m, 1 H, NC*H*), 3.66–3.73 (m, 1 H, NC*H*), 3.76–3.82 (m, 1 H, NC*H*), 4.25–4.29 (m, 1 H, NC*H*); ^{13}C NMR ($CDCl_3$) δ 9.6, 11.7, 12.8, 13.5, 13.9, 14.3, 22.4, 33.0, 45.3, 48.2, 49.0, 50.8, 83.6, 89.0, 106.9, 118.2, 179.6, 247.5, 250.2, 251.6; IR (thin film) 2970 m, 1936 vs, 1870 s, 1714 m, 1546 w, 1377 w cm^{-1}; mass spectrum m/z (relative intensity) 498 M^+ + 1 (15), 497 M^+ (39), 441 (22), 414 (36), 413 (100), 385 (11), 384 (21), 344 (33), 273 (29), 272 (25), 191 (18), 184 (11), 52 (17); calcd for $C_{25}H_{39}O_4N_3Cr$ m/z 497.2345, measd m/z 497.2337. Spectral data for **65** (minor): R_f = 0.83; yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, 6 H, J = 6.9 Hz, $2CH_2CH_3$), 1.14 (t, 6 H, J = 7.1 Hz, $2CH_2CH_3$), 1.23 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.42 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.45 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 3.04–3.26 (m, 8 H, $4NCH_2$), 3.56–3.64 (m, 1 H, NC*H*), 3.76–3.90 (m, 2 H, 2NC*H*), 4.16–4.24 (m, 1 H, NC*H*); ^{13}C NMR ($CDCl_3$) δ 8.6, 10.43, 13.3, 13.4, 15.26, 21.5, 29.7, 45.1, 48.4, 48.9, 50.5, 84.4, 88.2, 108.6, 115.12, 119.3, 178.7, 245.4, 248.0, and 250.9; IR (thin film) 2970 m, 1936 vs, 1870 s, 1714 m, 1546 w cm^{-1}; mass spectrum m/z (relative intensity) 498 (10, M^+ + 1), 497 (23, M^+), 441 (21), 414 (35), 413 (100), 389 (10), 373 (12), 360 (13), 303 (14), 302 (50), 244 (13), 85 (14), 71 (21), 57 (35); calcd for $C_{25}H_{39}O_4N_3Cr$ m/z 497.2345; measd m/z 497.2334.

Reactions of the Pyrrolidino-η^4-vinyl Ketene Complex 62b with Pyrrolidine. The ketene complex **62a** (0.1694 g, 0.563 mmol) was dissolved in 8 mL of THF and stirred under nitrogen while pyrrolidine (0.19 mL, 0.16 g, 2.3 mmol) was injected. After 30 min, a dilute aqueous solution of HCl was added until the solution was red to litmus paper. The resulting mixture was stirred in air for 15 min and then refluxed for 15 min. The solution was diluted with a 2:1 mixture of ether/dichloromethane and washed with 5% aqueous $NaHCO_3$, water, and brine. The organic extracts were dried over magnesium sulfate, filtered, and concentrated. The product was obtained as a 2.2:1 mixture of isomers, and elution from a silica gel column (1:2 hexane/ethyl acetate) gave the major isomer of **63** cleanly (28.6 mg) and a 1:1.2 mixture of major/minor isomers of **63** (37.0 mg) for a combined yield of 56%. Spectral data for **63** (major): R_f = 0.28; ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 3 H, J = 7.1 Hz, CH_3), 1.81–2.26 (m, 11 H, $(CH_2)_3$, $(CH_2)_2$, CH), 2.97 (pentet, 1 H, J = 7.1 Hz, C*H*CH_3), 3.39–3.43 (m, 3 H, NCH_2, NCH), 3.56–3.62 (m, 1 H, NCH); ^{13}C NMR ($CDCl_3$) δ 15.7, 20.6, 24.2, 26.1, 26.8, 37.3, 38.4, 45.6, 46.6, 52.5, 173.4 (CO_{amide}), 220.7 (CO_{ketone}); IR (thin film) 2968 s, 2935 m, 2874 m, 1734 vs, 1636 vs, 1448 m, 1430 m cm^{-1}; mass spectrum (GC/MS) m/z (relative intensity) 210 (4, M^+ + 1), 209 (32, M^+), 180 (15), 166 (47), 127 (100), 98 (38), 83 (13), 70 (34), 56 (21), 55 (57); calcd for $C_{12}H_{19}O_2N$ m/z 209.1415, measd m/z 209.1414. Spectral data for **63** (minor, extracted from spectra of mixture): R_f = 0.23; ^{1}H NMR ($CDCl_3$) δ 1.08 (d, 3 H, J = 7.0 Hz, CH_3), 1.64–2.35 (m, 10 H, $(CH_2)_3$, $(CH_2)_2$), 2.54 (m, 1 H, CH), 2.81 (pentet, 1 H, J = 7.0 CH), 3.36–3.57 (m, 4 H, 2 NCH_2); ^{13}C NMR ($CDCl_3$) δ 14.4, 20.5, 24.2, 26.0, 26.5, 37.5, 37.8, 45.8, 46.4, 51.8, 174.1 (CO_{amide}) 219.6 (CO_{ketone}); mass spectrum, recorded by GC/MS m/z (relative intensity) 210 (5, M^+ + 1), 109 (34, M^+), 180 (6), 166 (89), 138 (8), 127 (24), 111 (27), 98 (49), 83 (22), 70 (60), 56 (34), 55 (100).

Reactions of the Pyrrolidino-η^4-vinyl Ketene Complex 62b with Sodium Methoxide. Ketene complex **62a** (0.0887, 0.295 mmol) was dissolved in 1 mL of THF, and a 25% solution of sodium methoxide in methanol (0.2 mL) was injected. The brown solution turned red within 10 min. The reaction was quenched by the addition of a dilute aqueous HCl solution until the mixture was red to litmus paper. After 3 min the solution was diluted with ether and was washed with an aqueous ceric ammonium nitrate solution, a saturated aqueous $NaHCO_3$ solution, water, and brine. The ethereal extract was dried over magnesium sulfate, filtered through Celite, and concentrated to give a yellow oil. The ^{1}H NMR spectrum of this crude mixture indicated that product **66** was formed as a 1:1.5 mixture of diastereomers. Silica gel chromatography (1:1 hexane/ethyl acetate) gave **66** (R_f = 0.79, 31.9 mg, 0.188 mmol) as a mixture of inseparable diastereomers in 64% yield. Spectral data for **66** (major, extracted from spectra of mixture): ^{1}H NMR ($CDCl_3$) δ 1.26 (d, 3 H, J = 7.3 Hz, CH_3), 1.72–1.81 (m, 2 H, CH_2), 2.03–2.31 (m, 5 H, $(CH_2)_2$, CH), 3.06 (dq, 1 H, J = 4.3 Hz, J = 7.3 Hz), 3.65 (s, 3 H, OCH_3); mass spectrum (GC/MS), t_R = 2.09 min, m/z (relative intensity) 171 (7, M^+ + 1), 170 (70, M^+), 139 (53), 138 (35), 127 (29), 111 (64), 110 (38), 88 (39), 84 (53), 83 (70), 59 (33), 55 (100). Spectral data for **66** (minor, extracted from spectra of mixture): ^{1}H NMR ($CDCl_3$) δ 1.11 (d, 3 H, J = 7.1 Hz, CH_3), 1.58–1.73 (m, 1 H, HC*H*), 2.03–2.31 (m, 5 H, $(CH_2)_2$, CH), 2.53–2.62 (m, 1 H, C*H*CH_3), 2.80 (dq, 1 H, J = 13.1 Hz, J = 7.3 Hz) 3.71 (s, 3 H, OCH_3); mass spectrum (GC/MS); t_R = 2.19 min, m/z (relative intensity) 170 (26, M^+), 139 (20), 138 (15), 111 (34), 110 (22), 83 (48), 59 (30), 55 (100). Spectral data for **66** (mixture): IR (thin film) 2956 m, 2927 w, 2872 w, 1736 br s, 1458 w, 1203 m, 1159 m cm^{-1}. The methyl esters **66** were identical to the mixture of esters that is obtained from the hydrolysis of the methanol trapping product **48a**.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8821326). The National Institutes of Health has provided a predoctoral training grant for C.A.C. (GM 07183). Some of the mass spectral data were obtained at the Midwest Center for Mass Spectrometry with partial support by the National Science Foundation, Biology Division (Grant No. DIR 9017262). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program.