

# Three-Component Intramolecular Two-Alkyne Annulations of Fischer Carbene Complexes: New Strategies for Steroid Synthesis

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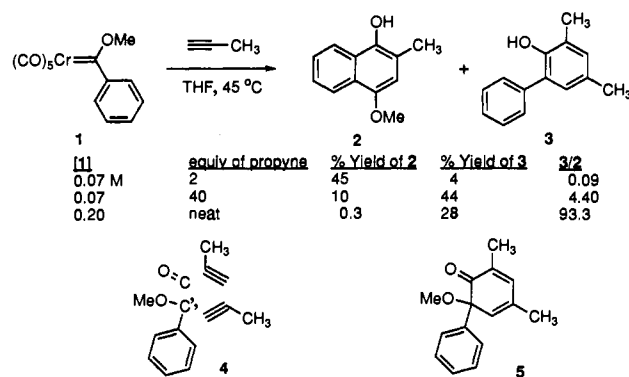
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**Abstract:** The two-alkyne annulations of a variety of chromium and tungsten carbene complexes are examined in which both of the alkynes are tethered to the carbene complex. The reactions of complexes in which the two alkynes and the first alkyne and the carbene carbon are connected by methylene groups were investigated for their potential in the construction of tricyclic phenols. This methodology was screened for a number of different ring sizes, and it was found that the efficiency of phenol formation depended on the nature of the metal, the solvent, and the sizes of the rings produced. In the reactions of chromium complexes, for certain ring sizes an unprecedented lactone product was also observed which resulted from the incorporation of the two alkynes as well as two carbon monoxide ligands from the metal. A new strategy for entry to the tetracyclic ring system of steroids is developed that involves a tandem coupling of a Diels-Alder reaction of carbene complexes with the double-intramolecular two-alkyne annulation. In a model system where the A and C rings are aromatic, the feasibility of this strategy was demonstrated in a reaction where all four rings of the steroid ring system can be generated in a one-pot reaction. In a second generation of this strategy, it was demonstrated that the tandem coupling of these reactions can also lead to the generation of nonaromatic steroidal ring systems.

The reactions of Fischer carbene complexes with alkynes is one of great mechanistic allure and considerable synthetic utility.<sup>1</sup> This reaction normally produces naphthols<sup>2</sup> (or phenols) of the type **2**, where a new benzene ring is generated with the incorporation of 1 equiv of the alkyne. It is this reaction that to date has been of the greatest synthetic value of all the reactions of Fischer carbene complexes that have been studied.<sup>3</sup> This is not the case for the two-alkyne annulation products, which initially were observed as side products in the normal benzannulation reaction.<sup>4</sup> It was found that the two-alkyne annulated phenols of the type **3** were most predominant from reactions with small alkynes such as 1-propyne, but in reactions with larger alkynes such as 1-pentyne, significantly reduced quantities of the two-alkyne phenols were observed. As illustrated by the reaction in Scheme 1, the two-alkyne phenols were favored by increased concentrations, but only to a point. This is probably due to competing oligomerization and polymerization of the alkyne at

Scheme 1



very high concentrations.<sup>5</sup> The formation of the two-alkyne phenol **3** is the result of the assembly of pieces indicated by **4** and is believed to involve the intermediacy of the cyclohexadienone **5**, which is reduced *in situ* by a chromium(0) species.<sup>6a</sup>

The selectivity for two-alkyne annulation products can be increased by a number of techniques, and, as indicated in Scheme 2, one of the more important strategies involves the utilization of intramolecular processes. This is illustrated for reactions that we have previously reported involving an intramolecular tethering of the two alkynes<sup>6a,b</sup> and an intramolecular tethering of the carbene complex to one of the alkynes.<sup>7</sup> In the case of the reaction

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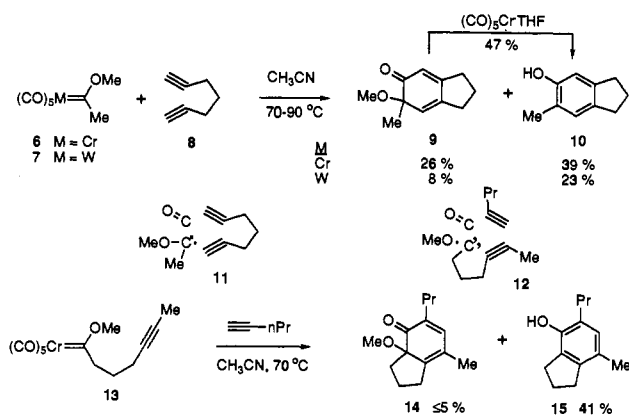
(1) For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Casey, C. P. *React. Interm.* **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, MA, 1989. (g) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (h) Harrington, P. J. *Transition Metals in Total Synthesis*; John Wiley: New York, 1990; pp 346-399. (i) McQuillin, F. J.; Parker, D. G.; Stephenson, G. R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge University Press: Cambridge, U.K., 1991. (j) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5.

(2) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

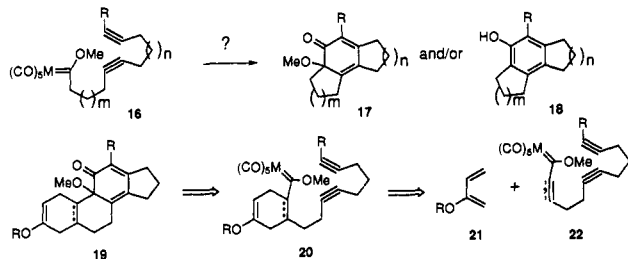
(3) For a list of citations to applications of this reaction in synthesis, see: Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102.

(4) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132.

## Scheme 2



## Scheme 3



of the carbene complexes **6** and **7** with 1,6-heptadiyne (**8**), the purported 6-methoxycyclohexadienone intermediate in these reactions was isolated. Furthermore, it was demonstrated that the dienone product **9** could be reduced to the two-alkyne phenol **10** by pentacarbonyl(THF)chromium, thereby providing support for the *in situ* reduction of these species by a chromium(0) intermediate produced during the course of the reaction.<sup>6a</sup> In the intramolecular reaction of the alkynylcarbene complex **13**, the cyclohexadienone product **14** was not detected, but rather only the two-alkyne phenol product **15** was isolated.<sup>7</sup> The two-alkyne phenols **10** and **15** are the result of the overall assembly of pieces indicated by **11** and **12** in Scheme 2.

Whereas the stoichiometry of the two-alkyne annulation involves 2equiv of the alkyne and 1equiv of the carbene complex, the process itself involves an overall [2 + 2 + 1 + 1] coupling reaction of the two-alkynes, the carbene ligand, and a carbon monoxide ligand, presumably occurring in a sequential fashion in the coordination sphere of the metal. The success of the studies on the two possible modes of two-component intramolecular processes, illustrated in Scheme 2, allowed a consideration of developing the three-component intramolecular version of the two-alkyne annulation indicated in Scheme 3. This reaction would have the feature of producing tricyclic compounds of the type **17** or **18**, and, in addition, if coupled with a Diels–Alder reaction of a carbene complex of the type **22**,<sup>8</sup> would provide for an entirely new strategy for steroid synthesis. In this report we describe the three-component intramolecular two-alkyne annulations of diynylcarbene complexes of the type **16**. These reactions were found to produce a number of products, including an unprecedented lactone product resulting from the incorporation of two alkynes and two carbon monoxide ligands. The selectivity for the two-alkyne phenol product **18** (or **17**) is a function of the metal, the solvent, and the ring sizes. We also report our initial studies on the tandem Diels–Alder/double-intramolecular two-alkyne an-

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Table 1. Preparation of Alkyl-Tethered Chromium Carbene Complexes

The reaction scheme shows the preparation of alkyl-tethered chromium carbene complexes. It involves the reaction of an alcohol (with a diynyl group) with a methyl(methoxy)carbene complex (CO)<sub>5</sub>Cr(OCH<sub>3</sub>)CH<sub>2</sub>OMe in the presence of Ti<sub>2</sub>O<sub>3</sub>, Et<sub>3</sub>N, and CH<sub>2</sub>Cl<sub>2</sub> at 0 °C for 2 h, followed by reaction with (CO)<sub>5</sub>Cr(OCH<sub>3</sub>)CH<sub>2</sub>OMe in THF at 0 °C for 0.5 h. The resulting carbene complex has an alkyl chain of length m and a diynyl group of length n.

alcohol	m	n	carbene complex	yield of carbene complex (%)	yield of dialkylated carbene complex (%)
<b>34</b>	1	0	<b>47</b>	38	17
<b>35</b>	1	1	<b>49</b>	35	25
<b>36</b>	1	2	<b>51</b>	49	18
<b>37</b>	2	1	<b>53</b>	51	ND <sup>a</sup>
<b>38</b>	2	2	<b>55</b>	39	ND <sup>a</sup>

<sup>a</sup> Not determined.

annulation process for steroid synthesis for both diynyl- and triynylcarbene complexes of the type **22**.<sup>9</sup>

## Preparation of Diynylcarbene Complexes of the Type 16

The diynyl chromium complexes were prepared by alkylation of the anion of the methyl(methoxy)carbene complex with the appropriate diynyl triflate.<sup>10</sup> As indicated in Table 1, these triflates were generated *in situ* from their corresponding alcohols, whose preparations are described in the Experimental Section. The moderate yields observed in the preparation of these complexes is a function of the fact that dialkylation was a serious competing side reaction in these preparations. Dialkylation was observed for all of the entries in Table 1, but the yield of the dialkylation product was not determined for entries 4 and 5. All of the desired monoalkylated complexes, which were quite stable and could be handled in air, were obtained as orange oils after separation from the dialkylated products by silica gel chromatography.

The diynyl tungsten complexes also could be prepared by alkylation of diynyl triflates in the same manner as were the chromium complexes; however, dialkylation was an even more serious side reaction for tungsten, resulting in reduced yields. In addition, the separation of these complexes from the unreacted methyl(methoxy)pentacarbonyltungsten carbene complex and unreacted diynyl triflates proved to be a difficult problem. Thus the tungsten complexes were instead prepared directly from tungsten hexacarbonyl and the corresponding diynyl lithiums, which were generated from the diynyl iodides shown in Table 2 by the method of Bailey and Negishi.<sup>11</sup> The procedures for the preparation of the diynyl iodides are described in the Experimental Section. No effort was made to optimize the reactions in Table 2, which were usually accompanied by the formation of products resulting from the reduction of the diynyl iodide. The source of this side reaction was not identified. The separation of the desired diynyl tungsten carbene complexes from the diacetylenic hydrocarbon side products on silica gel was straightforward and gave the tungsten complexes indicated in Table 2 as orange oils which were more stable than their chromium counterparts.

## Double-Intramolecular Two-Alkyne Annulation

Our initial studies were carried out on the carbene complexes **49** and **50**, which upon thermolysis gave the phenol **58** along with the nonreduced cyclized cyclohexadienone **62** (Table 3). This system was also the subject of attempts to optimize these products by variation of solvent. The total yield of the annulation products

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(11) (a) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404. (b) Negishi, I.; Swanson, D. R.; Rousset, C. J. *J. Org. Chem.* **1990**, *55*, 5406.

**Table 2.** Preparation of Alkyl-Tethered Tungsten Carbene Complexes

alkyl iodide	<i>m</i>	<i>n</i>	<i>o</i>	carbene complex	yield of carbene complex (%)
<b>42</b>	1	0	2	<b>48</b>	44
<b>43</b>	1	1	2	<b>50</b>	57
<b>44</b>	1	2	2	<b>52</b>	31
<b>45</b>	2	1	3	<b>54</b>	37
<b>46</b>	2	2	3	<b>56</b>	44

**Table 3.** Double Intramolecular Two-Alkyne Annulation of Diynyl Carbene Complexes<sup>a</sup>

Carbene Complex	solvent	Phenol Product	Other products
 <b>47</b> M = Cr <b>48</b> M = W	benzene benzene CH <sub>3</sub> CN/CO <sup>b</sup>	 <b>57</b> 30% <b>57</b> 48%	 <b>61</b> 41%
 <b>49</b> M = Cr <b>50</b> M = W	benzene Bu <sub>2</sub> O THF CH <sub>3</sub> CN DMF CH <sub>3</sub> CN/CO <sup>b</sup>	 <b>58</b> 57% <b>58</b> 50% <b>58</b> 61% <b>58</b> 31% <b>58</b> 10% <b>58</b> 61%	 <b>62</b> 5% <b>62</b> 7% <b>62</b> 41% <b>62</b> 16%
 <b>51</b> M = Cr <b>52</b> M = W	benzene CH <sub>3</sub> CN/CO <sup>b</sup>	 <b>59</b> 33% <b>59</b> 38%	
 <b>53</b> M = Cr <b>54</b> M = W	benzene CH <sub>3</sub> CN/CO <sup>b</sup>	 <b>60</b> 24% <b>60</b> 36%	 <b>63</b> 19%
 <b>55</b> M = Cr <b>56</b> M = W	benzene CH <sub>3</sub> CN/CO <sup>b</sup>		 <b>64</b> 39%

<sup>a</sup> All reactions were carried out at 0.005 M in carbene complex and required 16–24 h. Reactions of the chromium complexes were at 70 °C and those of tungsten at 110 °C. <sup>b</sup> Reaction mixtures were sealed in a reaction flask<sup>19</sup> at 25 °C under 1 atm of CO and heated to 110 °C.

(**58** + **62**) increases with increasing coordinating ability of the solvent up to acetonitrile and then drops off in DMF. The ratio of the nonreduced product **62** to the reduced product **58** increases with increasing coordinating ability of the solvent. This result was anticipated from previous studies and is believed to be due to the ability of the solvent to coordinate to reduced metal species and prevent reduction of **62**.<sup>6a</sup>

The use of two methylene spacers between the diyne function permits the generation of the benzocyclobutene **57** from the tungsten complex **48**.<sup>12</sup> The yield of this product could be increased by 50% by a change in solvent from benzene to acetonitrile and by a change in the atmosphere from argon to carbon monoxide. The chromium complex **47** did not give any detectable amount of the benzocyclobutene **57** but rather gave the unexpected lactone product **61**. This is an unprecedented product type from the reactions of carbene complexes and alkynes and was assigned the indicated structure on the basis of its spectral data. This is the second example of a product from the reactions of carbene complexes and alkynes that is the result of incorporation of two molecules of the alkyne and two carbon monoxide ligands.<sup>7b</sup>

The formation of five-membered rings fused to the central phenol ring is more efficient than the formation of six-membered rings, and this is true whether the six-membered ring is formed in the first cyclization (phenol **60** versus phenol **58**) or in the second cyclization (phenol **59** versus **58**). The low yields in the formation of phenol **60** from the thermolysis of both complexes **53** and **54** were disappointing since phenol **60** was to serve as a model for the generation of the BCD ring system of the steroid skeleton. In the case of the chromium complex **55**, designed to generate two six-membered rings fused to the central phenol, the reaction pathway is completely diverted from the two-alkyne phenol to give the lactone **64**. The thermolysis of the analogous tungsten complex **56** produced a complex mixture of products, none of which was formed in an amount significant to isolate.

### Mechanistic Considerations

An explanation of these results can be put forth upon consideration of the mechanistic possibilities outlined in Scheme 4.<sup>13</sup> In the following discussion, we will first describe the results from the reactions of the chromium complexes since changes in the product distributions were observed for chromium complexes but not for those of tungsten.

After initial dissociation of a CO ligand, the next step in the formation of the products observed in these reactions is undoubtedly the insertion of the alkyne closest to the carbene carbon in **16** to give the  $\eta^1, \eta^2$ -vinylcarbene complexed intermediate **65**. It is proposed that one of the main factors in determining the distribution between the phenol and lactone products is the relative amount of reaction flux occurring through the two conformations of the alkyne-chelated intermediate **66a** and **66b**. For reasons of least motion, the coupling of the alkyne and the carbene ligand in **66a** with the perpendicular arrangement of the two ligands to give **72** is expected to be much more facile than the same coupling from the parallel arrangement **66b** to give **72**. This issue has been addressed theoretically in model systems, and the finding was that both processes should be allowed by symmetry.<sup>15</sup> Furthermore, whereas it was found that the coupling in a parallel arrangement (**66b**) is predicted to have a very high barrier, the coupling in the perpendicular arrangement (**66a**) is predicted to occur with essentially no barrier.<sup>15</sup> In addition, it was shown by calculations that the perpendicular arrangement is lower in energy by ~5 kcal than the parallel arrangement.<sup>15</sup> In synergism with the expectation that the coupling product **72** be formed from **66a** and not **66b** is the anticipation that the CO coupling product **74** be formed from **66b** and not **66a**. Whereas the coupling of the

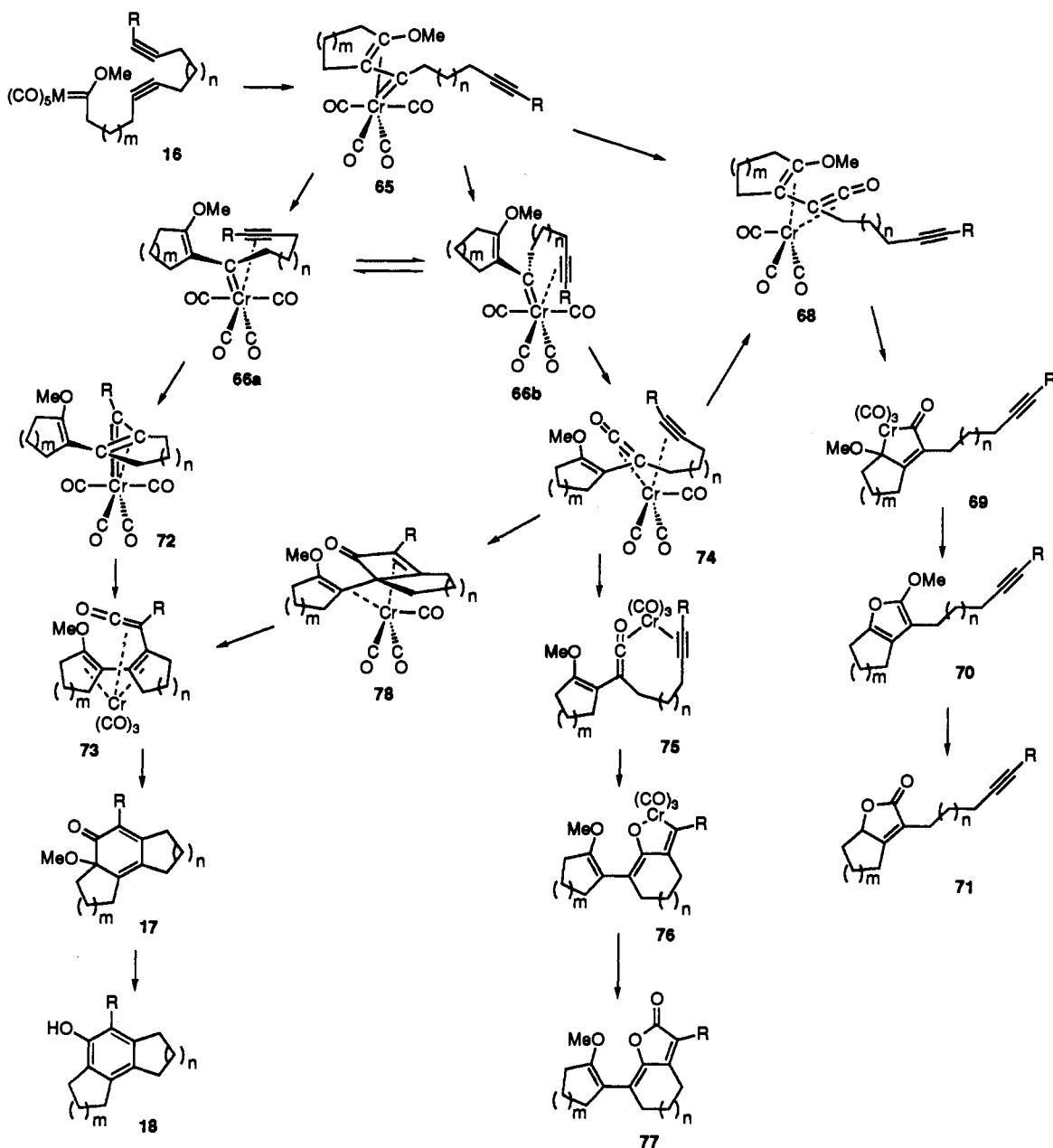
(12) For the chemistry of benzocyclobutenes, see: (a) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967. (b) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471. (c) Thummel, R. P. *Acc. Chem. Res.* **1980**, *13*, 70. (d) For citations to the recent literature, see: Kündig, E. P.; Bernardinelli, G.; Leresche, J. *J. Chem. Soc., Chem. Commun.* **1991**, 1713.

(13) For recent discussions on the mechanisms of the reactions of carbene complexes with alkynes, see refs 3 and 14.

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Scheme 4



carbene ligand with a carbon monoxide ligand in **66b** is geometrically constrained to occur with one of two COs that are mutually trans to give the ketene complex **74** with a facial arrangement of the remaining CO ligands, the same coupling in **66a** is constrained to occur with the CO ligand that would give a ketene complex that has a meridional arrangement of the remaining CO ligands (not shown). Thus, the expectation is that, due to the trans effect of the carbonyls in **66b**, the CO insertion step should be more energetically feasible for **66b** than for **66a**.

The expected reactivities of the two conformations of the alkyne chelate complexes **66a** and **66b** discussed above can be used to formulate an explanation for the different product distributions seen from the reactions of the chromium complexes **47** and **49**. The reasonable assumption must be made that, for energetic reasons, the perpendicular conformation **66a** can be reached easily with three methylene spacers between the two alkynes but not as easily with two methylene spacers. If this condition pertains, then the reaction of complex **47** would be expected to give more lactone (**77** in Scheme 4) than complex **49**, as is observed. What

remains unexplained at this point is why there is some lactone product formed from intermediate **66** when  $m = 2$  but not when  $m = 1$  (complex **53** versus **49**).

The lactone product **64** (**71** in Scheme 4) is likely the result of hydrolysis of the furan product **70**, which is a structural type that is well preceded from the reactions of carbene complexes with alkynes.<sup>16</sup> It is obvious that this product occurs as the result of the failure to incorporate the second alkyne and thus is generated from the vinylketene complex **68**. One could argue that the observation of this lactone product from the complex **55** but not from **47**, **49**, or **53** is the result of a favored CO insertion in **65** relative to alkyne coordination when  $n = 2$ . An explanation is not obvious for the more subtle effect of the value of  $m$  on CO insertion versus alkyne coordination in **65** when  $n = 2$  (complex **51** versus **55**).

In all cases, the reactions of the tungsten complexes in Table 3 give only phenol products. This can be explained by the well

(16) (a) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177. (b) McCallum, J. S.; Kung, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

established propensity of tungsten carbene complexes to give fewer CO-inserted products than chromium carbene complexes.<sup>3,17</sup> Thus, if in all of the branch points in Scheme 4 that involve CO versus non-CO insertion processes the non-CO insertion process wins out, then the phenol **18** would be expected to be the only product. There is, however, an additional pathway to the phenol **18** that has not been considered yet: the pathway via the cyclobutenone intermediate **78**. In this mechanism, the branch point would not be at the alkyne chelates **66** but rather at the ketene complex **74**. By this mechanism, one could explain the difference between the chromium complexes **47** and **49** by the strain energy in the formation of two fused four-membered rings in the formation **78** from **47**. According to this pathway, complex **49** ( $n = 1$ ) gives only the phenol product **58**, but for complex **47**, where  $n = 0$ , the lactone product **61** (**77** in Scheme 4) is formed as the result of the high strain energy in **78** when  $n = 0$ . However, we tentatively rule out the pathway involving the intermediate **78** since the tungsten complex **48** can produce the benzocyclobutene **57**. We see no reason why the chromium complex **78** with  $n = 0$  could not be formed if the tungsten analog of **78** with  $n = 0$  is formed. Furthermore, we see no reason why alternative reaction pathways from **74** for tungsten should be less facile than those for chromium. While there are no such data for formation of lactones of the type **77**, it is known that the formation of furans of the type **70** is more facile for tungsten than for chromium.<sup>3</sup> Finally, as will be seen later (Scheme 13), we have observed the formation of a furanone product of the type **71** (Scheme 4) from the reaction of a tungsten complex.

Lastly, acetonitrile as solvent and carbon monoxide as the atmosphere for the reactions of tungsten complexes in Table 3 were chosen to optimize the phenol product **18**. By replacing chromium with tungsten, it was expected that CO insertion to give **74** would be slowed relative to alkyne-carbene coupling to give **72**. However, a CO insertion is still required from **72** to **74**, and thus the conditions of solvent and atmosphere were chosen to help maximize this step which is not at a branch point.

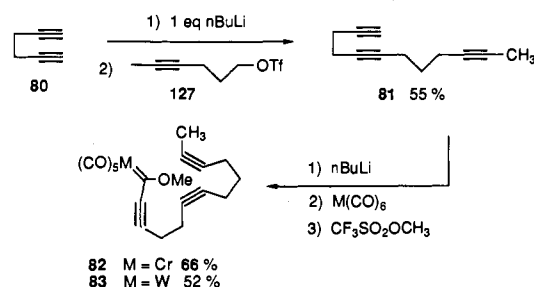
#### Steroid Ring System from a Triynylcarbene Complex

Subsequent to the demonstration of the viability of the three-component intramolecular two-alkyne annulations of diynylcarbene complexes described above, we began to pursue their application in an approach to the steroid ring system. Our first efforts were directed to the evaluation of triynylcarbene complexes of the general type **22** to be used in an overall strategy that involves a tandem Diels-Alder/two-alkyne annulation of these complexes as outlined in Scheme 3. The specific complexes **82** and **83** were prepared in two steps from the commercially available 1,5-hexadiyne (**80**) and 1-hex-4-ynyl triflate. Generation of the monoanion of **80** by addition of 1 equiv of butyllithium followed by 1 equiv of 1-hex-4-ynyl triflate gave a 55% yield of the desired monoalkylated product **81** along with an 18% yield of the dialkylated product, which can be easily separated by distillation. The chromium and tungsten triynylcarbene complexes can both be prepared from the triene **81** by the standard Fischer procedure as indicated in Scheme 5.

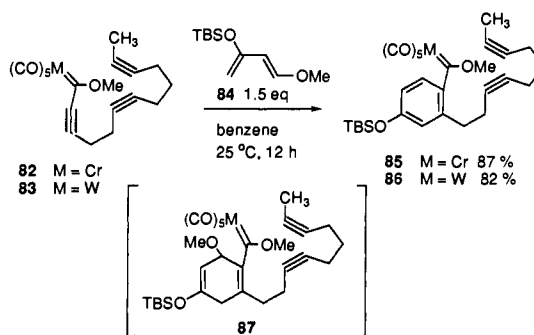
It has been well established that the dienophilicity of carbon-carbon double bonds and triple bonds is greatly enhanced when the bonds are in conjugation with a Fischer carbene complex.<sup>8</sup> In cases where kinetics have been measured, it has been found that a carbene complex can enhance the dienophilicity of a double bond by a factor of  $2 \times 10^4$  over that of an ester group. Thus, in considering the reactions of the triynyl complexes **82** and **83** with dienes, it is not expected that the two nonactivated diynes would compete with the conjugated alkyne.

The chromium complex **82** would not react with 2,3-dimethylbutadiene or 2-(trimethylsilyloxy)butadiene at room temperature, and at elevated temperatures these reactions produced complex

#### Scheme 5



#### Scheme 6



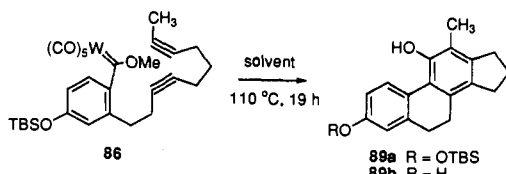
mixtures of products which were not analyzed. The chromium complex **82** reacts with Danishefsky's diene **84** at room temperature in 12 h and after purification on silica gel the aromatized cycloadduct **85** was obtained in 87% yield (Scheme 6). A second product was observed from this reaction by TLC which was more polar than **85** but which was quickly converted to the aromatized product when exposed to silica gel. It is suspected that the more polar compound was the expected cycloadduct **87**, but its identity was not confirmed. The chromium complexes **85** and **82** are both red oils, but the cycloadduct **85** is more stable than the triynyl complex **82**, which slowly polymerizes. The tungsten complex **86** can be prepared in an almost identical fashion in 82% yield.

In consideration of the thermolysis of the aryl diynyl chromium carbene complex **85**, there is reason to expect that this two-alkyne annulation may be more efficient than the two-alkyne annulation of the simple diynyl complex **53** (Table 3), which was a model system for the construction of the BCD steroid ring system but which was disappointing in terms of the low yields of the phenol product **60**. Although there are four atoms between the carbene carbon and the first alkyne in both the complexes **85** and **53**, intramolecular incorporation of the alkyne may be expected to be more favorable for complex **85** for entropy reasons since two of the connecting carbons in **85** are  $sp^2$  and since the carbene carbon and the alkyne function are cis-disposed relative to these two  $sp^2$  carbons. This expectation presumes that the mechanism of the three-component two-alkyne annulation begins with a first-order process involving a dissociation of a carbon monoxide ligand from the metal center and then a competition between inter- and intramolecular reactions with an alkyne function. This is supported by the effects of concentration on the reaction of complex **86** (Table 4), where the total yield of **89** drops off with increasing concentration (entries 4 and 5). These types of effects have been seen in other two-alkyne annulations<sup>5-7</sup> and presumably lead to oligo- or polymeric materials that are not mobile on silica gel and are not isolated from these reactions.<sup>18</sup>

The thermolysis of **85** in benzene gives the phenol **89a** in 30% yield and the lactone **90** in 23% yield (Scheme 7). This result is very similar to the thermolysis of **53**, where the same two types of products are formed in approximately the same ratio and only

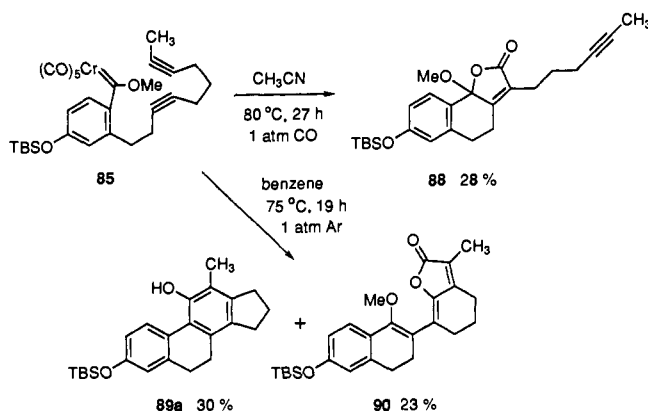
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Table 4. Two-Alkyne Annulation of Tungsten Complex **86**

solvent	conc (M)	89a:89b	yield 89 (%)
heptane	0.005	100:0	48
benzene	0.005	100:0	51
THF	0.005	100:0	53
CH <sub>3</sub> CN	0.005	100:0	63
CH <sub>3</sub> CN	0.05	100:0	50
CH <sub>3</sub> CN/CO	0.005	60:40	78

Scheme 7



a slight higher total mass balance for **85**. Surprisingly, the thermolysis of **85** in acetonitrile gives none of the phenol **89a**, and the only major product that is silica gel mobile is the methoxyfuranone **88**, which is a product that was not seen in any of the model reactions that we have studied (Table 3). This was surprising since the optimal solvent for the formation of the normal two-alkyne annulation products (phenol plus dienone) for the complex **49** was acetonitrile (Table 3). The methoxyfuranone product **88** is related to the furanone **64** observed from the thermolysis of the chromium complex **55** (Table 3) by the fact that, in each case, the first but not the second alkyne is incorporated. While it is reasonable that the furanone **64** resulted from the hydrolysis of the furan **70** (Scheme 4), it is clear that the 5-methoxyfuranone **88** could not. Two likely sources of the 5-methoxyfuranone product **88** are indicated in Scheme 8. The vinylketene intermediate **98** could undergo  $\eta^4$  to  $\eta^2$ -tautomerization to the metallacycle **99** and then reductive elimination to give the cyclobutenone **100**. It has been demonstrated that cyclobutenone formation is favored in coordinating solvents such as acetonitrile.<sup>19</sup> While cyclobutenones from these reactions are known to undergo oxidation to 5-methoxyfuranones in the presence of metal oxidants,<sup>19</sup> we have no way of knowing whether the cyclobutenone **100** can be oxidized to the 5-methoxyfuranones **88** by air. An alternate possibility is that the vinylketene complex **98** is formed as a primary product of the reaction and when the reaction mixture is exposed to air during the workup it is oxidized to the furanone **88**. It has been shown that an isolable vinylketene complex of cobalt can be oxidized to a 5-methoxyfuranone.<sup>20</sup> It is to be expected that the vinylketene complex **98** (Scheme 8) would be more stable than the vinylketene complex **68** (Scheme 4) since **98** has a *p*-(silyloxy)phenyl substituent in conjugation with the vinylketene. It has been shown that replacement of the

methoxy group in the starting carbene complex with a dimethylamino group in reactions related to the those described here is sufficient to lead to an isolable vinylketene complex.<sup>7c,d</sup> An X-ray structure revealed that the metal in these complexes is stabilized by coordination to the nitrogen, and thus the vinylketene complex **98** may also be stabilized by coordination to the methoxyl where the metal is coordinated to the vinylketene in an  $\eta^5$ -manner.

In an effort to change the partition between the phenol product **89a** and the lactone product **90** in favor of the phenol product, the dimethylamino complex **101** was prepared by treatment of the methoxy complex **85** with dimethylamine, as indicated in Scheme 9. It is known that amino complexes give fewer CO-inserted products than methoxyl complexes.<sup>21</sup> In the present reactions, it is thought, as indicated in Scheme 4, that the partition between the phenol and lactone products is determined by the relative rates of CO insertion in intermediate **66b** and alkyne insertion in intermediate **66a**. Thus it might be expected that the amino group in amino analogs of these intermediates disfavors CO insertion relative to alkyne insertion. The thermolysis of the amino complex **101** required a much higher temperature than that of the methoxyl complexes, which was anticipated on the basis of the expected higher thermal requirement for CO dissociation from an amino complex than from a methoxyl complex. Although this reaction exclusively gave the phenol **89a**, it cannot be determined whether the amino group had the anticipated effect on the partition between intermediates **66a** and **66b** (Scheme 4), since the mass balance dropped precipitously from that of the methoxyl complex **85**. The workup with reduced titanium chloride is employed to ensure that any unreduced aminocyclohexadienone product is reduced to the phenol **89a**.<sup>7c,d</sup>

Although switching the heteroatom stabilizing group in carbene complex **85** from alkoxy to amino did not lead to efficient formation of the phenol **89a**, switching the metal from chromium to tungsten did. It is known<sup>3,17</sup> that the reactions of tungsten carbene complexes with alkynes give fewer CO-inserted products than those of chromium, and thus it was not a surprise that the thermolysis of the tungsten complex **86**, like those of all of the tungsten complexes in this study, is chemoselective for the formation of the phenol product **89**. The thermolysis of the tungsten complex **86** required a higher temperature (110 °C) than that of the chromium complex (80 °C), in keeping with the known higher thermal barrier to dissociation of CO ligands in tungsten carbene complexes than in chromium carbene complexes.<sup>22</sup> Since it was found that the outcome of the thermolysis of the chromium complex **85** was highly dependent on the nature of the solvent, a solvent study was carried out for the tungsten complex **86**, and the results are given in Table 4. No surprises were found, and all solvents were chemoselective for phenol formation. No significant amount of any other product such as lactones or furanones was detected in these reactions. The optimal conditions were in acetonitrile with an atmosphere of carbon monoxide and were the same as those for the thermolysis of tungsten complex **54** (Scheme 4). It should also be noted that the 78% yield of phenol **89** from the thermolysis of **86** is more than double the yield of the thermolysis of the model system for the tungsten complex **54**, which gives the phenol **60** in 36% yield under exactly identical conditions. This may be due to the effect of entropy that was anticipated (but not observed) for the reaction of the chromium complex **85** discussed above. Upon dissociation of a CO ligand, it can be expected that an intramolecular reaction with an alkyne would be more favorable than an intermolecular reaction with an alkyne more so for complex **86** than for complex **54**. This is consistent with the observation that the efficiency of the thermolysis of complex **86** is concentration dependent, with the yield of phenol **89** dropping from 63% to 50% when the concentration is raised from 0.005 to 0.05 M.

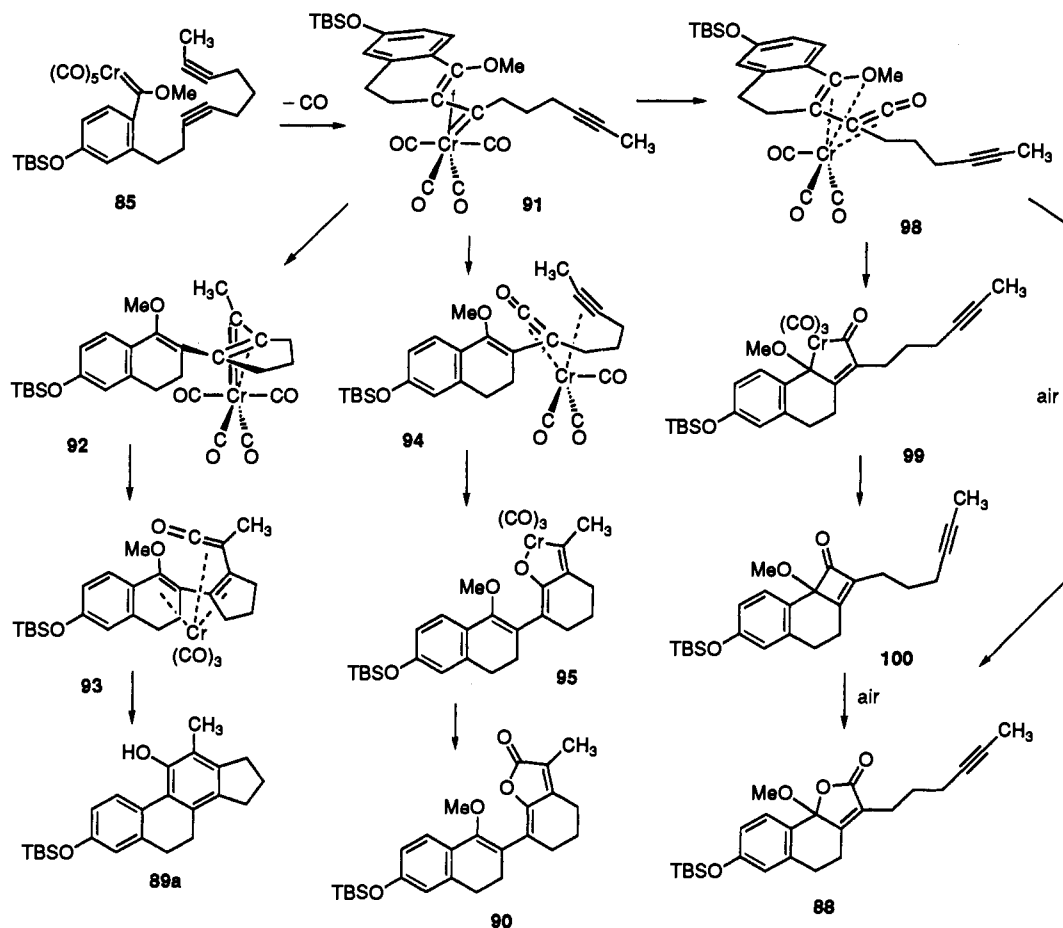
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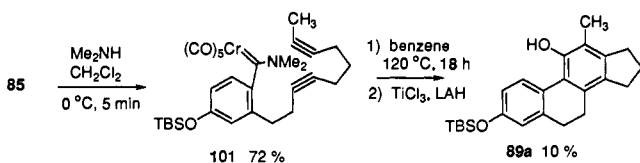
(21) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915.

(22) Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87.

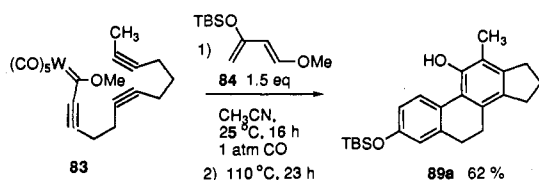
Scheme 8



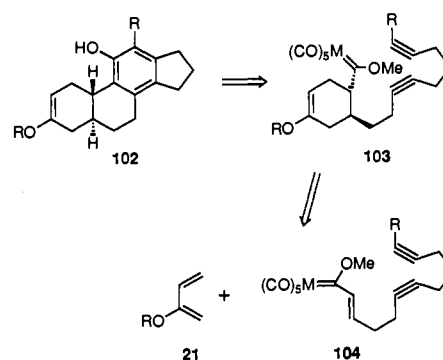
Scheme 9



Scheme 10



Scheme 11



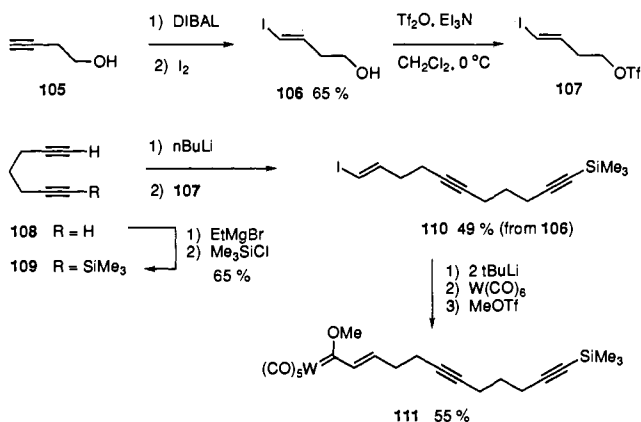
### Second Generation Approach to the Steroid Ring System

Since the Diels–Alder reaction of tungsten triynylcarbene complex **83** with Danishefsky's diene is faster than the intramolecular two-alkyne annulation of the cycloadduct **86**, the possibility exists of carrying out both reactions in a single flask. After the triyne complex **83** (0.05 M) was reacted with 1.5 equiv of diene **84** for 16 h at room temperature in acetonitrile and under a carbon monoxide atmosphere, the reaction mixture was diluted 10-fold with acetonitrile and heated at  $110^\circ\text{C}$  for 23 h to give a 62% yield of the phenol **89a** (Scheme 10). This is close to the overall yield of 67% for the two steps carried out separately. This process adds a new entry for strategies for the synthesis of steroids in the class  $\text{O} \Rightarrow \text{ABCD}$ .<sup>23</sup>

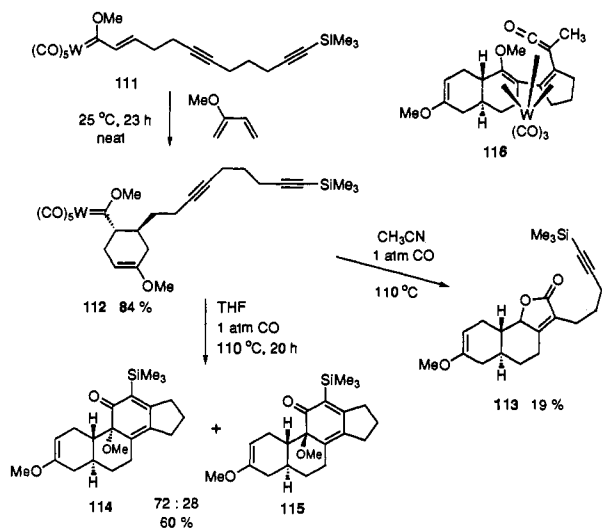
The success of the tandem Diels–Alder/two-alkyne annulation of the triynylcarbene complex **83** in a one-pot construction of all four rings of the steroid ring system demonstrated the feasibility of this approach and furthermore revealed that the arene ring in the Diels–Alder adduct **86** favorably assists the two-alkyne annulation as judged by the much lower yields obtained from the thermolysis of the conformationally unconstrained complex **54** (Table 3). However, it is not clear whether the arene ring in **86** assists the annulation for entropic or electronic reasons. In addition, from the synthetic point of view, this approach is less than ideal since the entire ring system of phenol **89** is devoid of chiral centers. In an effort to address both of these issues, we decided to pursue a more advanced version of this general strategy that is outlined in Scheme 11. This required a Diels–Alder

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Scheme 12



Scheme 13



reaction of a *trans*-substituted vinylcarbene complex (**104**) with a 2-alkoxybutadiene which we had previously found to be quite facile.<sup>8a</sup>

The requisite diynylcarbene complex **111** for this study was prepared by the standard Fischer procedure in 55% yield from the diynyl iodide **110** (Scheme 12). This iodide in turn was prepared from the commercially available 1,6-heptydiyne and 3-butyne-1-ol. *trans*-4-Iodo-3-buten-1-ol<sup>24</sup> was generated cleanly as a single olefin isomer in a single step from 3-butyne-1-ol by hydroalumination<sup>25</sup> with DIBAL followed by iodination. The desired alcohol was produced together with a small amount of the overreduced 4-iodobutan-1-ol, but these alcohols were not separated and were taken on as a mixture of their triflates. This mixture of triflates was filtered through a short plug of silica gel and directly treated with the anion of the monosilylated diyne **109** to give the diynyl iodide **110** in 49% overall yield from *trans*-4-iodo-3-buten-1-ol (**106**).

The Diels–Alder reaction of carbene complex **111** with 2-methoxybutadiene (Scheme 13) proceeded at room temperature to give the adduct **112**, which was isolated in 84% yield after purification by silica gel chromatography. The thermolysis of complex **112** in acetonitrile gave the lactone product **113** as the major mobile component on silica gel in 19% yield. Furanone products are most likely the result of the hydrolysis of furans of the type **70** (Scheme 4), and the only other furanone observed

in this work was from the reaction of the chromium complex **55**. The result was not expected on the basis of any of the observations made in this study. In every case that was examined in the present work, the two-alkyne annulation of a tungsten complex always gave a higher yield of phenol in acetonitrile than in any other solvent. This result is further distinguished by the fact that it is the only thermolysis of a tungsten complex that gave anything but a phenol product. The low mass balance in the thermolysis of **112** in acetonitrile is not likely due to unfavorable competition between inter- and intramolecular alkyne insertion after initial CO loss from **112** since the thermolysis of **112** in THF gave a 60% yield of the desired two-alkyne annulation products **114** and **115**. It is interesting to note that only cyclohexadienone products are isolated from this reaction and none of the phenol of the type **102**, which would have resulted from a reduction of the methoxyl group  $\alpha$  to the carbonyl. This difference from the reaction of the aryl complex **85** is most likely due to the fact that the methoxyl in the cyclohexadienone intermediate **94** (Scheme 8) is benzylic as well as  $\alpha$  to the carbonyl. The cyclohexadienone product was produced as 72:28 mixture of diastereomers, and the stereochemistry of the major product **114** was determined by an X-ray diffraction study. The results of this study can be found in the supplementary material. The source of the stereoselectivity that leads to the preferential formation of the dienone **114** is not understood at this time. One possible explanation is that there is a preferential formation of the intermediate vinylketene complex **116** in which a tungsten tricarbonyl group is bound to the face of the vinylketene that is syn to the hydrogen on the sp<sup>3</sup> carbon adjacent to the methoxyl group. Further experiments are planned to identify the factors that contribute to selective formation of **114** and hopefully to identify methodology that will lead to a stereocontrolled entry to these tetracyclic systems.

The initial goals of this work were (1) to develop a three-component intramolecular version of the two-alkyne annulation for the preparation of tricyclic phenols and (2) if step 1 was successful, to couple the three-component intramolecular two-alkyne annulation and a Diels–Alder reaction of a Fischer carbene complex in a tandem sequence for the overall generation of the tetracyclic ring system of steroids. Both of these goals have been realized, and at the same time a number of interesting issues associated with the reactions of carbene complexes and alkynes have been raised. Among the more interesting issues are (1) whether the different conformers of the alkyne complexed intermediates **66a** and **66b** are really related to the partition between phenol **18** and lactone **77** and (2) the source of the stereoselectivity in the preferential formation of **114** over **115**. In addition to attention to these issues, future efforts will be directed toward the development of synthetic intermediates of the type **114** and **115** for steroid syntheses and the development of asymmetric methods for the preparation of these and related intermediates.

## Experimental Section

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran, ether, and benzene were distilled from benzophenone ketyl under nitrogen. Dichloromethane and hexane were distilled from calcium hydride. Proton NMR data were obtained on either a University of Chicago-built DS-1000 500-MHz instrument or a QE-300 instrument. Carbon-13 spectral data were obtained on the QE-300 instrument at 75 MHz. Infrared spectra were taken on a Nicolet 20SX FTIR. Low-resolution mass spectra were recorded on a Finnigan 1015 mass spectrometer. High-resolution mass spectra were recorded on a VG 70-250 instrument or obtained from the Midwest Center for Mass Spectrometry in Lincoln, NE. Elemental analyses were done by Galbraith Laboratories in Knoxville, TN. 3-Butyn-1-ol, 4-pentyn-1-ol, 5-hexyn-1-ol, and 3-pentyn-1-ol (**120**) were purchased

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(25) (a) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* 1967, 2753. (b) Reich, H. J.; Eisenhart, E. K.; Kelly, M. J. *J. Am. Chem. Soc.* 1986, 108, 7791.



Table 5. Synthesis of Diynols 34–41

<i>m</i>	<i>n</i>	ynol	ynyl ether, M = H	diynol	yield of diynol from 120–122 (%)
1	0	120	123	34	36
1	1	121	123	35	52
1	2	122	123	36	55
2	1	121	124	37	74
2	2	122	124	38	74
2	0	120	124	39	54
3	1	121	125	40	67
3	2	122	125	41	79

from either Aldrich or Farchan. 4-Hexyn-1-ol (121) and 5-heptyn-1-ol (122) were prepared as described in the literature.<sup>26</sup>

**General Procedure for the Preparation of Diynyl Alcohols 34–41.** The alkynyl alcohols 120–122 were converted to their triflates by treatment of a methylene chloride solution of alcohol with 1.0 equiv of triethylamine and 1.2 equiv of triflic anhydride at 0 °C for 2 h, after which time the volatiles were removed, and the triflate was partially purified by rapid elution through a short silica gel column with a 1:1:8 mixture of ether:CH<sub>2</sub>Cl<sub>2</sub>:hexane as eluent. After removal of solvent, the triflates were not stored but were immediately employed in the next step.

The ynyl tetrahydropyranyl ethers 123–125 were dissolved in THF and cooled to –78 °C. To this solution was added 1–1.1 equiv of butyllithium. After 10 min, the dry ice bath was removed to allow the solution to slowly warm to room temperature for 1.5 h. The solution was then cooled to –78 °C, and the proper ynyl triflate was added via cannula. The resulting solution was allowed to warm to room temperature overnight. The THF was removed under vacuum, and the residue was extracted with ether and washed with brine twice. After removal of ether, the THP-protected alcohol was purified by flash chromatography on silica gel with a 1:15 mixture of ethyl acetate/hexane as eluent. Deprotection of the THP ether was effected by refluxing a solution of the protected alcohol in ethanol containing 0.15 equiv of PPTS for 24–48 h. The ethanol was removed by vacuum, and the residue was extracted with ether and washed with water and brine. After removal of the ether, the diynol was purified by flash chromatography on silica gel.

The syntheses of diynols 34–41 are summarized in Table 5.

**3,7-Nonadiyn-1-ol (34).** This compound was obtained in 36% yield along with a 10% recovery of the THP ether 123. Spectral data for 34: *R<sub>f</sub>* = 0.24 (1:1:4, ether:CH<sub>2</sub>Cl<sub>2</sub>:hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.78 (s, 3 H), 2.12 (bs, 1 H), 2.33 (brd s, 4 H), 2.42 (t, 2 H, *J* = 6.0 Hz), 3.66 (t, 2 H, *J* = 6.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.36, 19.24, 19.30, 23.16, 61.16, 76.63, 77.58, 77.70, 81.37; IR (neat) 3283 (bs), 2945 (s), 2919 (s), 2886 (s), 2867 (s), 2246 (m), 1732 (w), 1441 (s), 1341 (m), 1261 (m), 1182 (w), 1116 (w), 1046 (s), 1022 (s), 912 (s), 849 (w), 732 (s), 648 (w) cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 136 (*M*<sup>+</sup>, 5), 135 (55), 121 (100), 105 (56), 93 (66), 91 (94), 79 (78), 77 (72), 65 (51).

**3,8-Decadiyn-1-ol (35).** This compound was obtained in 52% yield along with a 3% recovery of the THP ether 123 and an 11% yield of 3,8-decadiyn-1-ene. Spectral data for 35: colorless oil; *R<sub>f</sub>* = 0.20 (1:1:4, ether:CH<sub>2</sub>Cl<sub>2</sub>:hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.63 (p, 2 H, *J* = 7.0 Hz), 1.75 (t, 3 H, *J* = 2.5 Hz), 2.09 (bs, 1 H), 2.20–2.26 (m, 4 H), 2.37–2.43 (m, 2 H), 3.65 (t, 2 H, *J* = 6.3 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.33, 17.82 (two carbons), 23.09, 28.29, 61.29, 76.02, 76.92, 78.15, 81.56; IR (neat) 3396 (bs), 2938 (s), 2919 (s), 2866 (m), 2845 (m), 2216 (w), 1732 (w), 1678 (w), 1434 (s), 1333 (w), 1239 (w), 1185 (w), 1046 (s), 850 (w) cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 150 (*M*<sup>+</sup>, 34), 131 (33), 123 (34), 117 (84), 105 (70), 91 (100), 79 (77), 67 (68). Spectral data for 3,8-decadiyn-1-ene: colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.70 (pentet, 2 H, *J* = 7.0 Hz), 1.78 (t, 3 H, *J* = 2.5 Hz), 2.21–2.29 (m, 2 H), 2.42 (d of t, 2 H, *J* = 6.0, 1.9 Hz), 5.38 (d of d, 1 H, *J* = 11.0, 2.3 Hz), 5.55 (d of d, 1 H, *J* = 15.5, 2.3 Hz), 5.78 (ddt, 1 H, *J* = 17.5, 11.0, 2.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.42, 17.90, 18.43, 28.07, 76.11, 78.10, 79.72, 90.10, 117.48, 125.62.

**3,9-Undecadiyn-1-ol (36).** This compound was obtained in 55% yield along with an 8% recovery of the THP ether 123. Spectral data for 36: *R<sub>f</sub>* = 0.16 (1:1:4, ether:CH<sub>2</sub>Cl<sub>2</sub>:hexane); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.55–1.60 (m, 4 H), 1.75 (s, 1 H), 1.77 (t, 3 H, *J* = 2.3 Hz), 2.12–2.19 (m, 4 H), 2.40–2.44 (m, 2 H), 3.66 (t, 2 H, *J* = 6.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.38, 18.29, 18.34, 23.22, 28.08, 28.20, 61.40, 75.70, 76.42, 78.80, 82.28; IR (neat) 3370 (bs), 2940 (s), 2922 (s), 2862 (s), 2245 (w), 1715 (w), 1435 (s), 1378 (m), 1332 (m), 1186 (w), 1046 (s), 913 (m), 849 (w), 734 (s) cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 163 (*M*<sup>+</sup>, 1), 149 (7), 145 (4), 133 (54), 117 (56), 105 (85), 93 (52), 91 (100), 79 (84), 77 (83), 67 (84), 65 (92), 63 (42).

**4,9-Undecadiyn-1-ol (37).** 74% yield; *R<sub>f</sub>* = 0.32 (1:3, EtOAc:hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.55 (brd s, 1 H), 1.64 (pentet, 2 H, *J* = 6.9 Hz), 1.73 (pentet, 2 H, *J* = 6.5 Hz), 1.77 (t, 3 H, *J* = 2.2 Hz), 2.20–2.28 (m, 6 H), 3.73 (t, 2 H, *J* = 6.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.38, 15.28, 17.80 (two carbons), 28.38, 31.50, 61.76, 75.96, 78.24, 79.80, 79.93; IR (neat) 3341 (s), 2945 (s), 2867 (s), 2845 (m), 1452 (m), 1435 (s), 1346 (w), 1331 (w), 1058 (s), 1038 (m), 931 (w) cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 165 (*M*<sup>+</sup> + 1, 28), 164 (14), 163 (*M* – 1, 15), 147 (44), 137 (40), 123 (55), 121 (75), 119 (100), 105 (95), 95 (94), 81 (88), 71 (46), 67 (52).

**4,10-Dodecadiyn-1-ol (38).** This compound was obtained in 74% yield. Spectral data for 38: *R<sub>f</sub>* = 0.20 (1:1:4, ether:CH<sub>2</sub>Cl<sub>2</sub>:hexane); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.53–1.60 (m, 5 H), 1.73 (pentet, 2 H, *J* = 6.5 Hz), 1.77 (t, 3 H, *J* = 2.5 Hz), 2.13–2.16 (m, 4 H), 2.25–2.28 (m, 2 H), 3.74 (t, 2 H, *J* = 6.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.29, 15.28, 18.19, 18.21, 28.08 (two carbons), 31.59, 61.77, 75.55, 78.78, 79.50, 80.44; IR (neat) 3350 (bs), 2942 (s), 2862 (m), 2233 (w), 1435 (m), 1331 (w), 1057 (m), 913 (w), 734 (m) cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 178 (*M*<sup>+</sup>, 2), 177 (4), 163 (12), 149 (29), 133 (32), 119 (42), 105 (72), 91 (100), 79 (66), 67 (33).

**4,8-Decadiyn-1-ol (39).** This compound was obtained in 54% yield along with a 12% recovery of the THP ether 124. Spectral data for 39: *R<sub>f</sub>* = 0.16 (1:1:4, ether:CH<sub>2</sub>Cl<sub>2</sub>:hexane); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.65 (pentet, 2 H, *J* = 7.2 Hz), 1.74 (s, 1 H), 1.77 (t, 3 H, *J* = 2.2 Hz), 2.21–2.28 (m, 4 H), 2.40–2.43 (m, 2 H), 3.66 (t, 2 H, *J* = 6.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.43, 15.45, 19.35, 19.37, 31.47, 61.99, 76.52, 77.76, 79.63, 80.30; IR (neat) 3552 (bs), 2921 (s), 2876 (m), 1739 (w), 1436 (m), 1377 (w), 1340 (w), 1260 (w), 1057 (s), 934 (w), 909 w cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 149 (*M* – 1, 16), 135 (60), 122 (86), 117 (72), 105 (72), 97 (47), 93 (45), 91 (100), 79 (84), 77 (99), 67 (64), 65 (73). Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O: C, 79.95; H, 9.39. Found: C, 79.37; H, 9.59.

**5,10-Dodecadiyn-1-ol (40).** This compound was obtained in 67% yield. Spectral data for 40: *R<sub>f</sub>* = 0.17 (1:1:4, ether:CH<sub>2</sub>Cl<sub>2</sub>:hexane); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.54–1.69 (m, 7 H), 1.77 (t, 3 H, *J* = 2.5 Hz), 2.16–2.27 (m, 6 H), 3.67 (t, 2 H, *J* = 6.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.38, 17.88, 17.91, 18.51, 25.32, 28.57, 31.88, 62.46, 75.91, 78.36, 79.69, 80.32; IR (neat) 3367 (bs), 2937 (s), 2919 (s), 2864 (s), 2843 (s), 1453 (m), 1434 (s), 1332 (m), 1314 (w), 1209 (w), 1164 (w), 1059 (s), 1031 (m), 982 (w), 931 (w) cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 178 (*M*<sup>+</sup>, 1), 177 (4), 163 (2), 149 (16), 133 (24), 119 (96), 105 (92), 92 (60), 90 (100), 78 (86); exact mass (*m/z*) calcd for C<sub>12</sub>H<sub>18</sub>O, 178.1358, found *m/z* 178.1301. Anal. Calcd for C<sub>12</sub>H<sub>18</sub>O: C, 80.85; H, 10.18. Found: C, 79.73; H, 9.74.

**5,11-Tridecadiyn-1-ol (41).** This compound was obtained in 79% yield. Spectral data for 41: *R<sub>f</sub>* = 0.31 (1:2, EtOAc:hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.43 (s, 1 H), 1.56–1.59 (m, 6 H), 1.64–1.70 (m, 2 H), 1.77 (s, 3 H), 2.13–2.20 (m, 6 H), 3.66 (t, 2 H, *J* = 6.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 3.39, 18.30, 18.31, 18.53, 25.36, 28.19, 28.22, 31.92, 62.51, 75.61, 78.92, 80.03, 80.23; IR (neat) 3336 (bs), 2940 (s), 2920 (s), 2862 (m), 2843 (w), 2236 (w), 1456 (m), 1435 (m), 1332 (m), 1059 (m), 1030 (w), 981 (w), 913 (m), 733 (s) cm<sup>-1</sup>; mass spectrum *m/z* (relative intensity) 192 (*M*<sup>+</sup>, 2), 191 (*M* – 1, 8), 177 (12), 163 (38), 147 (26), 133 (70), 119 (58), 105 (98), 90 (96), 78 (100); exact mass (*m/z*) calcd for C<sub>13</sub>H<sub>20</sub>O, 192.1514, found, 192.1493. Anal. Calcd for C<sub>13</sub>H<sub>20</sub>O: C, 81.20; H, 10.48. Found: C, 80.59; H, 10.80.

**General Procedure for the Preparation of Diynyl Iodides 42–46.** The appropriate alcohol (37–41) was dissolved in fresh distilled methylene chloride and treated with 7 equiv of finely ground potassium hydroxide and 2 equiv of tosylate chloride, which were added sequentially. This slurry was stirred at room temperature for 12 h and then washed with water and brine. After removal of the volatiles, the tosylate was purified by flash chromatography on silica gel with a 1:9 mixture of ethyl acetate:hexane as eluent. The tosylate was then refluxed in acetone for 4 h in the presence of 4 equiv of sodium iodide. The acetone was removed

(26) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W. D.; Zask, A. *Tetrahedron* 1985, 41, 5803.

Table 6. Synthesis of Diynyl Iodides 42–46

<i>m</i>	<i>n</i>	diynol	diynyl iodide	yield of diiodide from 37–41 (%)
2	0	39	42	71
2	1	37	43	81
2	2	38	44	85
3	1	40	45	95
3	2	41	46	46

under vacuum, and the residue was extracted with ether and washed twice with water. The diynyl iodide was purified by flash chromatography on silica gel as indicated below.

The syntheses of diynyl iodides 42–46 are summarized in Table 6.

**1-Iodo-4,8-decadiyne (42).** From 1.76 g (11.7 mmol) of 39 was isolated 2.17 g (8.34 mmol, 71%) of 42 after chromatography with a 1:30 mixture of EtOAc:hexane ( $R_f = 0.54$  (1:30, EtOAc:hexane)). Spectral data for 42:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.79 (s, 3 H), 1.95–1.98 (m, 2 H), 2.30 (brd s, 6 H), 3.31 (t, 2 H,  $J = 6.8$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.56, 5.63, 19.31 (two carbons), 19.76, 32.36, 76.53, 77.72, 78.77, 80.16; IR (neat) 2916 (s), 2843 (w), 1430 (s), 1341 (m), 1262 (m), 1222 (s), 1168 (m), 847 (w), 751 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 260 ( $\text{M}^+$ , 2), 259 (10), 245 (95), 232 (16), 155 (18), 133 (15), 117 (22), 105 (100), 91 (88), 77 (82).

**1-Iodo-4,9-undecadiyne (43).** From 0.59 g (3.57 mmol) of 37 was isolated 0.79 g (2.88 mmol, 81%) of 43 after chromatography with a 1:30 mixture of EtOAc:hexane ( $R_f = 0.24$  (hexane)). Spectral data for 43:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.64 (pentet, 2 H,  $J = 6.9$  Hz), 1.77 (s, 3 H), 1.95 (pentet, 2 H,  $J = 6.5$  Hz), 2.20–2.29 (m, 6 H), 3.28 (t, 2 H,  $J = 7.0$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.42, 5.45, 17.87 (two carbons), 19.78, 28.43, 32.49, 75.96, 78.22, 78.28, 80.60; IR (neat) 2934 (s), 2916 (s), 2857 (s), 2840 (s), 1733 (w), 1432 (s), 1345 (m), 1331 (m), 1265 (m), 1222 (s), 1167 (m), 847 (w), 722 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 273 ( $\text{M} - 1$ , 3), 259 (27), 246 (30), 219 (10), 180 (36), 155 (88), 147 (34), 131 (48), 119 (100), 105 (100). Anal. Calcd for  $\text{C}_{11}\text{H}_{15}\text{I}$ : C, 48.19; H, 5.52. Found: C, 48.32; H, 5.72.

**1-Iodo-4,10-dodecadiyne (44).** From 0.58 g (3.25 mmol) of 38 was isolated 0.79 g (2.73 mmol, 85%) of 44 after chromatography with a 1:50 mixture of EtOAc:hexane ( $R_f = 0.29$  (1:50, EtOAc:hexane)). Spectral data for 44:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.54–1.59 (m, 4 H), 1.77 (t, 3 H,  $J = 2.1$  Hz), 1.95 (pentet, 2 H,  $J = 6.5$  Hz), 2.12–2.16 (m, 4 H), 2.26–2.29 (m, 2 H), 3.28 (t, 2 H,  $J = 6.9$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.39, 5.36, 18.57, 18.62, 19.90, 28.42, 28.50, 32.72, 75.87, 78.34, 79.04, 81.22; IR (neat) 2939 (s), 2918 (s), 2859 (m), 2841 (m), 1431 (s), 1331 (m), 1265 (w), 1222 (s), 1167 (m), 847 (w), 744 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 288 ( $\text{M}^+$ , 2), 287 ( $\text{M} - 1$ , 14), 273 (5), 260 (7), 155 (28), 147 (23), 133 (100), 119 (62), 105 (92), 91 (87), 79 (90), 67 (57); exact mass ( $m/z$ ) calcd for  $\text{C}_{12}\text{H}_{17}\text{I}$ , 288.0375, found, 288.0420. Anal. Calcd for  $\text{C}_{12}\text{H}_{17}\text{I}$ : C, 50.02; H, 5.95. Found: C, 50.97; H, 6.30.

**1-Iodo-5,10-dodecadiyne (45).** From 1.07 g (5.99 mmol) of 40 was isolated 1.63 g (5.66 mmol, 95%) of 45 after chromatography with a 1:15 mixture of EtOAc:hexane ( $R_f = 0.64$  (1:15, EtOAc:hexane)). Spectral data for 45:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.55–1.67 (m, 4 H), 1.77 (s, 3 H), 1.89–1.96 (m, 2 H), 2.16–2.25 (m, 6 H), 3.19 (t, 2 H,  $J = 7.0$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.43, 6.19, 17.72, 17.90 (two carbons), 28.53, 29.69, 32.48, 75.92, 78.29, 79.67, 80.01; IR (neat) 2935 (s), 2859 (m), 2841 (m), 1433 (m), 1331 (w), 1288 (w), 1213 (m), 1166 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 288 (2), 188 (54), 185 (18), 171 (27), 159 (17), 145 (22), 133 (56), 119 (86), 105 (76), 91 (100), 79 (68), 67 (73); exact mass ( $m/z$ ) calcd for  $\text{C}_{12}\text{H}_{17}\text{I}$ , 288.0375, found, 288.0342. Anal. Calcd for  $\text{C}_{12}\text{H}_{17}\text{I}$ : C, 50.01; H, 5.95. Found: C, 49.90; H, 5.88.

**1-Iodo-5,11-tridecadiyne (46).** From 0.63 g (3.27 mmol) of 41 was isolated 0.45 g (1.49 mmol, 46%) of 46 after chromatography with a 1:1:60 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.33$  (1:1:60, ether: $\text{CH}_2\text{Cl}_2$ :hexane)). Spectral data for 46:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.53–1.63 (m, 6 H), 1.78 (t, 3 H,  $J = 2.5$  Hz), 1.93 (pentet, 2 H,  $J = 7.5$  Hz), 2.11–2.22 (m, 6 H), 3.21 (t, 2 H,  $J = 7.1$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.46, 6.41, 17.66, 18.24 (two carbons), 28.09 (two carbons), 29.64, 32.40, 75.58, 78.82, 79.34, 80.47; IR (neat) 2940 (s), 2918 (s), 2859 (m), 2840 (w),

1433 (m), 1332 (w), 1287 (w), 1212 (m), 1166 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 302 ( $\text{M}^+$ , 1), 301 (3), 287 (5), 274 (7), 183 (10), 175 (15), 155 (88), 147 (100), 133 (100). Anal. Calcd for  $\text{C}_{13}\text{H}_{19}\text{I}$ : C, 51.67; H, 6.34. Found: C, 51.83; H, 6.35.

**General Procedure for the Preparation of Diynyl Chromium Complexes 47, 49, 51, 53, and 55.** As indicated in Table 1, these chromium complexes were prepared by the alkylation of (methyl(methoxy)methylene)pentacarbonylchromium (6).<sup>27</sup> The appropriate diynyl alcohol (34–38) was dissolved in methylene chloride and stirred with 1 equiv of triethylamine and 1.5 equiv of triflic anhydride at 0 °C for 2 h. The solvent was removed, and the residue was quickly filtered through a 2-in. plug of silica gel with a 1:1:4 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane to afford the corresponding triflate, which was immediately used in the next step. At the same time, a solution of complex 6 in THF at  $-78$  °C was stirred with 1 equiv of *n*-butyllithium for 1 h. To the solution of the resulting anion at 0 °C was added 1.0 equiv of the appropriate triflate. After 0.5 h, the reaction mixture was diluted with ether and washed with water and brine. The desired carbene complex was purified by flash chromatography on silica gel as described below. Dialkylation products were observed as side products, but the amount of the dialkylated product was not determined in all cases.

**Deca-4,8-diynyl Chromium Complex 47.** From 0.418 g (1.67 mmol) of 6 and 0.23 g (1.67 mmol) of diynol 34 was obtained the complex 47 as an orange oil in 38% yield (0.23 g, 0.63 mmol) after flash chromatography on silica gel with a 1:1:30 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.22$  (1:1:60, ether: $\text{CH}_2\text{Cl}_2$ :hexane)). A 17% yield of the dialkylated product was also obtained which eluted more slowly off the column ( $R_f = 0.06$ ). Spectral data for 47:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.65 (pentet,  $J = 7.6$  Hz, 2 H), 1.77 (t,  $J = 2.2$  Hz, 3 H), 2.17 (t,  $J = 6.9$  Hz, 2 H), 2.27–2.33 (m, 4 H), 3.42 (t,  $J = 7.6$  Hz, 2 H), 4.75 (s, 3 H);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  3.35, 18.52, 19.71, 25.40, 62.15, 67.12, 76.57, 78.11, 79.81, 80.61, 216.71, 223.45, 362.14 (one carbon not found); IR (neat) 2961 (s), 2922 (s), 2852 (m), 2062 (s), 1934 (vs), 1454 (s), 1341 (w), 1250 (vs), 1157 (m), 1072 (m), 1039 (m), 944 (m), 845 (w), 695 (m), 667 (m), 653 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 368 ( $\text{M}^+$ , 18), 256 (6), 228 (88), 213 (100), 174 (22), 159 (53), 105 (64), 80 (26).

**Undeca-4,9-diynyl Chromium Complex 49.** From 0.418 g (1.67 mmol) of 6 and 0.251 g (1.67 mmol) of diynol 35 was obtained the complex 49 as an orange oil in 35% yield (0.217 g, 0.57 mmol) after flash chromatography on silica gel with a 1:1:30 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.5$  (1:1:30, ether: $\text{CH}_2\text{Cl}_2$ :hexane)). A 25% yield of the dialkylated product was also obtained which eluted more slowly off the column ( $R_f = 0.33$ ). In addition, a 13% recovery of carbene complex 6 was observed. Spectral data for 49:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.60–1.75 (m, 4 H), 1.77 (t,  $J = 2.5$  Hz, 3 H), 2.16–2.32 (m, 6 H), 3.42 (t,  $J = 7.8$  Hz, 2 H), 4.76 (s, 3 H);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  3.27, 18.14, 18.22, 25.50, 28.93, 62.15, 67.14, 76.22, 78.45, 79.50, 81.02, 216.73, 223.44 ( $\text{C}_{\text{carb}}$  not located); IR (neat) 2956 (m), 2936 (m), 2922 (m), 2859 (w), 2063 (s), 1932 (s), 1453 (m), 1249 (m), 1072 (w), 1039 (w), 956 (w), 694 (w), 667 (s), 633 (s), 623 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 382 ( $\text{M}^+$ , 33), 298 (1), 270 (3), 242 (100), 225 (5), 208 (100), 199 (7), 182 (28), 168 (33), 154 (7), 143 (11), 131 (7), 117 (20), 105 (15), 91 (15), 80 (24), 71 (7), 65 (5).

**Dodeca-4,10-diynyl Chromium Complex 51.** From complex 6 (0.189 g, 0.76 mmol) and 0.138 g (0.84 mmol) of diynol 36 was obtained the complex 51 as an orange oil in 49% yield (0.147 g, 0.37 mmol) after flash chromatography on silica gel with a 1:1:30 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.58$  (1:1:30, ether: $\text{CH}_2\text{Cl}_2$ :hexane)). An 18% yield of the dialkylated product was also obtained. Spectral data for 51:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.55–1.59 (m, 4 H), 1.66 (pentet, 2 H,  $J = 7.6$  Hz), 1.78 (t, 3 H,  $J = 2.5$  Hz), 2.15–2.19 (m, 6 H), 3.44 (t, 2 H,  $J = 7.8$  Hz), 4.79 (s, 3 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.34, 18.42, 18.54, 18.64, 25.50, 28.12, 28.50, 62.24, 67.10, 75.86, 78.99, 79.18, 81.49, 216.73, 223.43, 362.08; IR (neat) 2924 (w), 2861 (w), 2063 (s), 1925 (s), 1453 (m), 1249 (s), 1038 (w), 837 (w), 652 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 396 (20), 382 (4), 284 (6), 256 (96), 222 (100), 208 (18), 194 (16), 131 (14), 117 (16), 105 (22), 91 (15), 80 (20), 71 (16).

**Dodeca-5,10-diynyl Chromium Complex 53.** From complex 6 (0.375 g, 1.50 mmol) and 0.246 g (1.50 mmol) of diynol 37 was obtained the complex 53 as an orange oil in 51% yield (0.285 g, 0.72 mmol) after flash chromatography on silica gel with a 1:1:60 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.22$  (1:1:60, ether: $\text{CH}_2\text{Cl}_2$ :hexane)). The dialkylation product was also produced in this reaction, but the amount was not

(27) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* 1968, 101, 960. (b) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* 1987, 65, 140.

determined. Spectral data for **53**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.46–1.49 (m, 2 H), 1.50–1.61 (m, 2 H), 1.63 (pentet,  $J = 7.3$  Hz, 2 H), 1.77 (s, 3 H), 2.14 (t,  $J = 5.0$  Hz, 2 H), 2.15–2.25 (m, 4 H), 3.01 (t,  $J = 7.4$  Hz, 2 H), 4.76 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  3.28, 18.20 (two carbons), 18.78, 25.44, 28.59, 29.00, 62.68, 67.18, 76.13, 78.53, 80.07, 80.14, 216.76, 223.46, 362.60; IR (neat) 2938 (w), 2862 (w), 2063 (s), 1980 (m), 1925 (vs), 1454 (m), 1237 (m), 1022 (w), 942 (w), 691 (w), 668 (m), 653 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 396 ( $\text{M}^+$ , 18), 310 (5), 283 (7), 256 (100), 232 (29), 220 (46), 201 (95), 189 (23), 173 (60), 145 (35), 131 (34), 105 (30), 91 (35), 71 (38).

**Trideca-5,11-diyne Chromium Complex 55.** From complex **6** (0.415 g, 1.66 mmol) and **0.281 g** (1.58 mmol) of diyne **38** was obtained the complex **55** as an orange oil in 39% yield (0.252 g, 0.61 mmol) after flash chromatography on silica gel with a 1:1:60 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.23$  (1:1:60, ether: $\text{CH}_2\text{Cl}_2$ :hexane)). The dialkylation product was also produced in this reaction, but the amount was not determined. Spectral data for **55**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.46–1.64 (m, 8 H), 1.79 (t, 3 H,  $J = 2.5$  Hz), 2.15–2.16 (m, 6 H), 3.33 (t, 2 H,  $J = 7.0$  Hz), 4.79 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.36, 18.65 (two carbons), 18.84, 25.46, 28.55 (two carbons), 28.67, 62.67, 67.08, 75.81, 79.00, 79.75, 80.62, 216.75, 223.45, 362.63; IR (neat) 2942 (m), 2924 (m), 2863 (w), 2063 (s), 1959 (s), 1943 (vs), 1454 (s), 1276 (w), 1257 (s), 1154 (w), 1028 (w), 942 (w), 692 (w), 668 (s), 654 (s), 619 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 410 (8), 292 (7), 270 (35), 234 (51), 187 (48), 145 (41), 105 (34), 83 (100), 67 (37).

**General Procedure for the Preparation of Diyne Tungsten Complexes 48, 50, 52, 54, and 56.** As indicated in Table 2, these tungsten complexes were prepared by the standard Fischer procedure from tungsten hexacarbonyl and an organolithium. The proper iodide **42–46** was dissolved in ether, cooled to  $-78$   $^\circ\text{C}$ , and treated with 2.2 equiv of *tert*-butyllithium for 10 min. The resulting solution of diynyl lithium was transferred via cannula into a slurry of tungsten hexacarbonyl in ether at  $-78$   $^\circ\text{C}$ . After 45 min, the dry ice bath was removed, and the solution was allowed to warm to  $0$   $^\circ\text{C}$  over 1.5 h, after which time 4 equiv of methyl (trifluoromethane)sulfonate was added at  $0$   $^\circ\text{C}$ . After 30 min, the reaction mixture was washed twice with saturated aqueous sodium bicarbonate and once with water and brine. After removal of the volatiles, the desired carbene complex was purified by flash chromatography on silica gel as described below.

**Deca-4,8-diyne Tungsten Complex 48.** From 0.3436 g (1.32 mmol) of diyne iodide **42** and 0.465 g (1.32 mmol) tungsten hexacarbonyl was isolated the carbene complex **48** as an orange oil in 44% yield (0.2938 g, 0.59 mmol) after flash chromatography on silica gel with a 1:1:60 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.20$  (1:1:60, ether: $\text{CH}_2\text{Cl}_2$ :hexane)). Spectral data for **48**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.68 (pentet,  $J = 7.6$  Hz, 2 H), 1.77 (s, 3 H), 2.19 (t,  $J = 6.9$  Hz, 2 H), 2.31 (m, 4 H), 3.31 (t,  $J = 7.6$  Hz, 2 H), 4.59 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.52, 18.32, 19.32, 25.35, 64.00, 70.46, 76.42, 77.75, 79.64, 80.22, 197.16, 203.17, 336.27 (one carbon not found); IR (neat) 2928 (w), 2841 (w), 2070 (s), 1982 (m), 1914 (vs), 1448 (m), 1249 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 500 ( $\text{M}^+$ , 1,  $^{184}\text{W}$ ), 388 (1,  $^{184}\text{W}$ ), 376 (3,  $^{184}\text{W}$ ), 360 (16,  $^{184}\text{W}$ ), 342 (9,  $^{184}\text{W}$ ), 131 (21), 91 (45), 43 (100); exact mass ( $m/z$ ) calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_6^{184}\text{W}$ , 500.0457, found, 500.0452. Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_6\text{W}$ : C, 40.82; H, 3.22. Found: C, 40.84; H, 3.30.

**Undeca-4,9-diyne Tungsten Complex 50.** From 0.38 g (1.39 mmol) of diyne iodide **43** and 0.494 g (1.39 mmol) of tungsten hexacarbonyl was isolated the carbene complex **50** as an orange oil in 57% yield (0.408 g, 0.79 mmol) after flash chromatography on silica gel with a 1:30 mixture of EtOAc:hexane ( $R_f = 0.31$  (1:30, EtOAc:hexane)). Spectral data for **50**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.63–1.69 (m, 4 H), 1.77 (t,  $J = 2.3$  Hz, 3 H), 2.16–2.26 (m, 6 H), 3.31 (t,  $J = 7.7$  Hz, 2 H), 4.59 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.45, 17.85 (two carbons), 18.32, 25.44, 28.41, 64.06, 70.45, 75.97, 78.26, 79.19, 80.73, 197.14, 203.19, 336.21; IR (neat) 2954 (w), 2922 (w), 2070 (s), 1916 (vs), 1450 (m), 1249 (m), 1038 (w), 929 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 514 ( $\text{M}^+$ , 3,  $^{184}\text{W}$ ), 428 (3,  $^{184}\text{W}$ ), 402 (2,  $^{184}\text{W}$ ), 374 (8,  $^{184}\text{W}$ ), 370 (8,  $^{184}\text{W}$ ), 357 (11,  $^{184}\text{W}$ ), 71 (100); exact mass ( $m/z$ ) calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_6^{184}\text{W}$ , 514.0624, found, 514.0629. Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_6\text{W}$ : C, 42.05; H, 3.53. Found: C, 41.83; H, 3.76.

**Dodeca-4,10-diyne Tungsten Complex 52.** From 0.39 g (1.35 mmol) of diyne iodide **44** and 0.476 g (1.35 mmol) of tungsten hexacarbonyl was isolated the carbene complex **52** as an orange oil in 31% yield (0.222 g, 0.42 mmol) after flash chromatography on silica gel with a 1:1:60 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.29$ ). Spectral data for **52**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.56–1.57 (m, 4 H), 1.68 (pentet, 2 H,  $J = 7.5$  Hz), 1.77 (t, 3 H,  $J = 2.4$  Hz), 2.12–2.19 (m, 6 H), 3.31 (t, 2 H,  $J = 7.7$  Hz),

4.59 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.35, 15.53, 18.47, 18.63, 25.55, 28.46, 28.54, 64.23, 69.92, 75.84, 79.00, 79.25, 81.50, 197.49, 203.35, 335.72; IR (neat) 2943 (m), 2923 (m), 2863 (m), 2847 (w), 2070 (vs), 1917 (vs), 1450 (s), 1354 (w), 1332 (m), 1298 (m), 1249 (s), 1157 (w), 1073 (m), 1039 (m), 936 (m), 801 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 528 ( $\text{M}^+$ , 2,  $^{184}\text{W}$ ), 388 (9,  $^{184}\text{W}$ ), 382 (6,  $^{184}\text{W}$ ), 364 (8,  $^{184}\text{W}$ ), 267 (6,  $^{184}\text{W}$ ), 133 (30), 71 (100); exact mass ( $m/z$ ) calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_6^{184}\text{W}$ , 528.0769, found, 528.0765. Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_6\text{W}$ : C, 43.20; H, 3.82. Found: C, 43.72; H, 4.22.

**Undeca-5,10-diyne Tungsten Complex 54.** From 0.262 g (0.91 mmol) of diyne iodide **45** and 0.476 g (1.35 mmol) of tungsten hexacarbonyl was isolated the complex **54** as an orange oil in 37% yield (0.180 g, 0.34 mmol) after flash chromatography on silica gel with a 1:1:30 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.38$ ). Spectral data for **54**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.47–1.53 (m, 2 H), 1.58–1.66 (m, 4 H), 1.77 (t,  $J = 2.4$  Hz, 3 H), 2.13–2.16 (m, 2 H), 2.20–2.25 (m, 4 H), 3.21 (t,  $J = 7.5$  Hz, 2 H), 4.59 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  3.32, 18.21 (two carbons), 18.86, 25.53, 28.56, 29.01, 64.60, 69.99, 76.19, 78.54, 80.07, 80.19, 197.57, 203.39, 336.41; IR (neat) 2937 (m), 2845 (w), 2862 (w), 2070 (s), 1919 (vs), 1451 (s), 1333 (w), 1257 (s), 1166 (w), 1087 (w), 1029 (m), 940 (w), 987 (w), 657 (w), 595 (m), 571 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 528 (2,  $^{184}\text{W}$ ), 380 (3,  $^{184}\text{W}$ ), 366 (4,  $^{184}\text{W}$ ), 352 (7,  $^{184}\text{W}$ ), 296 (6,  $^{184}\text{W}$ ), 268 (12,  $^{184}\text{W}$ ), 240 (5,  $^{184}\text{W}$ ), 212 (5,  $^{184}\text{W}$ ), 189 (15), 173 (18), 157 (20), 145 (19), 131 (20), 118 (31), 105 (28), 85 (100). Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_6\text{W}$ : C, 43.20; H, 3.82. Found: C, 44.77; H, 4.66.

**Dodeca-5,11-diyne Tungsten Complex 56.** From 0.174 g (0.58 mmol) of diyne iodide **46** and 0.203 g (0.58 mmol) of tungsten hexacarbonyl was isolated the complex **56** as an orange oil in 44% yield (0.137 g, 0.25 mmol) after flash chromatography on silica gel with a 1:1:60 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane ( $R_f = 0.23$ ). Spectral data for **56**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.47–1.62 (m, 8 H), 1.77 (t, 3 H,  $J = 2.3$  Hz), 2.12–2.16 (m, 6 H), 3.21 (t, 2 H,  $J = 7.6$  Hz), 4.59 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  3.37, 18.67 (two carbons), 18.90, 25.56, 28.56 (two carbons), 28.63, 64.62, 69.95, 75.86, 79.05, 79.78, 80.67, 197.56, 203.34, 336.40; IR (neat) 2935 (w), 2924 (w), 2070 (s), 1980 (m), 1917 (vs), 1449 (w), 1275 (w), 1238 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 542 (21,  $^{184}\text{W}$ ), 402 (40,  $^{184}\text{W}$ ), 378 (32,  $^{184}\text{W}$ ), 376 (30,  $^{184}\text{W}$ ), 267 (21,  $^{184}\text{W}$ ), 175 (18), 145 (66), 143 (22), 139 (27), 131 (36), 105 (70), 91 (100).

**General Procedure for the Thermolysis of Chromium and Tungsten Diyne Complexes.** The appropriate carbene complex was placed in a single-necked flask equipped with a threaded high-vacuum stopcock and diluted with proper solvent to 0.005 M. The mixture was deoxygenated by the freeze-thaw method ( $-196$   $^\circ\text{C}$  to  $25$   $^\circ\text{C}$ , three cycles). The flask was back-filled with argon or carbon monoxide at 1 atm and sealed at  $25$   $^\circ\text{C}$ . The flask was heated at  $70$   $^\circ\text{C}$  for chromium complexes and  $110$   $^\circ\text{C}$  for tungsten complexes for 16–24 h. The flask was then cooled to room temperature, opened, and the contents removed. The solvent was removed under vacuum on a rotary evaporator, and products were separated by flash chromatography on silica gel.

**Thermolysis of the Deca-4,8-diyne Complexes 47 and 48.** The thermolysis of 0.126 g (0.34 mmol) of the chromium complex **47** in 69 mL of benzene provided 0.0329 g (0.14 mmol, 41%) of the lactone **61** after chromatography on silica gel with a 1:1:8 mixture of  $\text{CH}_2\text{Cl}_2$ :ether:hexane. Spectral data for **61**: light yellow solid, mp =  $141$ – $142$   $^\circ\text{C}$ ;  $R_f = 0.33$  (1:5, EtOAc:hexane);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.77 (s, 3 H), 1.83 (pentet,  $J = 7.6$  Hz, 2 H), 2.52–2.65 (m, 6 H), 3.03–3.06 (m, 2 H), 3.64 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.97, 20.49, 22.55, 30.29, 30.74, 35.00, 57.37, 108.08, 110.84, 122.08, 147.10, 162.93, 163.25, 176.05; IR (neat) 2935 (m), 2913 (m), 2853 (m), 1738 (vs), 1642 (w), 1610 (vs), 1433 (w), 1370 (m), 1321 (m), 1255 (m), 1234 (m), 1121 (w), 973 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 232 ( $\text{M}^+$ , 100), 217 (14), 189 (36), 175 (32), 161 (6), 91 (7), 77 (6); exact mass ( $m/z$ ) calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_3$ , 232.1099, found, 232.1138. Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_3$ : C, 72.39; H, 6.94. Found: C, 72.29; H, 7.19.

The thermolysis of 0.127 g (0.25 mmol) of the tungsten complex **48** in 51 mL of benzene provided 0.0132 g (0.076 mmol, 30%) of the phenol **57** after chromatography on silica gel with a 1:1:16 mixture of  $\text{CH}_2\text{Cl}_2$ :ether:hexane. Spectral data for **57**:  $R_f = 0.31$  (1:9, EtOAc:hexane); white solid, mp =  $147$ – $148$   $^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.06 (s, 3 H), 2.10 (pentet,  $J = 7.4$  Hz, 2 H), 2.73–2.78 (m, 4 H), 2.97–2.98 (m, 2 H), 3.03 (s, 2 H), 4.28 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.07, 25.72, 26.98, 28.05, 28.62, 30.09, 115.78, 128.56, 132.00, 137.53, 143.74, 149.41; IR (neat) 3310 (bs), 2953 (m), 2915 (s), 2852 (w), 1435 (w), 1369 (w), 1286 (w), 1195 (w), 1057 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 174 ( $\text{M}^+$ , 100), 173 (17), 159 (26), 131 (17), 91 (12); exact mass ( $m/z$ ) calcd

for  $C_{12}H_{14}O$ , 174.1045, found, 174.1045. Anal. Calcd for  $C_{12}H_{14}O$ : C, 82.72; H, 8.10. Found: C, 82.80; H, 8.25.

The thermolysis of 0.106 g (0.21 mmol) of the tungsten complex **48** in 42 mL of  $CH_3CN$  under 1 atm of CO provided 0.0176 g (0.10 mmol, 48%) of the phenol **57** after chromatography on silica gel with a 1:5 mixture of EtOAc:hexane.

**Thermolysis of the Undeca-4,9-diyne Complexes 49 and 50.** The thermolysis of 0.1191 g (0.312 mmol) of the chromium complex **49** in 62 mL of  $CH_3CN$  provided 0.0178 g (0.095 mmol, 31%) of the phenol **58** and 0.0281 g (0.129 mmol, 41%) of the dienone **62** upon elution from silica gel with a 1:9 mixture of ethyl acetate and hexanes. Spectral data for **58**: white solid, mp = 125–127 °C;  $R_f$  = 0.28 (1:9, EtOAc:hexane);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.07 (pentet,  $J$  = 7.4 Hz, 2 H), 2.11 (pentet,  $J$  = 7.1 Hz, 2 H), 2.14 (s, 3 H), 2.73–2.85 (m, 8 H), 4.31 (s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  12.06, 25.25, 25.39, 28.84, 31.04, 31.60, 31.75, 116.84, 126.66, 131.20, 138.13, 143.03, 148.55; IR (neat) 3264 (s), 2943 (s), 2925 (s), 2842 (m), 1435 (w), 1368 (w), 1289 (w), 1244 (w), 1075 (w)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 188 ( $M^+$ , 100), 173 (59), 160 (23), 145 (10), 128 (6), 115 (8), 91 (6), 83 (11), 77 (5), 65 (4), 57 (3), 53 (2). Anal. Calcd for  $C_{13}H_{16}O$ : C, 82.94; H, 8.57. Found: C, 83.06; H, 8.65. Spectral data for **62**:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.23–1.42 (m, 1 H), 1.81 (s, 3 H), 1.85–1.98 (m, 2 H), 1.98–2.08 (m, 1 H), 2.13–2.19 (m, 1 H), 2.28–2.37 (m, 2 H), 2.37–2.47 (m, 1 H), 2.47–2.56 (m, 2 H), 2.56–2.63 (m, 2 H), 3.10 (s, 3 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  10.83, 21.28, 23.99, 27.07, 29.14, 31.94, 32.61, 51.44, 80.92, 124.35, 134.55, 142.88, 158.71, 201.83; IR (neat) 2952 (s), 2820 (m), 1943 (w), 1695 (w), 1655 (s), 1611 (s), 1452 (m), 1432 (m), 1375 (w), 1336 (s), 1294 (w), 1123, 1075 (s), 1036 (w), 1017 (w), 924 (w), 762 (w)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 218 ( $M^+$ , 97), 203 (10), 189 (96), 175 (100), 159 (33), 147 (16), 141 (7), 128 (18), 115 (24), 105 (15), 91 (35), 77 (21), 65 (14).

The thermolysis of the chromium complex **49** was carried out in the same manner in a number of other solvents on approximately the same scale to give the following results. Benzene, **58** (57%); THF, **58** (61%) and **62** (7%); *n*-butyl ether, **58** (50%) and **62** (5%); DMF, **58** (10%) and **62** (16%). The thermolysis of 0.088 g (0.17 mmol) of the tungsten complex **50** in 34 mL of  $CH_3CN$  under 1 atm of CO provided 0.0196 g (0.10 mmol, 61%) of the phenol **58** after chromatography on silica gel with a 1:1:16 mixture of  $CH_2Cl_2$ :ether:hexane.

**Thermolysis of Dodeca-4,10-diyne Complexes 51 and 52.** The thermolysis of 0.1807 g (0.46 mmol) of the chromium complex **51** in 91 mL of benzene provided 0.0236 g (0.12 mmol, 33% yield) of the phenol **59** after chromatography on silica gel with a 1:1:8 mixture of  $CH_2Cl_2$ :ether:hexane. Spectral data for **59**: white solid, mp = 120–121 °C;  $R_f$  = 0.30 (1:1:8,  $CH_2Cl_2$ :ether:hexane);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.73–1.81 (m, 4 H), 2.10 (pentet, 2 H,  $J$  = 7.5 Hz), 2.10 (s, 3 H), 2.56 (t, 2 H,  $J$  = 6.4 Hz), 2.60 (t, 2 H,  $J$  = 5.8 Hz), 2.77 (t, 2 H,  $J$  = 7.4 Hz), 2.82 (t, 2 H,  $J$  = 7.3 Hz), 4.31 (s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  10.79, 22.80, 23.47, 24.72, 27.14, 27.44, 28.94, 31.50, 119.36, 125.30, 125.66, 134.92, 141.47, 147.63; IR (neat) 3338 (bs), 2950 (w), 2925 (s), 2848 (m), 2823 (w), 1716 (w), 1576 (w), 1449 (m), 1354 (w), 1284 (m), 1226 (w), 1093 (w), 1036 (w)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 202 ( $M^+$ , 100), 201 (43), 187 (92), 174 (78), 159 (30), 145 (15), 128 (12), 115 (15), 91 (17), 87 (14), 77 (15); exact mass ( $m/z$ ) calcd for  $C_{14}H_{18}O$ , 202.1358, found, 202.1438. Anal. Calcd for  $C_{14}H_{18}O$ : C, 83.12; H, 8.97. Found: C, 83.36; H, 9.02.

The thermolysis of 0.095 g (0.18 mmol) of the tungsten complex **52** in 36 mL of  $CH_3CN$  under 1 atm of CO provided 0.0137 g (0.068 mmol, 38%) of the phenol **59** after chromatography with a 1:1:16 mixture of  $CH_2Cl_2$ :ether:hexane.

**Thermolysis of Undeca-5,10-diyne Complexes 53 and 54.** The thermolysis of 0.1006 g (0.25 mmol) of the chromium complex **53** in 51 mL of benzene provided, in order of elution, 0.0125 g (0.062 mmol, 24%) of the phenol **60** and 0.012 g (0.049 mmol, 19%) of the lactone **63** after chromatography with a 1:1:8 mixture of  $CH_2Cl_2$ :ether:hexane. Spectral data for **60**:  $R_f$  = 0.25 (1:1:5, EtOAc:hexane); white solid, mp = 86–88 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.69–1.84 (m, 4 H), 2.06 (pentet,  $J$  = 7.6 Hz, 2 H), 2.14 (s, 3 H), 2.53–2.60 (m, 4 H), 2.73 (t,  $J$  = 7.4 Hz, 2 H), 2.82 (t,  $J$  = 7.4 Hz, 2 H), 4.46 (s, 1 H, exchangeable with  $D_2O$ );  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  12.24, 22.65, 22.77, 23.34, 24.54, 27.09, 30.90, 31.82, 115.85, 120.22, 130.96, 133.86, 140.81, 150.09; IR (neat) 3490 (bs), 2929 (vs), 2857 (m), 2837 (m), 1735 (w), 1592 (w), 1457 (m), 1313 (w), 1205 (m), 1065 (w)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 202 ( $M^+$ , 100), 187 (25), 159 (16), 91 (10), 77 (6); exact mass ( $m/z$ ) calcd for  $C_{14}H_{18}O$ , 202.1358, found, 202.1351. Anal. Calcd for  $C_{14}H_{18}O$ : C, 83.12; H, 8.97. Found: C, 82.85; H, 9.09. Spectral data for **63**:  $R_f$  = 0.22 (1:5, EtOAc:hexane); white solid, mp = 90–91 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.62–

1.85 (m, 4 H), 1.86 (s, 3 H), 1.88–2.23 (m, 4 H), 2.32–2.63 (m, 6 H), 3.78 (dd,  $J$  = 12.3, 1 H,  $J$  = 5.6 Hz);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  8.37, 22.69, 22.76, 24.87, 25.36, 27.18, 31.49, 42.13, 51.50, 119.03, 121.10, 145.91, 148.58, 171.20, 208.77; IR (neat) 2937 (m), 2864 (w), 1756 (vs), 1708 (s), 1681 (w), 1647 (m), 1449 (w), 1126 (m), 1024 (s), 759 (w)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 246 ( $M^+$ , 12), 218 (40), 202 (18), 189 (7), 176 (7), 150 (22), 91 (13), 83 (100); exact mass ( $m/z$ ) calcd for  $C_{15}H_{18}O_3$ , 246.1260, found, 246.1272.

The thermolysis of 0.0739 g (0.14 mmol) of the tungsten complex **54** in 28 mL of  $CH_3CN$  under 1 atm of CO provided 0.0103 g (0.051 mmol, 36%) of the phenol **60** after chromatography with a 1:1:5 mixture of EtOAc:hexane.

**Thermolysis of Dodeca-5,11-diyne Complexes 55 and 56.** The thermolysis of 0.131 g (0.32 mmol) of the chromium complex **55** in 64 mL of benzene provided 0.0287 g (0.12 mmol, 39%) of the furanone **64** as an oil after flash chromatography with a 1:1:4 mixture of  $CH_2Cl_2$ :ether:hexane. Spectral data for **64**:  $R_f$  = 0.32 (1:1:4,  $CH_2Cl_2$ :ether:hexanes);  $^1H$  NMR ( $CD_3CN$ )  $\delta$  1.06–1.66 (m, 8 H), 1.71 (t, 3 H,  $J$  = 2.6 Hz), 1.78–1.88 (m, 1 H), 2.07–2.22 (m, 5 H), 2.39–2.45 (m, 1 H), 2.78–2.85 (m, 1 H), 4.61 (dd, 1 H,  $J$  = 6.1, 11.2 Hz);  $^{13}C$  ( $CD_3CN$ )  $\delta$  3.30, 18.84, 23.05, 23.30, 26.75, 27.17, 28.22, 29.16, 35.20, 76.40, 79.75, 80.66, 123.50, 165.06, 175.00; IR (neat) 2940 (s), 2860 (m), 1749 (s), 1679 (m), 1447 (m), 1348 (w), 1107 (w), 1089 (w), 1035 (s)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 232 ( $M^+$ , 18), 217 (5), 203 (13), 187 (35), 176 (16), 164 (23), 152 (56), 145 (18), 133 (18), 119 (20), 107 (22), 91 (33), 81 (100), 77 (22), 67 (29); exact mass ( $m/z$ ) calcd for  $C_{15}H_{20}O_2$ , 232.1463, found, 232.1426.

The tungsten complex **56** (0.114 g, 0.21 mmol) was dissolved in 42 mL of freshly distilled acetonitrile, and the solution was deoxygenated by the freeze-thaw method (one cycle). The flask was sealed at 25 °C under 1 atm of carbon monoxide and placed in a 110 °C oil bath for 22 h. After the removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:1:4 mixture of ether: $CH_2Cl_2$ :hexane. Five fractions were collected, but none of them were isolated in quantities significant enough to warrant characterization.

**Preparation of 1,5,10-Dodecatriyne 81.** To a solution of 0.626 g (8.03 mmol) of 1,5-hexadiyne in 50 mL of THF was added 3.05 mL of 2.5 M *n*-butyllithium (7.63 mmol) at –78 °C. After 5 min, the solution was allowed to warm to room temperature for 1 h. After the solution was recooled to –78 °C, the triflate of 4-hexyn-1-ol was added, which was prepared from 0.75 g (7.6 mmol) of 4-hexyn-1-ol by treatment with triethylamine (0.82 mL, 5.9 mmol) and triflic anhydride (1.13 mL, 6.7 mmol) at 0 °C. After 12 h, the reaction was quenched with brine, and the organic layer was washed with water. Upon removal of solvent from the organic layer, 0.523 g (3.31 mmol, 55% yield) of triyne **81** was isolated after bulb-to-bulb distillation as a colorless oil. Octadeca-2,7,11,16-tetrayne was left as a white solid (0.154 g, 0.65 mmol, 18%) after the distillation. Spectral data for **81**: colorless oil; bp 105–107 °C/3 mmHg,  $R_f$  = 0.48 (1:1:30, ether: $CH_2Cl_2$ :hexane);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.65 (pentet,  $J$  = 7.0 Hz 2 H), 1.77 (t,  $J$  = 2.2 Hz, 3 H), 2.00 (s, 1 H), 2.21–2.26 (m, 4 H), 2.37 (m, 4 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  3.47, 17.83, 17.87, 18.87, 19.08, 28.38, 69.01, 75.95, 78.34, 78.67, 80.57, 83.01; IR (neat) 3293 (s), 2936 (s), 2919 (s), 2859 (m), 2842 (m), 2112 (w), 1434 (s), 1338 (m), 1316 (w), 1292 (w), 1259 (w), 1003 (w), 643 (s)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 158 ( $M^+$ , 2), 157 (12), 143 (38), 128 (100), 119 (32), 115 (47), 91 (97), 77 (43), 65 (44). Anal. Calcd for  $C_{12}H_{14}$ : C, 91.08; H, 8.92. Found: C, 89.82; H, 9.14. Spectral data for octadeca-2,7,11,16-tetrayne: white solid, mp = 44–45 °C;  $R_f$  = 0.38 (1:1:30, ether: $CH_2Cl_2$ :hexane);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.64 (pentet, 4 H,  $J$  = 7.0 Hz), 1.77 (t, 6 H,  $J$  = 2.4 Hz), 2.21–2.26 (m, 8 H), 2.32 (s, 4 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  3.44, 17.81, 17.89, 19.40, 28.42, 75.88, 78.38, 79.26, 80.21; IR (neat) 2948 (m), 2935 (s), 2919 (s), 2858 (m), 2842 (m), 1434 (m), 1339 (w), 1315 (w), 1258 (w)  $cm^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 238 ( $M^+$ , 0.5), 237 (2), 223 (6), 208 (15), 195 (34), 185 (22), 167 (20), 155 (24), 129 (43), 115 (36), 91 (100), 77 (54), 65 (47). Anal. Calcd for  $C_{18}H_{22}$ : C, 90.70; H, 9.30. Found: C, 90.38; H, 9.34.

**Preparation of Triynyl Chromium Complex 82.** Triyne **81** (0.201 g, 1.27 mmol) was dissolved in 20 mL of THF and cooled to –78 °C with a dry ice bath. To this solution was added 0.87 mL of a 1.6 M solution of *n*-butyllithium in hexanes. After 5 min, the cold bath was removed, and the reaction mixture was allowed to warm to room temperature for 1 h. This solution of the anion of **81** was then transferred into a flask containing 0.309 g of chromium hexacarbonyl in 5 mL of THF at –78 °C. After 30 min, the solution was allowed to warm to room temperature slowly for 1 h. The THF was removed, and 20 mL of methylene chloride

was added. To this solution was added 0.5 mL of methyl (trifluoromethane)sulfonate, and the mixture was stirred for 10 min at 0 °C. The reaction was quenched with pH 7 buffer and washed twice with saturated aqueous sodium bicarbonate and once with water and brine. After removal of the volatiles, the residue was loaded onto a silica gel column. Elution with a 1:9 mixture of EtOAc:hexane gave 0.330 g (0.84 mmol, 66%) of carbene complex **82** as a dark red-brown oil. Spectral data for **82**:  $R_f$  = 0.15 (1:15, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.63 (pentet,  $J$  = 6.8 Hz), 1.77 (t,  $J$  = 2.1 Hz, 3 H), 2.20–2.26 (m, 4 H), 2.52 (m, 2 H), 2.96 (t,  $J$  = 7.1 Hz, 2 H), 4.32 (s, 3 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.44, 17.75, 17.82, 18.37, 21.38, 28.25, 65.95, 76.06, 77.85, 78.12, 81.27, 86.46, 137.71, 216.07, 225.23, 318.98; IR (neat) 2950 (w), 2922 (w), 2845 (w), 2169 (m), 2063 (s), 1994 (m), 1935 (vs), 1429 (m), 1330 (w), 1244 (m), 1126 (s), 943 (w), 685 (m), 650 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 392 ( $\text{M}^+$ , 20), 280 (16), 252 (100), 237 (22), 222 (90), 106 (54), 91 (72).

**Preparation of Triynyl Tungsten Complex 83.** Tryine **81** (0.206 g, 1.30 mmol) was dissolved in 20 mL of THF and cooled to 0 °C with an ice bath. To this solution was added 0.89 mL of a 1.6 M solution of *n*-butyllithium in hexanes. After 5 min, the cold bath was removed, and the solution was warmed to room temperature for 1 h. This solution of the anion of **81** was then transferred into a flask containing a slurry of 0.504 g of tungsten hexacarbonyl in 5 mL of THF at 0 °C. After 5 min, the solution was allowed to warm to room temperature slowly for 1 h. To this solution was added 0.7 mL of methyl fluorosulfonate, and the mixture was stirred for 15 min at 0 °C. The reaction was quenched with pH 7 buffer solution and washed twice with saturated aqueous sodium bicarbonate and once with water and brine. Upon removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:1:16 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane gave 0.354 g (0.68 mmol, 52%) of carbene complex **83** as a dark red-brown oil along with 0.204 g of tungsten hexacarbonyl. Spectral data for **83**:  $R_f$  = 0.35 (1:1:16, ether: $\text{CH}_2\text{Cl}_2$ :hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.63 (pentet,  $J$  = 7.1 Hz, 2 H), 1.76 (s, 3 H), 2.19–2.26 (m, 4 H), 2.51 (t,  $J$  = 7.0 Hz, 2 H), 2.81 (t,  $J$  = 7.0 Hz, 2 H), 4.26 (s, 3 H);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  3.31, 17.99, 18.15, 18.23, 21.67, 28.71, 65.58, 76.32, 78.16, 78.32, 81.45, 91.41, 135.61, 197.83, 205.62, 290.85; IR (neat) 2946 (m), 2921 (m), 2843 (w), 2367 (w), 2180 (m), 2070 (s), 1942 (vs), 1437 (m), 1315 (w), 1246 (s), 1131 (s), 953 (w), 643 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 524 ( $\text{M}^+$ , 5,  $^{184}\text{W}$ ), 412 (4,  $^{184}\text{W}$ ), 384 (12,  $^{184}\text{W}$ ), 364 (9,  $^{184}\text{W}$ ), 352 (10,  $^{184}\text{W}$ ), 268 (18,  $^{184}\text{W}$ ), 240 (7,  $^{184}\text{W}$ ), 212 (6,  $^{184}\text{W}$ ), 137 (8), 95 (9), 71 (10), 69 (52). Anal. Calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_6\text{W}$ : C, 43.53; H, 3.08. Found: C, 45.12; H, 3.68.

**Diels–Alder Reaction of Chromium Complex 82 with Danishefsky's Diene 84.** A 25-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with 0.179 g (0.46 mmol) of carbene complex **82**, 0.147 g (0.68 mmol) of 1-methoxy-3-(*tert*-butyldimethylsilyloxy)butadiene, and 2 mL of benzene. The solution was deoxygenated by the freeze–thaw method (1 cycle) and back-filled with 1 atm of carbon monoxide. After the solution was stirred at 25 °C for 12 h, the volatiles were removed, and the residue was loaded onto a silica gel column. Elution with a 1:30 mixture of EtOAc:hexane gave 0.226 g (0.39 mmol, 87%) of carbene complex **85** as a red oil. Spectral data for **85**:  $R_f$  = 0.41 (1:15, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.21 (s, 6 H), 0.98 (s, 9 H), 1.60 (pentet,  $J$  = 6.8 Hz, 2 H), 1.76 (t,  $J$  = 2.6 Hz, 3 H), 2.15–2.22 (m, 4 H), 2.40–2.43 (m, 2 H), 2.51 (t,  $J$  = 6.9 Hz, 2 H), 4.38 (s, 3 H), 6.72 (m, 2 H), 6.80 (m, 1 H);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  –4.43, 3.33, 18.16, 18.36, 18.51, 19.68, 25.74, 28.34, 32.12, 65.44, 78.44, 79.64, 80.78, 81.84, 118.16, 120.54, 123.26, 131.97, 146.24, 156.10, 216.49, 224.61, 359.36; IR (neat) 2954 (w), 2932 (w), 2859 (w), 2062 (s), 1988 (w), 1939 (vs), 1599 (m), 1558 (w), 1485 (w), 1448 (w), 1292 (m), 1252 (m), 1136 (w), 1097 (w), 979 (w), 838 (m), 649 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 574 ( $\text{M}^+$ , 2), 525 (4), 438 (67), 410 (46), 395 (56), 380 (87), 323 (20), 276 (8), 220 (42), 108 (56), 89 (98), 80 (100).

**Diels–Alder Reaction of Triynyl Tungsten Complex 83 with Danishefsky's Diene 84.** A 100-mL flask was charged with carbene complex **83** (0.9098 g, 1.74 mmol), 1-methoxy-3-(*tert*-butyldimethylsilyloxy)butadiene (**84**) (0.56 g, 2.61 mmol), and 20 mL of benzene. The solution was stirred under a blanket of nitrogen at 25 °C for 12 h. After removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:30 mixture of EtOAc:hexane gave 1.01 g (1.43 mmol, 82% yield) of carbene complex **86** as a red oil. Spectral data for **86**:  $R_f$  = 0.25 (1:30, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.21 (s, 6 H), 0.98 (s, 9 H), 1.62 (pentet,  $J$  = 7.0 Hz, 2 H), 1.76 (t,  $J$  = 2.4 Hz, 3 H), 2.17–2.24 (m, 4 H), 2.37 (t,  $J$  = 7.7 Hz, 2 H), 2.55 (t,  $J$  = 7.5 Hz, 2 H), 4.60 (s, 3 H), 6.67 (d,  $J$  = 1.6 Hz, 1 H), 6.70 (dd,  $J$  = 8.3, 2.1 Hz, 1 H), 7.04 (d,  $J$  = 7.3 Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  –4.40, 3.50, 17.85, 17.93, 18.24, 20.39, 25.63, 28.40, 32.82, 69.26, 75.96, 78.30, 79.46, 80.35, 117.31,

120.94, 126.67, 133.04, 150.04, 156.24, 196.96, 204.25, 330.78; IR (neat) 2952 (w), 2922 (w), 2860 (w), 2070 (s), 1925 (m), 1928 (vs), 1592 (m), 1252 (m), 1230 (s), 1170 (m), 997 (w), 829 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 706 ( $\text{M}^+$ , 1,  $^{184}\text{W}$ ), 650 (1,  $^{184}\text{W}$ ), 622 (1,  $^{184}\text{W}$ ), 400 (32), 343 (58), 143 (100).

**Thermolysis of the Triynyl Chromium Complex 85 in Benzene.** A 50-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with 0.081 g (0.14 mmol) of the chromium carbene complex **85** and 23.2 mL of benzene. The solution was deoxygenated by the freeze–thaw method (three cycles), and the flask was sealed at 25 °C under 1 atm of argon. The flask was heated at 73–75 °C for 19 h. Upon the removal of solvent from the reaction mixture, the residue was loaded onto a silica gel column. Elution with a 1:1:16 mixture of  $\text{CH}_2\text{Cl}_2$ :ether:hexane gave 0.0161 g (0.042 mmol, 30%) of phenol **89a** and 0.0142 g (0.032 mmol, 24%) of the lactone **90**. Spectral data for **89a**: colorless oil,  $R_f$  = 0.38 (1:1:16,  $\text{CH}_2\text{Cl}_2$ :ether:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.25 (s, 6 H), 1.02 (s, 9 H), 2.10 (pentet,  $J$  = 7.5 Hz, 2 H), 2.23 (s, 3 H), 2.65 (m, 2 H), 2.68 (m, 2 H), 2.88 (pentet,  $J$  = 7.5 Hz, 4 H), 5.20 (s, 1 H, exchangeable with  $\text{D}_2\text{O}$ ), 6.74 (m, 1 H), 6.76 (s, 1 H), 7.88 (d,  $J$  = 8.0 Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  –4.14, 12.56, 18.19, 24.55, 25.69, 26.54, 30.00, 31.28, 32.16, 117.83, 118.25, 119.28, 119.94, 126.45, 126.64, 131.98, 132.71, 140.68, 142.78, 149.25, 154.01; IR (neat) 3567 (bs), 3028 (w), 2952 (s), 2894 (m), 2857 (m), 1608 (m), 1495 (s), 1471 (m), 1419 (w), 1287 (s), 1247 (s), 1224 (w), 1169 (m), 1073 (m), 999 (w), 969 (m), 852 (s), 839 (s), 781 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 380 ( $\text{M}^+$ , 100), 339 (14), 323 (36), 161 (8), 75 (29), 57 (14); exact mass ( $m/z$ ) calcd for  $\text{C}_{24}\text{H}_{32}\text{O}_2\text{Si}$ , 380.2173, found, 380.2162. Anal. Calcd for  $\text{C}_{24}\text{H}_{32}\text{O}_2\text{Si}$ : C, 75.74; H, 8.48. Found: C, 75.36; H, 8.58. Spectral data for **90**:  $R_f$  = 0.08 (1:1:16,  $\text{CH}_2\text{Cl}_2$ :ether:hexane); light yellow solid, mp = 134–135 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.21 (s, 6 H), 0.98 (s, 9 H), 1.88 (s, 3 H), 1.91 (pentet,  $J$  = 6.2 Hz, 2 H), 2.57–2.61 (m, 4 H), 2.65 (t,  $J$  = 5.9 Hz, 2 H), 2.72 (t,  $J$  = 7.0 Hz, 2 H), 3.65 (s, 3 H), 6.61 (d,  $J$  = 1.6 Hz, 1 H), 6.64 (dd,  $J$  = 8.2, 2.2 Hz, 1 H), 7.21 (d,  $J$  = 8.3 Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  –4.33, 8.52, 18.44, 23.3, 23.70, 25.77, 28.20, 28.83 (two carbons), 60.36, 93.65, 117.92, 118.30, 119.55, 121.94, 124.17, 125.31, 140.23, 145.05, 149.39, 152.98, 155.97, 171.13; IR (neat) 2952 (s), 2931 (s), 2885 (m), 2858 (m), 2835 (w), 1756 (vs), 1645 (m), 1603 (s), 1560 (w), 1493 (s), 1472 (w), 1426 (w), 1283 (s), 1252 (s), 1157 (m), 1133 (m), 1098 (m), 1023 (m), 980 (m), 944 (m), 864 (m), 841 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 438 ( $\text{M}^+$ , 100), 410 (47), 395 (32), 379 (82), 367 (16), 351 (15), 323 (12), 225 (21), 73 (44); exact mass ( $m/z$ ) calcd for  $\text{C}_{26}\text{H}_{34}\text{O}_4\text{Si}$ , 438.2226, found, 438.2200. Anal. Calcd for  $\text{C}_{26}\text{H}_{34}\text{O}_4\text{Si}$ : C, 71.19; H, 7.81. Found: C, 70.98; H, 8.30.

**Thermolysis of Chromium Complex 85 in Acetonitrile.** A 100-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with the chromium carbene complex **85** (0.155 g, 0.27 mmol) and 53.8 mL of acetonitrile. The solution was deoxygenated by the freeze–thaw method (three cycles), and the flask was sealed at 25 °C under 1 atm of carbon monoxide. The flask was placed in a 80 °C oil bath for 27 h. After the removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:9 mixture of EtOAc:hexane gave 0.0323 g (0.076 mmol, 28%) of the furanone **88**. Spectral data for **88**: colorless oil;  $R_f$  = 0.24 (1:9, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.19 (s, 6 H), 0.97 (s, 9 H), 1.71–1.73 (m, 2 H), 1.75 (s, 3 H), 2.01–2.12 (m, 2 H), 2.40 (t, 2 H,  $J$  = 7.4 Hz), 2.74–2.78 (m, 1 H), 2.83–2.91 (m, 2 H), 3.12–3.18 (m, 1 H), 3.20 (s, 3 H), 6.60 (d, 1 H,  $J$  = 1.2 Hz), 6.70 (d of d, 1 H,  $J$  = 7.0 Hz,  $J$  = 1.4 Hz), 7.46 (d, 1 H,  $J$  = 8.4 Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  –4.41, 3.44, 18.16, 18.23, 21.30, 22.55, 25.61, 26.77, 28.92, 51.15, 76.40, 78.10, 103.66, 118.50, 119.36, 126.95, 127.30, 127.45, 137.91, 156.67, 158.87, 171.45; IR (neat) 2955 (s), 2930 (s), 2858 (m), 1768 (vs), 1609 (s), 1576 (w), 1498 (m), 1472 (w), 1329 (w), 1155 (w), 1107 (s), 956 (s), 837 (s), 782 (s)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 426 ( $\text{M}^+$ , 5), 395 (100), 367 (10), 339 (22), 163 (10), 135 (8), 73 (56); exact mass ( $m/z$ ) calcd for  $\text{C}_{25}\text{H}_{34}\text{O}_4\text{Si}$ , 426.2226, found, 426.2263. Anal. Calcd for  $\text{C}_{25}\text{H}_{34}\text{O}_4\text{Si}$ : C, 70.38; H, 8.03. Found: C, 70.54; H, 8.07.

**Thermolysis of Triynyl Amino Chromium Carbene Complex 101.** A solution of the triynyl methoxy chromium carbene complex **85** (0.315 g, 0.55 mmol) in 10 mL of dichloromethane at 0 °C was purged with dimethylamine for 5 min. The color of the solution immediately changed from red to brown-yellow. The crude reaction mixture was washed with pH 7 buffer and dried with anhydrous magnesium sulfate. Upon removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:5 mixture of EtOAc:hexane gave 0.2308 g (0.40 mmol, 72% yield) of the aminocarbene complex **101** as a dark yellow oil. Spectral data for



**101:**  $R_f = 0.30$  (1:5, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.20 (s, 6 H), 0.99 (s, 9 H), 1.27 (brd s, 2 H), 1.61 (brd s, 2 H), 1.78 (brd s, 3 H), 2.19 (brd s, 4 H), 2.48 (brd s, 2 H), 3.08 (brd s, 3 H), 4.00 (brd s, 3 H), 6.57 (brd s, 1 H), 6.78 (brd s, 2 H).

A 200-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with the aminocarbene complex **101** (0.230 g, 0.39 mmol) and 65 mL of benzene. The solution was deoxygenated three times with the freeze-thaw method, and the flask was sealed at 25 °C under 1 atm of argon. The flask was heated at 120 °C in an oil bath for 18 h. The  $^1\text{H NMR}$  spectrum of the crude reaction mixture was very complex; therefore, the crude reaction mixture was dissolved in 15 mL of THF and reduced with  $\text{TiCl}_3/\text{LAH}$  (0.32 g) to destroy any cyclohexadienone metal complexes.<sup>7d</sup> After 1 h, the solution was quenched with water and diluted with ether. The organic layer was washed with brine and dried with anhydrous magnesium sulfate. Upon the removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:1:30 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane gave 0.015 g (0.039 mmol, 10%) of phenol **89a** as the major product.

**Effect of Solvent on the Thermolysis of Tungsten Complex 86.** A 100-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with 0.245 g (0.35 mmol) of the tungsten carbene complex **86** and 69 mL of acetonitrile. The solution was deoxygenated twice via the freeze-thaw method and sealed at 25 °C under 1 atm of carbon monoxide. The flask was placed in an oil bath at 110 °C for 19 h. The crude reaction mixture was filtered through Celite, stripped of volatiles, and loaded onto a silica gel column. Elution with a 1:30 mixture of EtOAc:hexane gave 0.0617 g (0.16 mmol, 47% yield) of the phenol **89a** and 0.0272 g (0.10 mmol, 31% yield) of the bis-phenol **89b**. The spectral data for **89a** were identical to those described above. Spectral data for **89b**:  $R_f = 0.14$  (1:1:16, ether: $\text{CH}_2\text{Cl}_2$ :hexane); white solid, softens at 50–120 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.08 (pentet,  $J = 7.4$  Hz, 2 H), 2.20 (s, 3 H), 2.62–2.68 (m, 4 H), 2.83–2.89 (m, 4 H), 4.88 (s, 1 H), 5.12 (s, 1 H), 6.71–6.73 (m, 2 H), 7.90 (d,  $J = 8.3$  Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  12.55, 24.55, 26.45, 29.96, 31.28, 32.17, 113.16, 115.21, 118.23, 119.19, 126.13, 127.20, 131.91, 132.78, 141.02, 142.79, 149.21, 153.84; IR (neat) 3372 (s), 2930 (s), 2895 (m), 2839 (m), 1612 (m), 1499 (m), 1438 (m), 1349 (m), 1285 (w), 1225 (s), 1153 (m), 1073 (m), 922 (w), 823 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 266 ( $M^+$ , 100), 251 (8), 129 (15), 97 (18), 83 (22), 69 (55), 57 (58); exact mass ( $m/z$ ) calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_2$ , 266.1307, found, 266.1306. Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_2$ : C, 81.17; H, 6.81. Found: C, 81.39; H, 7.19.

The thermolysis of **86** was carried out on similar scales in a number of different solvents with the same procedure described above except that an argon atmosphere was employed. The following results unless otherwise specified were obtained at 0.005 M in **86**: heptane, **89a** (48%); benzene, **89a** (51%); acetonitrile **89a** (63%); acetonitrile at 0.05 M, **89a** (50%), THF, **89a** (53%).

**Synthesis of the Tetracyclic Phenol 89a via a One-Pot Tandem Diels-Alder Reaction/Two-Alkyne Annulation of the Triynyl Tungsten Complex 83 and Danishefsky's Diene.** A 100-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with the triynyl tungsten carbene complex **83** (0.147 g, 0.28 mmol), diene **84** (0.0902 g, 0.42 mmol), and 5.6 mL of acetonitrile. The solution was deoxygenated three times via the freeze-thaw method, and the flask was back-filled with 1 atm of carbon monoxide. The flask was sealed and stirred at room temperature for 16 h. The flask was opened, and the reaction mixture was diluted with 50.6 mL of acetonitrile. The solution was degassed twice with the freeze-thaw method, and then the flask was back-filled with 1 atm of carbon monoxide at 25 °C. The flask was sealed and placed in an oil bath at 110 °C for 23.5 h. The crude reaction mixture was filtered through Celite, and after removal of solvents, the product was purified by flash chromatography on silica gel with a 1:1:30 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane followed by a 1:1:4 solvent mixture to give 0.0635 g (0.17 mmol, 62% yield) of **89a** as an oil. The spectral data of **89a** from this reaction were identical to those of the phenol obtained from the thermolysis of complex **86**.

**Preparation of Iodoendiyne 110.** To 1.12 g (16.0 mmol) of 4-butyne-1-ol at  $-20$  °C was added 32.0 mL of a 1.0 M solution of DIBAL (32.0 mmol, in hexane). After the gas evolution stopped, the solution was stirred at 25 °C for 12 h. The hexane was removed, and the residue was dissolved in 20 mL of THF and treated at  $-78$  °C with a solution of 4.87 g (19.2 mmol) of iodine in 30 mL of THF, which was added via cannula. After being stirred for 20 min at  $-78$  °C, the solution was allowed to warm to room temperature for 1 h. The reaction mixture was quenched with water and diluted with ether. The organic layer was washed  $\text{Na}_2\text{S}_2\text{O}_3$  and water and dried with anhydrous  $\text{MgSO}_4$ . Upon removal of solvent,

3.21 g (98% yield) of an oil was obtained that was identified as a 2:1 mixture of **106** and 4-iodo-1-butanol. This mixture was dissolved in 60 mL of methylene chloride and treated with 2.27 mL (16.3 mmol) of triethylamine and 3.28 mL (19.5 mmol) of triflate anhydride at 0 °C. After the solution was stirred for 2 h, the methylene chloride was removed, and the residue was quickly eluted through a short column of silica gel with a 1:1:4 mixture of ether: $\text{CH}_2\text{Cl}_2$ :hexane. The solvent was removed to give a mixture of triflates that was immediately used in the next step.

At same time, 2.67 g of 1-(trimethylsilyl)-1,6-heptadiyne in 50 mL of THF at  $-78$  °C was treated with 10.7 mL of a 1.6 M solution *n*-butyllithium in hexane. After 5 min, the solution was allowed to warm to 25 °C for 1 h. The solution was cooled to 0 °C and treated with a THF (10 mL) solution of the triflates prepared as described above. After 10 h at 25 °C, the reaction mixture was diluted with ether, washed with water and brine, and dried with anhydrous  $\text{MgSO}_4$ . Upon the removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:10 mixture of chloroform:hexane gave 2.72 g (7.9 mmol, 49%) of iodoendiyne **110**. Spectral data for **110**: colorless oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.15 (s, 9 H), 1.68 (pentet, 2 H,  $J = 6.9$  Hz), 2.20–2.26 (m, 6 H), 2.31 (t, 2 H,  $J = 7.1$  Hz), 6.06 (d, 1 H,  $J = 14.1$  Hz), 6.50–6.53 (m, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.16, 17.88, 18.14, 19.03, 28.14, 35.46, 75.82, 79.14, 80.46, 84.98, 106.49, 144.69; IR (neat) 2957 (m), 2902 (w), 2174 (m), 1249 (s), 944 (w), 842 (s), 759 (m), 684 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 215 (6), 199 (12), 185 (58), 167 (10), 155 (6), 143 (24), 128 (11), 109 (16), 91 (14), 83 (14), 73 (100). Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{Si}$ : C, 48.84; H, 6.15. Found: C, 48.73; H, 6.18.

**Preparation of Endiynyl Tungsten Carbene Complex 111.** To a solution of 0.287 g (0.83 mmol) of iodoendiyne **110** in 20 mL of THF at  $-78$  °C was added *tert*-butyllithium (1.08 mL, 1.84 mmol as a 1.7 M solution in pentane) under argon. After 5 min, the solution was transferred into a slurry of tungsten hexacarbonyl (0.307 g, 0.87 mmol) in 20 mL of THF via cannula at  $-78$  °C. The solution was stirred for 3 h, during the which period the temperature slowly rose to 25 °C. The THF was removed under vacuum, and the residue was dissolved in 30 mL of methylene chloride. The metal acylate was methylated with methyl triflate (0.38 mL, 3.36 mmol) at 0 °C for 40 min. The reaction was quenched with saturated aqueous sodium bicarbonate, and the organic layer was washed with water and brine and dried with anhydrous  $\text{MgSO}_4$ . Upon the removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:30 mixture of EtOAc:hexane gave 0.267 g (0.46 mmol, 55%) of carbene complex **111** as a red oil. Spectral data for **111**:  $R_f = 0.27$  (1:30, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.15 (s, 9 H), 1.69 (pentet, 2 H,  $J = 7.1$  Hz), 2.22–2.36 (m, 8 H), 4.60 (s, 3 H), 6.52–6.57 (m, 1 H), 7.27 (d, 1 H,  $J = 15.2$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.16, 17.78, 17.91, 19.04, 28.09, 32.08, 69.13, 78.84, 80.74, 84.98, 106.45, 138.88, 148.23, 197.46, 203.61, 310.14; IR (neat) 3050 (w), 2957 (m), 2905 (w), 2846 (w), 2175 (m), 2067 (s), 1979 (m), 1919 (vs), 1630 (w), 1607 (m), 1448 (m), 1344 (w), 1249 (s), 1171 (m), 1072 (m), 986 (m), 760 (m), 843 (s), 699 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 584 ( $M^+$ , 15,  $^{184}\text{W}$ ), 472 (8,  $^{184}\text{W}$ ), 444 (26,  $^{184}\text{W}$ ), 409 (21,  $^{184}\text{W}$ ), 155 (16), 89 (28), 73 (100); exact mass ( $m/z$ ) calcd for  $\text{C}_{21}\text{H}_{24}\text{O}_6\text{Si}^{184}\text{W}$ , 584.0852, found, 584.0862. Anal. Calcd for  $\text{C}_{21}\text{H}_{24}\text{O}_6\text{Si}^{184}\text{W}$ : C, 43.17; H, 4.14. Found: C, 45.42; H, 3.91.

**Diels-Alder Reaction of the Endiynyl Tungsten Carbene Complex 111 with 2-Methoxy-1,3-butadiene.** A 25-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with endiynyl carbene complex **111** (0.457 g, 0.78 mmol) and 0.4 mL (3.9 mmol) of 2-methoxy-1,3-butadiene. The mixture was deoxygenated by the freeze-thaw method (two cycles), and the flask was back-filled with 1 atm of argon at 25 °C. After the mixture was stirred at room temperature for 23 h, the volatiles were removed, and the residue was loaded onto a silica gel column. Elution with a 1:30 mixture of EtOAc:hexane gave 0.439 g (0.66 mmol, 84%) of carbene complex **112** as a yellow oil. Spectral data for **112**:  $R_f = 0.36$  (1:30, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.20 (s, 9 H), 1.42–1.44 (m, 1 H), 1.53–1.59 (m, 1 H), 1.69 (pentet, 2 H,  $J = 7.0$  Hz), 1.85–1.89 (m, 2 H), 2.11–2.41 (m, 9 H), 3.50 (s, 3 H), 4.03 (m, 1 H), 4.63 (d, 1 H,  $J = 5.5$  Hz), 4.68 (s, 3 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.18, 16.97, 18.17, 19.22, 28.47, 28.69, 33.57, 33.90, 37.16, 52.40, 71.27, 74.09, 79.83, 80.08, 85.08, 91.36, 106.92, 154.71, 197.85, 204.12, 345.06; IR (neat) 3053 (w), 2996 (w), 2953 (s), 2936 (s), 2854 (m), 2837 (m), 2366 (w), 2175 (s), 2070 (s), 1928 (vs), 1675 (s), 1451 (s), 1378 (m), 1362 (m), 1287 (s), 1251 (s), 1225 (s), 1158 (s), 1045 (s), 967 (s), 920 (m), 843 (vs), 760 (m), 655 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 668 ( $M^+$ , 5,  $^{184}\text{W}$ ), 654 (37,  $^{184}\text{W}$ ), 638 (12,  $^{184}\text{W}$ ), 569 (20,  $^{184}\text{W}$ ), 543 (22,  $^{184}\text{W}$ ), 513 (35,  $^{184}\text{W}$ ), 331 (38), 227 (23), 209 (27), 89 (48), 73 (100). Anal. Calcd for  $\text{C}_{26}\text{H}_{32}\text{O}_7\text{SiW}$ : C, 46.71; H, 4.83. Found: C, 46.34; H, 4.81.

**Thermolysis of the Endiylne Tungsten Carbene Complex 112 in Acetonitrile.** A 200-mL single-necked flask equipped with a threaded high-vacuum stopcock was charged with carbene complex **112** (0.215 g, 0.32 mmol) and 64.2 mL of freshly distilled acetonitrile. The solution was deoxygenated by the freeze-thaw method (three cycles), and the flask was back-filled with 1 atm of carbon monoxide at 25 °C. The flask was sealed and placed in an oil bath at 110 °C for 20 h. After the removal of solvent, the residue was loaded onto a silica gel column. Elution with a 1:2 mixture of EtOAc:hexane gave 0.0212 g (0.062 mmol, 19%) of lactone **113** as a colorless oil. Spectral data for **113**:  $R_f = 0.37$  (1:2, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.16 (s, 9 H), 1.28–1.35 (m, 1 H), 1.42–1.50 (m, 1 H), 1.59–1.68 (m, 1 H), 1.75–1.84 (m, 3 H), 1.96–2.01 (m, 1 H), 2.10–2.51 (m, 9 H), 2.55–2.60 (m, 1 H), 2.94–3.00 (m, 1 H), 4.31 (d, 1 H,  $J = 10.1$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.09, 18.96, 21.88, 24.99, 26.30, 29.81, 33.86, 39.54, 40.04, 46.81, 48.51, 83.37, 85.41, 106.26, 123.32, 162.12, 173.74, 208.85; IR (neat) 2955 (s), 2930 (m), 2859 (m), 2173 (m), 1752 (vs), 1718 (s), 1683 (m), 1450 (w), 1341 (w), 1310 (w), 1248 (m), 1104 (w), 1040 (w), 1005 (m), 900 (w), 843 (s), 759 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 344 ( $\text{M}^+$ , 15), 329 (100), 292 (5), 254 (12), 169 (10), 129 (10), 117 (10), 109 (12), 91 (16), 73 (62); exact mass ( $m/z$ ) calcd for  $\text{C}_{20}\text{H}_{28}\text{O}_3\text{Si}$ , 344.1808, found, 344.1812.

**Thermolysis of the Endiylne Tungsten Carbene Complex 112 in THF.** With the same procedure as described above for the same reaction in acetonitrile, the residue from the thermolysis of 0.238 g (0.36 mmol) of complex **112** in 71.2 mL of THF was chromatographed with a 1:15 mixture of EtOAc:hexane to give 0.057 g (0.15 mmol, 43%) of dienone **114** and 0.0226 g (0.061 mmol, 17%) of dienone **115**. Spectral data for **114**: yellow solid, mp = 157–159 °C;  $R_f = 0.35$  (1:15, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  0.44 (s, 9 H), 1.30–2.40 (m, 15 H), 2.90–2.98 (m, 1 H), 3.18 (s, 3 H), 3.20 (s, 3 H), 4.46–4.47 (brd s, 1 H);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.01, 23.79, 24.27, 28.05, 28.30, 32.60, 34.63, 36.10, 36.52, 47.81, 52.97, 53.64, 84.50, 92.57, 129.94, 135.31, 147.32, 153.53, 167.47, 204.39; IR (neat) 3068 (w), 2949 (s), 2921 (s), 2875 (w), 2838 (m), 1675 (s), 1646 (s), 1562 (s), 1465 (w), 1448 (m), 1380 (w), 1304 (m), 1281 (w), 1243 (m), 1213 (s), 1174 (m), 1148 (m), 1089 (s), 1032 (w), 878 (w), 856 (s), 841 (s), 788 (w), 762 (w)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative

intensity) 372 ( $\text{M}^+$ , 85), 357 (15), 340 (30), 324 (30), 309 (12), 248 (58), 233 (37), 219 (36), 206 (64), 135 (26), 123 (19), 109 (78), 73 (100); exact mass ( $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{32}\text{O}_3\text{Si}$ , 372.2121, found, 372.2109. Anal. Calcd for  $\text{C}_{22}\text{H}_{32}\text{O}_3\text{Si}$ : C, 70.92; H, 8.66. Found: C, 70.76; H, 8.85. Spectral data for **115**: oil,  $R_f = 0.23$  (1:15, EtOAc:hexane);  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  0.46 (s, 9 H), 1.39–2.39 (m, 16 H), 3.02 (s, 3 H), 3.17 (s, 3 H), 4.33 (d, 1 H,  $J = 5.5$  Hz);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.33, 24.04, 27.43, 27.74, 28.04, 28.44, 34.69, 36.19, 38.06, 52.57, 53.21, 53.84, 82.58, 93.18, 102.98, 138.64, 144.00, 155.96, 168.85, 205.64; IR (neat) 3067 (w), 2943 (vs), 2843 (vs), 2898 (s), 2837 (m), 1665 (s), 1642 (vs), 1561 (s), 1438 (m), 1359 (w), 1312 (m), 1281 (w), 1244 (m), 1216 (vs), 1176 (w), 1147 (w), 1084 (s), 1010 (w), 922 (w), 857 (s), 839 (vs), 780 (m)  $\text{cm}^{-1}$ ; mass spectrum  $m/z$  (relative intensity) 372 ( $\text{M}^+$ , 40), 357 (17), 341 (88), 325 (20), 248 (30), 206 (35), 109 (64), 73 (100); exact mass ( $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{32}\text{O}_3\text{Si}$ , 372.2121, found, 372.2129.

The relative stereochemistry of **114** was determined by an X-ray analysis, and the results of this study are presented in the supplementary material.

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**Supplementary Material Available:** Crystal structure data for **114** including atomic parameters, anisotropic thermal parameters, bond distances, and bond angles (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.