Substrate Regulation of Product Distribution in the Reactions of Aryl Chromium Carbene Complexes with Alkynes

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Abstract: The reactions of arylcarbene complexes with alkynes were examined for six of the nine possible substitution patterns for mono- and dioxygenated aryl substituents of the carbene carbon. The product distributions were found to be highly dependent on a number of factors, including solvent, temperature, concentration of alkyne, and the nature of the aryl substituent. The product distributions were determined in nearly all cases for phenol and indene products and in some cases for furans, cyclobutenones, and cyclopentenediones, which were minor products in these reactions. The product distribution for the reaction of each arylcarbene complex was determined as a function of both temperature and alkyne concentration, since the combined product distribution profiles provided a much more sensitive measure of the relative influences of the aryl substituents on the reaction outcome. Furthermore, this distribution profile was determined for the reactions with 3-hexyne and 1-pentyne for each carbene complex. A series of monosubstituted arylcarbene complexes were examined to identify the effects of oxygen substituents at various positions on the aryl ring. The *m*-methoxy group has no effect on the product distribution, whereas the *o*-methoxy group influences the distribution by its ability to chelate to the metal center and the *p*-methoxy group influences the distribution by its ability to donate electrons by resonance. The product distributions from the reactions of the 2,3-, 2,4-, and 2,5-dimethoxy complexes followed the profile expected from the simple sum of the profiles of the monomethoxyl complexes. In all cases where an effect was observed, higher concentrations of alkyne led to a higher selectivity for phenol over indene products. The dependence of the product distribution on the concentration of the alkyne substrate is suggested to be due to a process in which a second molecule of alkyne coordinates to the metal center and determines the chemical outcome of an intermediate that has covalently incorporated the first alkyne. It is further suggested that the special ability of an alkyne to display this effect is related to the ability of an alkyne to readily switch from a 2 to a 4 e^- donor. This phenomenon of substrate regulation of product distribution is termed the allochemical effect, and a mechanistic explanation is developed that features this proposed process and that is refined to accommodate the observed effects of solvent, temperature, chelation, and steric and electronic effects that have been observed for the reaction of carbene complexes and alkynes.

The reaction of chromium Fischer carbene complexes with alkynes was first reported 15 years ago,[1] and since that time much has been learned about this reaction.[2] The reaction has been utilized in synthetic applications more than any other reaction of transition metal carbene complexes, and the full synthetic scope of this reaction has yet to be established.[3] All of the applications that have appeared to date have utilized the ability of this reaction to construct highly functionalized aromatic rings in regioselective fashion under neutral conditions near ambient temperature. For example, a synthesis of 11-deoxydaunomycinone has been reported from our laboratories where the key step is the reaction of the *o*-methoxy complex **2b** with the alkyne **3**, which occurs with high regio- and chemoselectivity in 80% yield.[4,5] Presently we have several syntheses of other natural products underway in which more highly oxygenated arylcarbene complexes will be required in the key benzannulation step, including the synthesis of 7-*con*-*O*-methylnogarol **4**[6] and olivin **7**,[7] the aglycone of olivomycin A.[9] Benzannulations of carbene complexes that bear more than one oxygen substituent on the aryl ring such as **5** and **9** have not been extensively studied,[10] and at the outset there was a certain degree of uncertainty with regard to the success of these proposed benzannulations (Scheme I).

Introduction

The uncertainty associated with the anticipated annulations of the highly substituted complexes **5** and **9** has to do with the fact that these reactions may not give rise to the exclusive formation of six-membered ring annulated phenol products. Under defined conditions, the reaction of arylcarbene complexes and alkynes is, in general, remarkably chemoselective for the formation of phenols. However, depending on the substrates and the reaction conditions, up to twelve structurally different organic products can be produced from this reaction, including 4-alkoxyphenols, indenes, furans, cyclobutenones, vinylcyclopentenediones, phenols, pyrones, vinyl ketenes, and lactones.[2,11,12] The effect of introducing a methoxyl group into the ortho position of an aryl substituent of a carbene complex was known prior to this work and is illustrated in Scheme II. The reaction of the parent phenylcarbene complex **2a** with diethylacetylene gives only the quinone **14a**, whereas, the more electron-rich *o*-methoxy complex **2b** gives both quinone and

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

(2) For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Brown, E. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Casey, C. P. *React. Intermed.* **1985**, 3. (e) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (f) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9. (g) Dötz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; Dieck, H. tom, de Meijere, A., Eds.; Springer: Berlin, 1988. (h) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (i) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, 1989. (j) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (k) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5.

(3) For a list of citations to syntheses, see: Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642, and ref 2k.

(4) Wulff, W. D.; Xu, Y. C. *J. Am. Chem. Soc.* **1988**, *110*, 2312.

(5) For references to other anthracycline syntheses with carbene complexes, see the citations listed in reference 4 and in Dötz, K. H.; Popall, M. *Chem. Ber.* **1988**, *121*, 665.

(6) For initial studies, see refs 2e, 2j, and 8.

(7) For initial studies, see: Peterson, G. A.; Kunng, F. A.; McCallum, J. S.; Wulff, W. D. *Tetrahedron Lett.* **1987**, *28*, 1381, and ref 2f.

(8) (a) Semmelhack, M. F.; Jeong, N. *Tetrahedron Lett.* **1990**, *31*, 605. (b) Semmelhack, M. F.; Jeong, N.; Lee, R. L. *Tetrahedron Lett.* **1990**, *31*, 609.

(9) *Antineoplastic Agents*; Remers, W. A., Ed.; Wiley Interscience: New York, 1984.

(10) The only previous examples of annulations of arylcarbene complexes with at least two oxygen substituents can be found in ref 8 and in Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1991**, *56*, 2115.

(11) Xu, Y. C.; Challener, C. A.; Dragisich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269.

(12) Brandvold, T. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1645.

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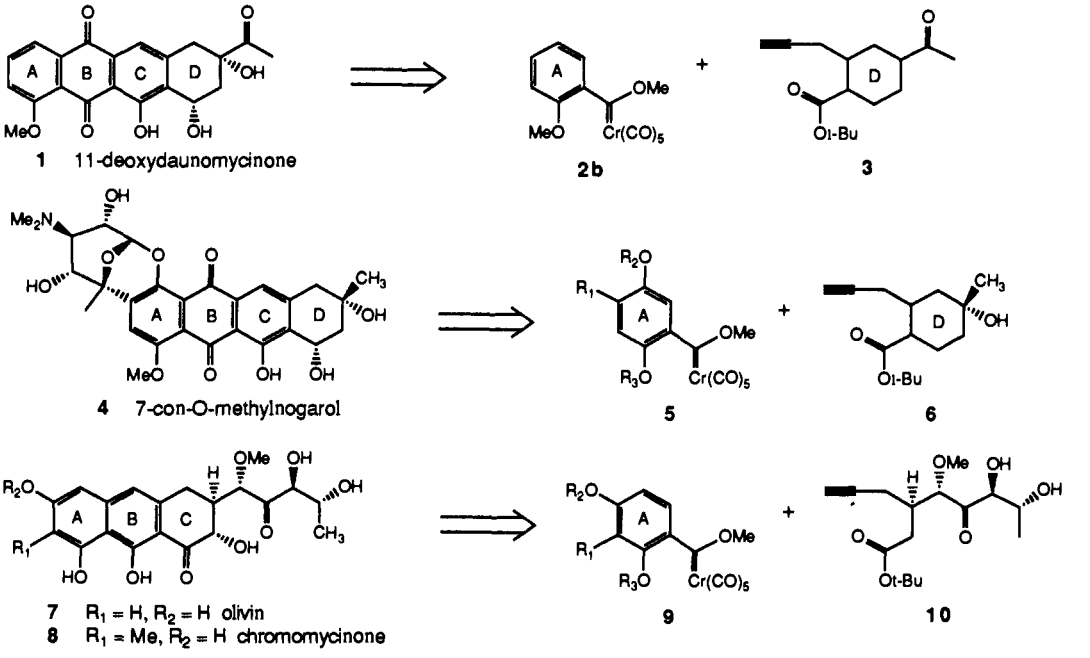
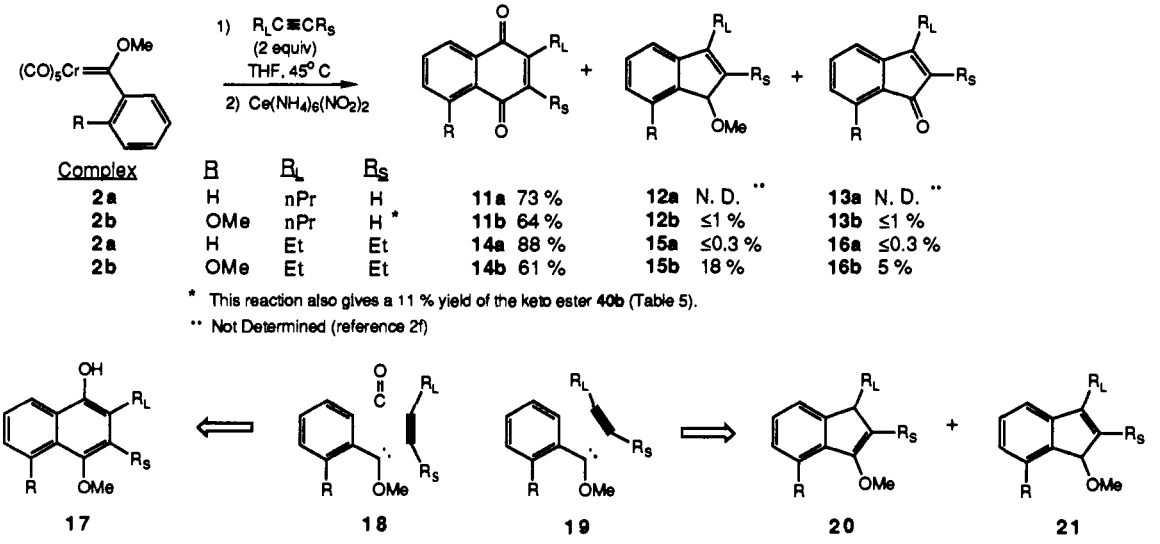
Scheme I



Scheme II



Complex	R	R_L	R_S			
2a	H	nPr	H	11a 73 %	12a N. D. **	13a N. D. **
2b	OMe	nPr	H *	11b 64 %	12b ≤1 %	13b ≤1 %
2a	H	Et	Et	14a 88 %	15a ≤0.3 %	16a ≤0.3 %
2b	OMe	Et	Et	14b 61 %	15b 18 %	16b 5 %

* This reaction also gives a 11 % yield of the keto ester **40b** (Table 5).

** Not Determined (reference 2f)

indene products.[2e,2f,2j,13] It should be noted that in previous studies[2f] it has been most convenient to employ an oxidative workup[14] for these reactions, in which case the phenol products **17** are typically isolated as the quinones, and the indene products **20** and **21** are isolated in either the unoxidized, oxidized (indenone), or hydrolyzed (indanone) form. The indene products differ from the phenol products only in that a CO ligand from the metal is incorporated into the phenols but not into the indenes (**18** versus **19**, Scheme II). The distribution between phenol and indene products from the reaction of **2b** is dependent on the nature of the alkyne. As indicated in Scheme II, internal alkynes give mixtures of the two products, whereas terminal alkynes are chemoselective for the phenol products. This chemoselectivity of the reactions of the *o*-methoxy complex **2b** with terminal alkynes has been taken advantage of in a number of synthetic applications.[2,4,5,15]

In planning syntheses such as those outlined in Scheme I, the preferred retroanalysis is back to a terminal acetylene since it has been firmly established that terminal acetylenes are incorporated with high regioselectivity[17] and since, as discussed above, key complexes such as the *o*-methoxy complex **2b** are more chemoselective for phenol products with terminal alkynes than internal

(13) A preference for indene products has also been observed for the more electron-rich amino carbene complexes. See ref 2f and (a) Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *111*, 2059. (b) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (c) Yamashita, A.; Toy, A.; Watt, W.; Muchmore, C. R. *Tetrahedron Lett.* **1988**, *29*, 3403.

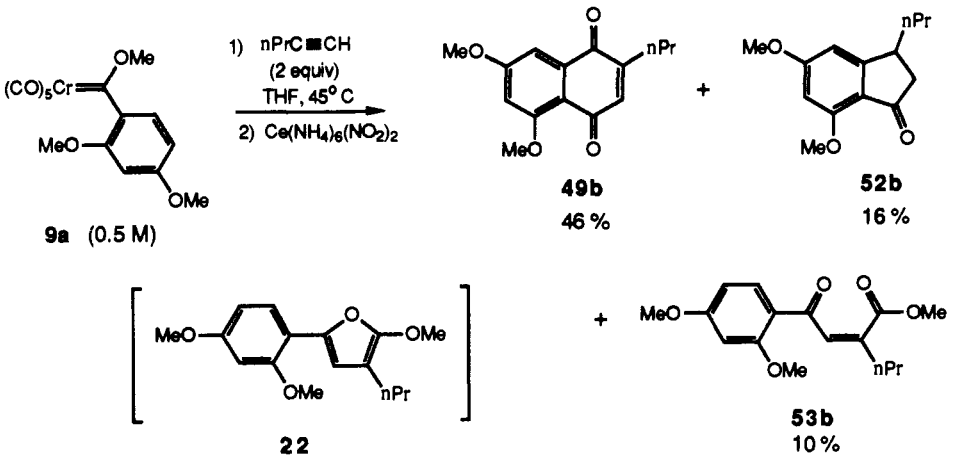
(14) The advantages of employing an oxidative workup are that many unstable metal complexes are destroyed, liberating their organic ligands and thus simplifying separation, and that the phenol products are in some cases somewhat unstable to air and are best isolated as their quinones. The disadvantage is that some minor organic products may be lost or the yields of major products may be affected if they are unstable to these conditions. In this work, oxidative workups will be employed, unless otherwise specified, to screen for phenol and indene products and, to a lesser extent, for furan[8,16] and vinylcyclopentenedione[11] products.

(15) (a) Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W. D.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* **1982**, *104*, 5850. (b) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W. D.; Zask, A. *Tetrahedron* **1985**, *41*, 5803.

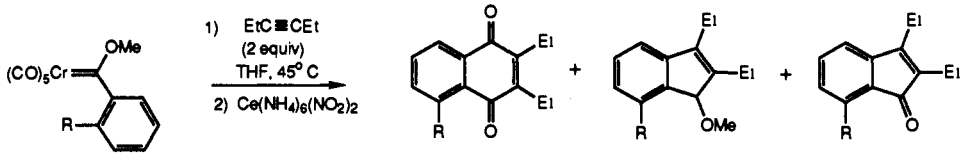
(16) (a) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177. (b) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520. (c) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

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

Scheme III



Scheme IV



2	R	[2]	Temp (°C)			
2b	OMe	0.5	45	14b 61 %	15b 18 %	16b 5 %
2b	OMe	0.005	45	14b 5 %	15b 66 %	16b 9 %
2b	OMe	0.5	110	14b 29 %	15b 53 %	16b 10 %
2a	H	0.12	45	14a 88 %	15a ≤ 0.3 %	16a ≤ 0.3 %

alkynes. However, it became readily apparent that a similar adaptation of the benzannulation of carbene complexes to the synthesis of olivin **7** (Scheme I) would not be as straightforward when it was found that the reaction of the 2,4-dimethoxyphenyl carbene complex **9a** with 1-pentyne was not chemoselective for the quinone **49b** (Scheme III, Table VIII). This reaction gave both the six- and five-membered ring annulation products **49b** and **52b** as well as keto ester **53b**, which is a result of the oxidation of furan **22**, a member of a known class of primary products of these reactions.[8,16] Clearly a reaction more chemoselective for phenol formation would be desirable in a planned synthesis of olivin. It was anticipated that the optimization of this reaction would be greatly aided by a deeper understanding of the reactions of arylcarbene complexes with acetylenes.

Although the effects of the *o*-methoxy substituent in the reactions of complex **2b** with alkynes were known, their origins had not been determined. Also complicating these reactions is the observation that we made 3 years ago that the product distribution from the reaction of the complex **2b** with diethylacetylene is dependent on the concentration (Scheme IV).[2f] The yield of the quinone **14b** falls from 61% to 5% when the concentration is dropped from 0.5 to 0.005 M. We further demonstrate here that the product distribution in the benzannulation reaction is dependent on the concentration of the alkyne and not on the concentration of the carbene complex.[18] We also report here the first observation of the dependence of the distribution between phenol and indene products on the reaction temperature. This effect is illustrated in Scheme IV in the reaction of **2b** with diethylacetylene where the yield of quinone **14b** drops from 61% to 29% when the temperature is raised from 45 to 110 °C. In the present work, the effect of concentration and temperature will both be carefully detailed for the reactions of carbene complexes and alkynes in general. In addition, the origin of the effect of the *o*-methoxy group on the partition between phenol and indene products will be examined.

One of the overall goals of the work described herein is to further establish the synthetic scope of the reactions of arylcarbene complexes with alkynes. In particular, this will be pursued with electron-rich arylcarbene complexes in an attempt to establish optimal procedures for application of the benzannulation reaction to the synthesis of olivin and 7-*con*-*O*-methylnogarol. The significance of this work will hopefully transcend our efforts toward the syntheses in Scheme I, since most polycyclic aromatic natural products contain predominantly electron-rich arene rings that are most typically substituted with oxygen.

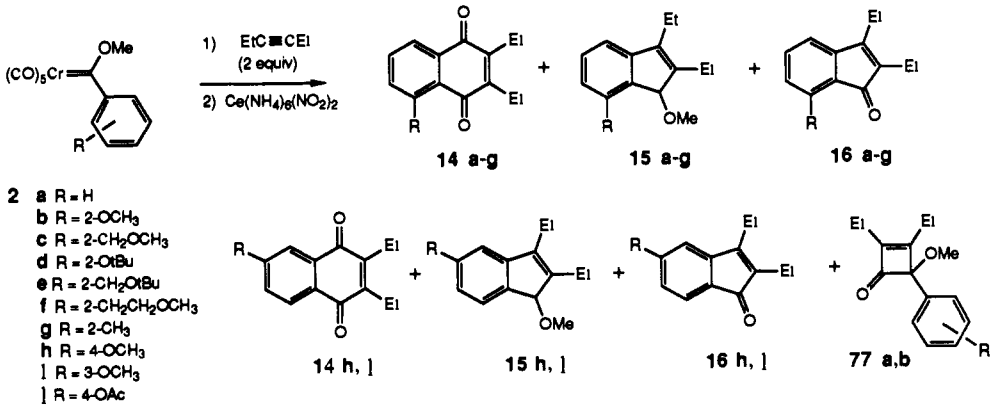
The other major goal of this work will be to gain a better understanding of the mechanism of the benzannulation reaction, with particular attention paid to the processes by which a variety of factors can influence the product distribution. Although the effect of alkyne concentration on product distribution has been previously observed in one particular reaction, the results to be found here more thoroughly define the scope of this phenomenon. The traditional mechanistic proposals for the benzannulation reaction cannot account for the effects of alkyne concentration nor can they account for many of the other factors observed in this study that influence product distribution, including temperature, solvent, and chelation effects. Specifically, it was the goal to identify, at the very least, a mechanistic explanation that is consistent with all of the presently known facts concerning the benzannulation reaction for the purpose of guiding considerations of the implementation and strategic deployment of the benzannulation reaction in synthetic organic chemistry.

Reactions of Monosubstituted Aryl Complexes with 3-Hexyne

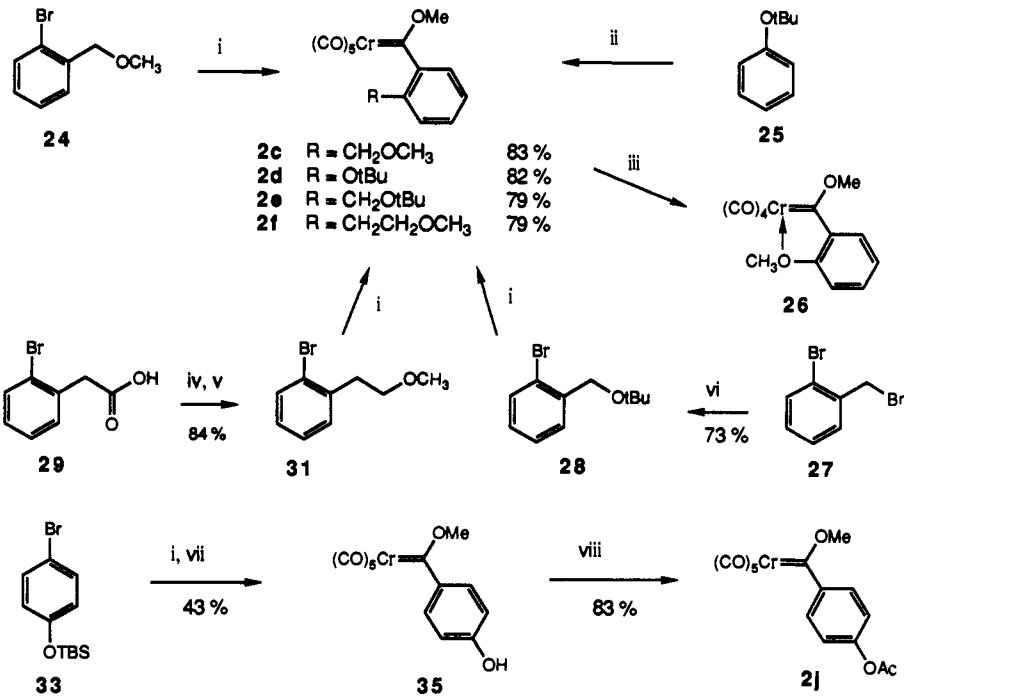
Before embarking directly on the optimization of the annulations of the dioxygenated complexes **5** and **9**, it was decided to first identify the effects of a single oxygen substituent on the aryl ring. As mentioned above, the reactions of the *o*-methoxy complex **2b** had been previously described; however, it had not been determined how the methoxyl group influences the product distribution.[2e,2f,2j,4,5,15] The role of the methoxyl group on the product partition could be due to steric effects, to electron donation to the aryl ring by resonance, or by chelation of the oxygen of the methoxyl group to the metal at an intermediate along the pathway to either of the two products. To distinguish between these possibilities, the series of monosubstituted complexes **2a–j** were prepared and their reactions with 3-hexyne and 1-pentyne were examined (Scheme V).

(18) This has also been demonstrated for a molybdenum complex: Brandvold, T. A.; Chan, K. S.; Wulff, W. D.; Mitchell, J.; Clardy, J. C. To be submitted for publication.

Scheme V



Scheme VI



i, (a) nBuLi, (bO $Cr(CO)_6$, (c) Me_3OBF_4. ii, (a) tBuLi/cyclohexane, reflux, (b) $Cr(CO)_6$, (c) Me_3OBF_4. iii, heat or vacuum. iv, BH_3. v, NaH, CH_3I. vi, tBuOH, NaH, THF/DMF. vii, $NaOCH_3$, CH_3OH. viii, Ac_2O, pyridine, DMAP.

Table I. Temperature and Solvent Effects in Reactions of **2b** with 3-Hexyne[a]

series	aux group R	solvent	[2] (M)	temp (°C)[b]	isolated yield (%) 14b	15b	16b	total mass recovery (%)	six/five
b	2-OCH_3	THF	0.5	45	61	18	5	84	2.7
			0.5	110	29	53	10	92	0.5
			0.5	180	13	38	18	69	0.2
		PhH	0.5	45	77	2	5	84	11.0
			0.5	110	29	6	37	72	0.7
			0.5	180	16	12	44	72	0.3
		heptane	0.5	45	81	<2	<4	~87	>14
			0.5	110	54	9	35	98	1.2

[a] Two equivalents of alkyne. [b] Reaction times are 16–24 h at 45 °C, 20–30 min at 110 °C, and 5 min at 180 °C.

The preparation of complexes **2b**, **2i**, and **2h** were accomplished according to published procedures.[19] The preparation of complex **2d** has been improved by modification of the published procedure,[2f] which is indicated in Scheme VI. The complexes **2c**, **2e**, **2f**, **2g**, and **2j** are new, and all could be prepared in good yields as outlined in Scheme VI and as detailed in the Experimental Section. The only preparation that needs special mention is the *p*-acetoxy complex **2j**. Since *p*-bromophenyl acetate was not expected to undergo clean metal–halogen exchange with *n*-butyllithium, the *p*-acetoxy complex **2j** was prepared in a two-step procedure from the silylated bromophenol **33**, where the silyl group was replaced by acetate after the carbene complex was prepared.[20] It has previously been reported that the *o*-methoxy complex **2b** can be converted with slight heating to the tetracarbonyl chelated species

(19) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Muller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

(20) For an alternate method of preparation of complexes of this type, see: Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839.

Table II. Concentration and Solvent Effects in Reactions of **2b** with 3-Hexyne

solvent	temp (°C)	[2] (M)	[alkyne]	time[a]	isolated yield (%)				total mass recovery (%)	six/five[b]
					14b	**15b**	**16b**	**77b**		
THF	45	0.5	1.0	24 h	61	18	5		84	2.7
		0.05	0.1	12 h	46	42	1	3	92	1.1
		0.005	0.01	2 days	5	66	9		80	0.07
		0.05	1.0	11 h	84	5	1	2	92	14.3
		0.005	1.0	37 h	81	5	<1	5	91	17.2
		0.05	8.8[e]	12 h	91	<1	<1		91[c,d]	>91
THF	110	0.5	1.0	30 min	29	53	10		92	0.41
		0.5	1.0	20 min	26	54	10		90[e]	0.47
		0.05	0.1	1 h	9	68	11		88	0.11
		0.005	0.01	2 h	Tr[f]	65	10		75	0.01
		0.05	1.0	1 h	38	46	7		91	0.72
		0.005	1.0	12 h	45	31	8		84	1.15
		0.5	1.0	2 h	28	47	<1		75[g]	0.60
		0.005	0.01	2 h	8	62	10		80[g]	0.11
DMTHF[h]	45	0.5	1.0	36 h	88	6	Tr[f]		94	14.7
		0.005	0.01	58 h	28	52	2		82	0.52
CH_3CN	45	0.5	1.0	24 h	6	5	6	78	95	7.6
		0.05	0.1	24 h	3	24	12	44	83	1.3
		0.005	0.01	48 h	Tr	31	25	25	81	0.45
PhH	45	0.5	1.0	24 h	77	2	5		84	11.0
		0.005	0.01	48 h	21		37		58	0.57
PhH	110	0.5	1.0	30 min	29	6	37		72	0.67
		0.05	0.1	13 h	5	8	53		66	0.08
		0.005	0.01	2 h	≤1	3	68		71	0.01
heptane	110	0.5	1.0	50 min	54	9	35		98	1.2
		0.5	1.0	25 min	60	1	38		99[e]	1.5
		0.5	1.0	25 min	36	Tr[f]	30		66[i,j]	1.2

[a] Not necessarily optimized. [b] For reactions where **77b** is formed, this ratio is (**14b** + **77b**)/(**15b** + **16b**). [c] Reaction carried out in neat alkyne. [d] See ref 25. [e] Run in the presence of 1.5 equiv of $tBuMe_2SiCl$. [f] Trace observed but amount not determined. [g] Reaction carried out in a flask sealed under 1 atm of CO at 45 °C and then heated to 110 °C. [h] 2,5-Dimethyltetrahydrofuran. [i] Run in the presence of 1.5 equiv of Ac_2O. [j] A 40% yield of *o*-anisaldehyde was also obtained.

26 (Scheme VI) and that either species gives the same distribution of products in their reactions with alkynes.[2e,4,5,21] In this work, all of the complexes with ortho oxygen substituents were isolated and all of their reactions examined on the pentacarbonyl species with the exception of complex **9**. In this case, both the complex **9d** and the nonchelated complex **9c** were examined (Table X), and this represents the first side-by-side comparison of a chelate, nonchelate pair under a variety of conditions.

A study of the effects of temperature and solvent on the reaction of the *o*-methoxy complex **2b** with 3-hexyne is presented in Table I. At 45 °C this reaction is slightly more selective for the quinone product versus the indene products (six/five ratio) in benzene versus THF, which is consistent with previous observations of the effect of solvent on the benzannulation reaction.[2f] The effect of temperature on the distribution of products from the reaction of Fischer carbene complexes and alkynes has not been previously reported. As indicated by the data in Table I, the selectivity of the reaction of the *o*-methoxy complex **2b** and 3-hexyne can be reversed by raising the temperature. At 45 °C the reaction is moderately selective for quinone formation, whereas at 180 °C the reaction is selective to approximately the same degree for indene formation.[22] It was actually surprising to find that the benzannulation reaction was successful at 180 °C, since it is known that these complexes will thermally dimerize at 130 °C.[23] While this level of sensitivity of the product distribution to the temperature is not seen for all complexes to be reported in this work, the direction of change (if any) is always the same; higher temperature is associated with higher proportions of indene products relative to quinones.

As indicated by the data in Table II, the proportion of indene products from the reaction of the *o*-methoxyphenyl complex **2b** with 3-hexyne increases with decreasing concentration. If this influence of the concentration is brought to bear in concert with the influence of temperature seen in Table I, the reaction of **2b** with 3-hexyne in THF can be essentially driven to give only indene products by raising the temperature to 110 °C and by lowering the concentration to 0.005 M. At the other extreme, this reaction can be driven exclusively to phenol products at 45 °C and 8.8 M alkyne (neat). The data in Table II also reveal that the product distribution from the reactions at 45 °C is dependent on the concentration of the alkyne (entries 1–3, entries 2, 4, and 6, and entries 3 and 5) and not on the concentration of the carbene complex (entries 1, 4, and 5). These same observations were also made at 110 °C with the effect that the whole distribution is shifted toward the indene products. Furthermore, it is to be noted that the presence of a carbon monoxide atmosphere does not affect the product distribution (entries 7, 9, 13, and 14). It was not possible to perform the reaction under carbon monoxide at 45 °C since after a week at this temperature there appeared to be little reaction. It is also to be noted that we have examined the effect of the presence of $tBuMe_2SiCl$ and Ac_2O on the reaction of **2b** with 3-hexyne (entries 8, 26, and 27 in Table II). These experiments were prompted by an observation made by Boger that the benzannulation reaction is accelerated by acetic anhydride.[10,24] However, the presence of these reagents had no effect on either the rate or the product distribution of this reaction. While the same level of sensitivity of the product distribution to the concentration of the alkyne is not seen for all complexes to be reported in this work, the direction of change (if any) is always the same; lower concentration of alkyne is associated with higher proportions of indene products relative to quinones.

(21) (a) Reference 2i, pp 216 and 241. (b) Dötz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267.

(22) Since the reaction of complex **2b** with 3-hexyne is sensitive to the concentration, it was deemed necessary as a control to examine the reaction of complex **2b** with a higher boiling alkyne to eliminate the possibility that the vapor-phase concentration of 3-hexyne in the head space of the sealed reaction vessel was higher than expected, thus contributing to an increase in indene formation as a result of a decreased solution concentration of 3-hexyne (bp 81.5 °C). The reaction of **2b** with 6-dodecyne (bp 209 °C) paralleled the reaction with 3-hexyne under indene-forming conditions (110 °C, 0.005 M), giving a 96% yield of the five-membered ring products (**36b** and **37b**) with no evidence for quinone formation (see Experimental Section).

(23) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Müller, J.; Merner, H. *J. Organomet. Chem.* **1969**, *16*, P29.

(24) (a) Boger, D. L.; Jacobson, I. C. *Tetrahedron Lett.* **1989**, *30*, 2037. (b) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1990**, *55*, 1919.

(25) We previously reported[2f] that this reaction gave a 44% yield of **14b**, but we have since found that this was due to an ~2% contamination of the 3-hexyne that was used by 3-hexyn-2-yl hydroperoxide.

Table III. Steric Effects of *o*-Methoxy Group in Reactions of **2b** with 3-Hexyne[a]

series	aux group R	solvent	[2] (M)	temp (°C)[b]	isolated yield (%) 14	15	16	77	total mass recovery (%)	six/five[c]
b	2-OCH_3	THF	0.5	45	61	18	5		84	2.7
			0.5	110	29	53	10		92	0.5
			0.005	110	Tr[d]	65	10		75	0.01
g	2-CH_3	THF	0.5	45	87	≤1	≤1		87	87
			0.5	110	77	≤1	≤1		77	77
			0.005	110	58	16	1		74	3.6
			0.001	110	37	17	≤1		54[e]	2.2
a	2-H	THF	0.12	45	88	≤0.3	≤0.3		88[f]	160
			0.005	110	87	≤1	≤1		87	87
		CH_3CN	0.5	45	57	Tr[d]	ND[g]	23	80	>80
			0.05	45	37	5	5	24	71	6.1
			0.005	45	24	14	15	19	72	1.5

[a] The initial concentration of the alkyne was twice that of **2**. [b] Reaction times are 16–24 h at 45 °C and 0.5 M, 30–40 min at 110 °C and 0.5 M, 1–2 h at 110 °C and 0.005 M, and 44 h at 45 °C and 0.005 M. [c] For reactions in acetonitrile this ratio is (**14** + **77**)/(**15** + **16**). [d] Trace observed but amount not determined. [e] Reaction time 14 h. [f] Reference 2f. [g] Yield not determined.

The effect of coordinating versus noncoordinating solvents on the partition between phenol and indene products has previously been examined, and it was found that coordinating solvents shift the distribution in favor of indene or non-carbonyl-inserted products.[2e,2f,13] The data in Tables II and III reveal that the reactions of the phenyl complex **2a** and the *o*-methoxy complex **2b** with 3-hexyne conform to the previous observations, with the exception of the reaction of **2b** in acetonitrile. In this solvent, substantial amounts of the carbonyl-inserted cyclobutenone product **77** is formed, and possible mechanisms for the formation of this product in this solvent for this complex have been discussed.[2f] The data in Tables II and III represent the first examination of the effects of the concentration on the product partition in both coordinating and noncoordinating solvents. In all cases and in all solvents it was found that the proportion of phenol products increased with increasing concentration of the alkyne substrate. Particularly informative are the reactions in THF versus 2,5-dimethyltetrahydrofuran (DMTHF). The reactions in DMTHF are much more selective for phenol products than those in THF under the same conditions. In fact, the product distributions in DMTHF are very similar to those for benzene (Table II) or heptane (Table I) under the same conditions and are the best evidence that the coordinating ability of the solvent is associated with increased proportions of indene products from the benzannulation reaction.

The initial experiments to determine the source of the effect of the methoxyl group on the product distribution in the reaction of the *o*-methoxy carbene complex **2b** with 3-hexyne were designed to probe the possibility that it was due to steric interactions. This was done by comparing the reactions of the *o*-methoxyphenyl complex **2b**, the *o*-methylphenyl complex **2g**, and the parent phenyl complex **2a** with 3-hexyne. It is clear from the data in Table III that sterics alone cannot account for the observed propensity of the *o*-methoxyphenyl complex **2b** to give indene products relative to either the parent phenyl complex **2a** or the *o*-methylphenyl complex **2g**. The data in Table III present product distributions over changes in both temperature and concentration that in combination provide a more sensitive profile of the reactivity of each complex than could be obtained by changing either variable independently. This tactic proved valuable in the study of the *o*-methylphenyl complex **2g** where indene products were only observed at high temperature (110 °C) and at low concentration (≤0.005 M). This type of product distribution profile over both temperature and concentration will be routinely presented for all reactions described in this work to provide a more sensitive indication of the effects of various substituents of the aryl ring of the carbene complex on the benzannulation reaction.

The data in Table III suggest that the effect of an *o*-methoxy group on the distribution between phenol and indene products is not steric, and the data in Table IV indicate that the product distribution correlates with the ability of a group in the ortho position to chelate to the metal center and not with its ability to donate electron density by resonance. Comparison of the reactions of the *o*-methoxy complex **2b** with the *p*-methoxy complex **2h** reveals a very different product profile, suggesting that the effect of the *o*-methoxy group is not an electronic effect. Unlike the *o*-methoxy complex **2b**, the *p*-methoxy complex gives very little indene product, if any at all. If the effect of the *o*-methoxy group were due to electron donation, then it should display a profile similar to the *p*-methoxy complex, since the *p*-methoxy group is constrained to have its effect via resonance delocalization. Therefore, electron donation by resonance cannot be the source of the effects seen for the *o*-methoxy group. The complex **2i**, which has a *m*-methoxy group, gives high yields of phenol products and no detectable amounts of indene products over the complete profile of temperature and concentration, and this indicates the absence of any inductive effects on the product distribution.

The case for the effect of an *o*-methoxy group on the product distribution being associated with its ability to chelate to the metal center at some point in the reaction is supported by the reactions of a number of complexes in Table IV, including the *o*-*tert*-butyloxy complex **2d**. While it is not possible to know if chelation should be completely eliminated by substitution of *tert*-butyl for methyl on the ortho oxygen in complex **2b**, it is certainly to be expected that chelation would be less favorable for an *o*-*tert*-butyloxy group versus an *o*-methoxy group. The data reveal that there is less tendency for the *o*-*tert*-butyloxy group to give indene products compared to the *o*-methoxy group over the same spectrum of temperature and concentration. Nonetheless, there is some residual effect of the *o*-*tert*-butyloxy group, since substitution with an *o*-*tert*-butyloxy group does not return the product distribution to that seen for the *o*-methyl complex **2g**. Isolation of the *o*-methoxy group from the arene ring by one methylene spacer also gives less indene product, and the product profile for this complex (**2c**) is very similar to that of the *o*-*tert*-butyloxy complex **2d**. If the methoxyl group in complex **2b** does chelate to the metal center at some point in the reaction and lead to indene formation, it would be expected that the *o*-methoxymethyl complex **2c** would have less of an effect since a larger ring size chelated intermediate would be required for complex **2c** relative to **2b**. This is supported by the observation that adding yet another methylene spacer (complex **2f**) produces an additional decrease in the amount of indene product and in fact essentially returns the reaction profile to that observed for the *o*-methyl complex **2g**. This can also be seen in the reaction of the *o*-*tert*-butyloxy complex that is separated by one methylene spacer; complex **2e** also has essentially the same product distribution profile as the *o*-methyl complex **2g**. The reactions of the complexes **2e**, **2f**, and **2g** can be taken to define the steric effects of a substituent in the ortho position on the product distribution, and together they show that this effect is small and not particularly sensitive to the bulk of the ortho substituent. The most reasonable conclusion to be drawn from the data in Table IV is that the effect of the *o*-methoxy group in complex **2b** on the product distribution from the reaction with 3-hexyne is due to the chelation of the methoxyl group to the metal center at some intermediate on the reaction pathway and that as

Table IV. Reactions of Chelation-Allowed and Chelation-Minimized Complexes **2** with 3-Hexyne[a]

series	aux group R	solvent	[2] (M)	temp (°C)	isolated yield (%)[b] 14	15	16	total mass recovery (%)	six/five
b	2-OCH_3	THF	0.5	45	61	18	5	84	2.7
			0.5	110	29	53	10	92	0.5
			0.005	110	Tr	65	10	75	0.01
c	2-CH_3OCH_3	THF	0.5	45	74	Tr	N	74	74
			0.5	110	59	17[c]	N	76	3.5
			0.005	110	6	37[d]	16	59	0.12
d	2-OtBu	THF	0.5	45	96	≤1.3	N	97	72
			0.5	110	52	21	6	79	1.9
			0.005	110	7	54	8	69	0.11
e	2-CH_2OtBu	THF	0.5	45	87	N	N	87	87
			0.5	110	71	N	N	71	71
			0.005	110	44	21[e]	N	65	2.1
f	2-$CH_2CH_2OCH_3$	THF	0.5	45	82	N	N	82	82
			0.5	110	76	Tr	N	76	76
			0.005	110	50	22	4	76[f]	1.9
h	4-OCH_3	THF	0.5	45	93	D	D	93	93
			0.5	110	88	N	N	88	88
			0.005	110	64	N	N	64	64
i	3-OCH_3	THF	0.5	45	94[g]	N	N	94	94
			0.5	110	94[h]	N	N	94	94
			0.005	110	94[i]	N	N	94	94
j	4-OAc	THF	0.5	45	94	N	N	94	94
			0.5	110	80	N	N	80	80

[a] All reactions run with 2 equiv of alkyne. Reaction times are 16–24 h at 45 °C and 0.5 M, 30–40 min at 110 °C and 0.5 M, and 1–2 h at 110 °C and 0.005 M. [b] N indicates that product was not detected in the 500 MHz ^1H NMR spectrum of the crude reaction mixture, Tr indicates that a trace was observed but the amount was not determined, and D indicates that several minor products were observed but were not separated, characterized, or quantified. [c] Includes a 9% yield of indene **15g**. [d] Includes a 5% yield of indene **15g** and a 9% yield of the enol ether **20c**. [e] Includes an 8% yield of indene **15g**. [f] Ratio of products determined by ^1H NMR. [g] Isolated as a 2:1 mixture of **14h** and **14b** (ref 17a). [h] Isolated as a 1.6:1 mixture of **14h** and **14b**. [i] Isolated as a 1.3:1 mixture of **14h** and **14b**.

Table V. Reactions of Monooxygenated Complexes **2** with 1-Pentyne[a]

series	aux group R	solvent	[2] (M)	temp (°C)	isolated yield (%)[b] 11	38	40	total mass recovery (%)	six/five
g	2-CH_3	THF	0.5	45	59	N	N	59	>59
			0.5	110	55	N	N	55	>55
			0.005	110	77	N	7	84	>77
b	2-OCH_3	THF	0.5	45	64	N	11	75	>64
			0.5	110	57	N	11	68	>57
			0.005	110	23	41[c]	6	70	0.6
		THF	0.5	45	60[d]	D	D		
		heptane	0.5	45	56[d]	D	D		
		PhH	0.5	45	60	N	Tr	60[e]	>60
			0.5	110	52	N	N	52[e]	>52
c	2-CH_2OCH_3	THF	0.5	45	56	N	N	56	>56
			0.5	110	63	<6	7	76	>10
			0.005	110	59	<18	5	82	>2.5
h	4-OCH_3	THF	0.5	45	30	37	9	76	0.8
			0.5	110	41	39[f]	13[f]	93	1.1
			0.005	110	41	25[f]	7[f]	73	1.6
		PhH	0.5	45	36	40	Tr	76[e]	0.9
			0.5	110	50	23	2	75[e]	2.0
i	3-OCH_3	THF	0.5	45	74[g]	N	7	81	>74
			0.5	110	80[h]	N	9	89	>80
			0.005	110	84[i]	N	N	84	>84
j	4-OAc	THF	0.5	45	61	N	N	61	>61
			0.5	110	50	N	N	50	>50

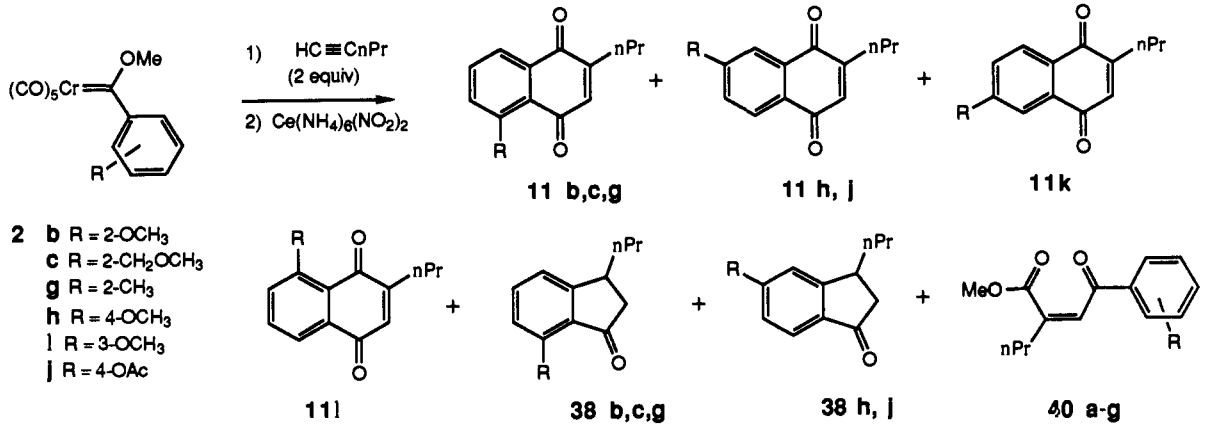
[a] All reactions run with 2 equiv of alkyne. Reaction times are 16–24 h at 45 °C and 0.5 M, 30–40 min at 110 °C and 0.5 M, and 1–2 h at 110 °C and 0.005 M. [b] N indicates that product was not detected in the 500 MHz ^1H NMR spectrum of the crude reaction mixture, D indicates that the reaction was not screened for this product but may have been present, and Tr indicates that a trace was observed but the amount was not determined. [c] Isolated as 28% indanone **38b** and 13% indene **12b**. [d] Reaction was only screened for quinone and was not deoxygenated by the freeze–thaw method but rather was performed in a flask flushed with argon. [e] Cyclopentenedione products were likely formed as minor products (ref 11) but were not detected since they are destroyed by Ce^{IV}. [f] Isolated as a mixture; ratio determined by ^1H NMR integration. [g] Obtained as a 11.3:1.0 mixture of **11k/11i** (ref 17a). [h] Obtained as a 5.6:1.0 mixture of **11k/11i**. [i] Obtained as a 5.0:1.0 mixture of **11k/11i**.

a result indene formation is favored.

Reactions of Monosubstituted Aryl Complexes with 1-Pentyne

The data in Tables IV and V reveal that there are significant differences in the product distributions from the reactions of oxygenated arylcarbene complexes with simple internal alkynes versus reactions with simple terminal alkynes. The most striking difference is that, to a first approximation, the roles of the *o*-methoxy and the *p*-methoxy groups are reversed. In reactions with 1-pentyne (Table V), the reaction of the *p*-methoxy complex **2h** produces more indene product than the reaction of the *o*-methoxy complex **2b**, whereas in the same reactions with 3-hexyne (Table IV), the reverse is true. At low temperature and high concentration the reaction of the *o*-methoxy complex **2b** with 1-pentyne gives only quinone products, which is not true of the same reaction of **2b** with 3-hexyne (Table IV). Only at high temperatures and at low concentrations does the reaction of the *o*-methoxy complex **2b** with 1-pentyne give any detectable amount

Scheme VII



of indene products. As was seen in the reactions with 3-hexyne, the formation of indene products from the reaction of the *o*-methoxy complex **2b** with 1-pentyne seems to be associated with the ability of the methoxyl group to chelate to the metal center at some point during the reaction, since the *o*-methoxymethyl complex **2c** gives less indene product relative to quinone (Scheme VII).

The reaction of the *p*-methoxy complex **2h** with 1-pentyne gives substantial amounts of indene products just as was observed for the reaction of the *o*-methoxy complex **2b** with 3-hexyne (Table IV). The similarity between these two reactions ends there, however, since unlike the reaction of the *o*-methoxy complex **2b** with 3-hexyne, the product distribution from the reaction of the *p*-methoxy complex **2h** with 1-pentyne is not significantly affected by either temperature or concentration and this was found to be true with either THF or benzene as the solvent. The different profiles of these reactions must be the result of different effects of the *o*-methoxy and *p*-methoxy groups, since the effect of the *o*-methoxy group was shown to be due to chelation and in the case of the *p*-methoxy group chelation is impossible. In fact it is clear that the effect of the *p*-methoxy group on the reactions of **2h** with 1-pentyne is due to the ability of the *p*-methoxy group to donate electron density by resonance, since the *p*-acetoxy complex **2j** will react with 1-pentyne to give only quinone products. Given the conclusion that the *p*-methoxy group in complex **2h** must be exerting its influence via resonance delocalization and the fact that this influence can be completely attenuated by replacing the *p*-methoxy group with the more electron-withdrawing *p*-acetoxy group, the possibility was explored as to whether the effect of the *p*-methoxy group could also be attenuated by in situ complexation with a Lewis acid. This was attempted by carrying out the reaction of the *p*-methoxy complex **2h** with 1-pentyne in the presence of a number of Lewis acids and electrophiles (see the Experimental Section); however, no significant change in the product distribution was observed for any of these reactions.

All of the complexes in Table V except **2j** give furans as minor products in their reactions with 1-pentyne in THF. The furan products **39** are not isolated from these reactions as they are not stable to oxidation by cerium(IV), which is employed in the workup, but rather they are isolated as the unsaturated keto esters **40** upon oxidation.[2f] Furan products were not seen in the reactions of these complexes with 3-hexyne (Table IV), and this preference for the formation of furans from reactions of terminal versus internal alkynes has been observed previously.[16c] There does not appear to be any significant dependence of the percentage of the furan product formed on either the temperature or on the concentration. There does seem to be an influence of solvent on furan formation, however, as furan formation is essentially suppressed from the reactions of 1-pentyne with both the *o*- and *p*-methoxy complexes **2b** and **2h** when the solvent is changed from THF to benzene.[26] In the reaction of **2b** and **2h** with 1-pentyne in benzene it is expected that 2-vinylcyclopentenediones would be produced as minor products, and in fact this has been observed for the reaction of **2h** with 1-pentyne.[11] These products are often destroyed by ceric ammonium nitrate and thus were not observed in the reactions listed in Table V; however, the amounts of these products that were formed were determined for the reactions listed in Table VIII.

In summary, the benzannulation reaction with simple terminal alkynes is reasonably selective for phenol or quinone formation from the reactions of monooxygenated arylcarbene complexes, except for the case of para substitution with alkoxy groups. Even in this case the reaction can be made essentially completely selective for phenol or quinone products over indene products by proper choice of the para oxygen substituent, since the product distribution is dependent on the resonance electron-donating ability of the para substituent.

Reactions of the 2,5-Dimethoxyphenyl Complex 5a with 3-Hexyne and 1-Pentyne

The synthesis of 7-*con*-*O*-methylnogarol outlined in Scheme I would require a 2,5-dioxygenated carbene complex of type **5**. If the methoxyl substituents in complex **5a** exert their effects independently, then the overall distribution of products would have a profile that was intermediate between the *o*-methoxyphenyl complex **2b** and the *m*-methoxyphenyl complex **2i**. In considering first the *m*-methoxyphenyl complex **2i**, it can be seen from the data in Tables IV and V that a *m*-methoxy substituent has no effect on the normal propensity of the benzannulation reaction to selectively produce phenol products in high yields in reactions with either 1-pentyne or 3-hexyne. It is anticipated then that the reactions of the 2,5-dimethoxyphenylcarbene complex **5a** with 3-hexyne and 1-pentyne will have product distribution profiles that resemble those of the complex **2b**.

As can be seen from the data in Table VI, the product distribution profile from the reactions of the 2,5-dimethoxyphenyl complex **5a** with both 3-hexyne and 1-pentyne do in fact closely mirror those of the *o*-methoxyphenyl complex **2b**. The reactions of **5a** are not quenched with an oxidant in the workup since a substantial amount of the quinone form of **41** is lost in aqueous extractions due to its solubility. The reaction mixtures are simply opened to air and chromatographed. Furans are formed in the reactions of **5a** with 1-pentyne as minor products and are isolated as the keto esters **48** since the furans are unstable to oxidation by air. The product distribution profiles from the reactions of **5a** and the *o*-methoxy complex **2b** (Table V) reveal that both complexes give nearly the same proportions of phenol, indene, and furan products, and also that they give nearly the same changes in distribution of these products over the same changes in temperature and concentration. Thus in terms of synthetic applications, those conditions that optimize the reaction of the *o*-methoxyphenyl complex **2b** should also provide optimal conditions for the benzannulations of the 2,5-dimethoxyphenylcarbene complexes **5a** (Scheme VIII). One very surprising difference between the reactions of **5a** and **2b** is that whereas the reaction of the latter

(26) In contrast, a lack of solvent effect has been reported on the formation of furan products in the reactions of furylcarbene complexes.[16c]

Table VI. Reaction of Complex **5a** with 3-Hexyne and 1-Pentyne[a]

product series	R_L	R_S	[2] (M)	temp (°C)	isolated yield (%)[b] 41	42	44	45	46	47	48	total mass recovery (%)	six/five
a	Et	Et	0.5	45	52	<2	<2	9	N	N	N	61	>4.0
			0.5	110	11	Tr	31	46	N	N	N	88[c]	0.14
			0.005	110	<1	<1	34	54	N	N	N	88[c]	<0.01
			0.005	45	<4	<7	20	43	N	N	N	63	<0.06
b	nPr	H	0.5	45	71[d]	2[e]	N	N	<1	N	<2	71[f]	>71
			0.5	110	52	N	N	17	8	N	10	87	2.1
			0.005	110	15	N	N	36	N	20	N	71	0.27
			0.005	45	65	13[e]	N	N	4	N	<3	85[f]	3.8

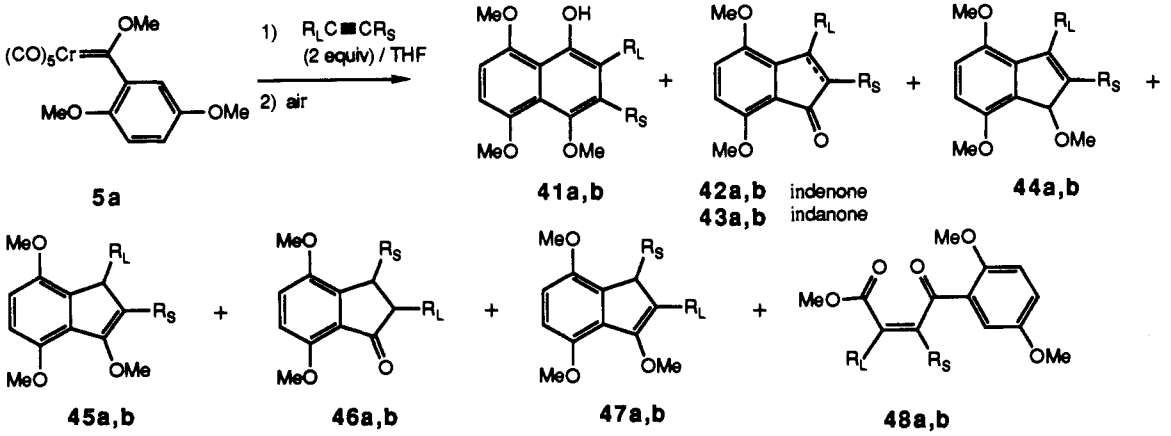
[a] Initial concentration of alkyne is twice that of **2**. Reaction times are 16–24 h at 45 °C and 0.5 M, 30–40 min at 110 °C and 0.5 M, 1–2 h at 110 °C and 0.005 M, and 48–72 h at 45 °C and 0.005 M. [b] N indicates that product was not detected in the 500 MHz ^{1}H NMR spectrum of the crude reaction mixture, and Tr indicates that a trace was observed but the amount was not determined. [c] Oxidative workup with $FeCl_3$–DMF complex (ref 55). [d] Determined in a separate workup without acid. [e] Obtained as indanone **43b**. [f] Acid workup (see Experimental Section).

Table VII. Reaction of Complex **9a** with 3-Hexyne and 1-Pentyne[a]

product series	R_L	R_S	solvent	[9] (M)	temp (°C)	isolated yield (%)[b] 49	50	51	52	53	54	total mass recovery (%)	six/five
a	Et	Et	THF	0.5	45	83	<2	<2	N	N	N	83	>20.0
				0.5	110	15	19	34	N	N	N	68	0.28
				0.005	110	<2	54	<2	N	N	N	54	<0.04
				0.005[c]	45	24	31	<2	N	N	N	55	0.8
b	nPr	H	THF	0.5	45	46	N	N	<16	<10	<2[d]	72	2.9
				0.5	110	43	N	N	12	3	D	58	3.6
				0.005	110	<6	N	N	43	<2	D	<49	<0.14
			PhH	0.5	45	47	N	N	14	<2	10[d]	71	3.4
				0.5	110	35	N	N	8	4	D	47	4.4
			hexane	0.5	45	49	N	N	7	<2	16[d]	72	7.0

[a] Initial alkyne concentration is twice that of **2**. Reaction times are 16–24 h at 45 °C and 0.5 M, 30–40 min at 110 °C and 0.5 M, 1–2 h at 100 °C and 0.005 M, and 48–72 h at 45 °C and 0.005 M. [b] N indicates that the product was not detected in the 500 MHz ^{1}H NMR spectrum of the crude reaction mixture, and D indicates that the reaction was not screened for this product but was most likely present. [c] Reaction carried out on the chelated complex **9b**. [d] Determined in a separate experiment in which an oxidative workup was not used (ref 11).

Scheme VIII



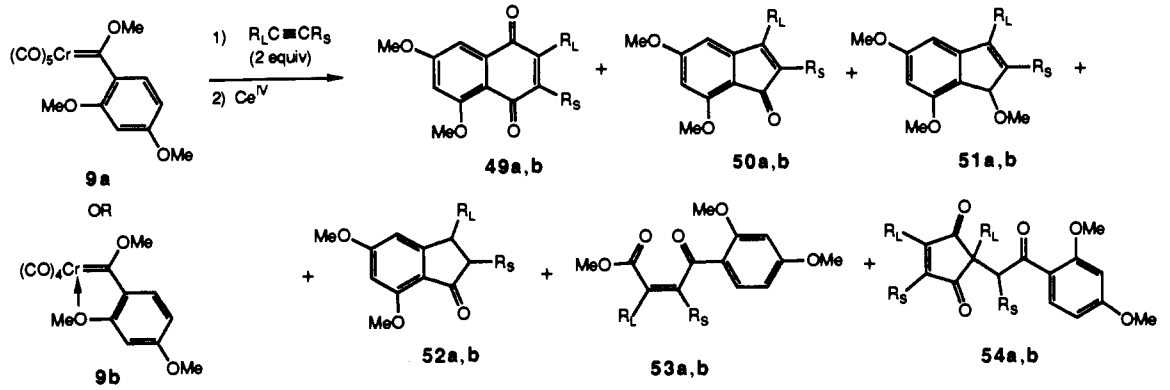
with 1-pentyne gives a single regioisomer (from the two possible orientations of the alkyne incorporation) for both the indene and phenol products complex **5a** gives both regioisomers for the indene products (but not the phenol). The ratio of the "normal" to "abnormal" regioisomers of the indene products ((**42b** + **43b** + **44b** + **45b**):(**46b** + **47b**)) is approximately 2:1. We have not observed any of the abnormal regioisomers of indene (or phenol) products for any of the other reactions described in this work, and the reasons for this are of interest but will be discussed elsewhere. Interestingly, Semmelhack has reported indenes from reactions of complex **5a** with a number of terminal alkynes and all were reported to have the normal regiochemistry.[8]

Reactions of the 2,4-Dimethoxyphenyl Complex 9a with 3-Hexyne and 1-Pentyne

In anticipating the effects of the two methoxyl groups on the benzannulations of the 2,4-dimethoxyphenyl complex **9a**, consideration needs to be given separately to the reactions with 3-hexyne and 1-pentyne. As can be seen from the reactions with 3-hexyne (Table IV), a *p*-methoxy group does not divert the product distribution from phenol or quinone formation and the benzannulation is quite efficient, occurring with high yield and selectivity. The *o*-methoxy group, on the other hand, gives a distribution of phenol and indene products that is dependent on the concentration and temperature and that can vary in favor of either product. If the effects of the *o*- and *p*-methoxy substituents were additive, the reaction of the 2,4-dimethoxyphenyl complex **9a** with 3-hexyne would be expected to be dominated by the *o*-methoxy group, and this is in fact what is observed as indicated by the data in Table VII. The product distribution profile for the reaction of the 2,4-dimethoxyphenyl complex **9a** with 3-hexyne very closely follows that of the *o*-methoxyphenyl complex **2b** over variations in both temperature and concentration.

Reactions of 1-pentyne with the *p*-methoxy complex **2h** (Table V) give nearly equal amounts of phenol and indene products with little variation in product ratios over the profile of temperature and concentration. As observed from the same reaction with **2b**, the presence of an *o*-methoxy group leads to reactions that are selective for phenol products, but which decay to a nonselective mixture of the two products only at high temperatures and low

Scheme IX



Scheme X

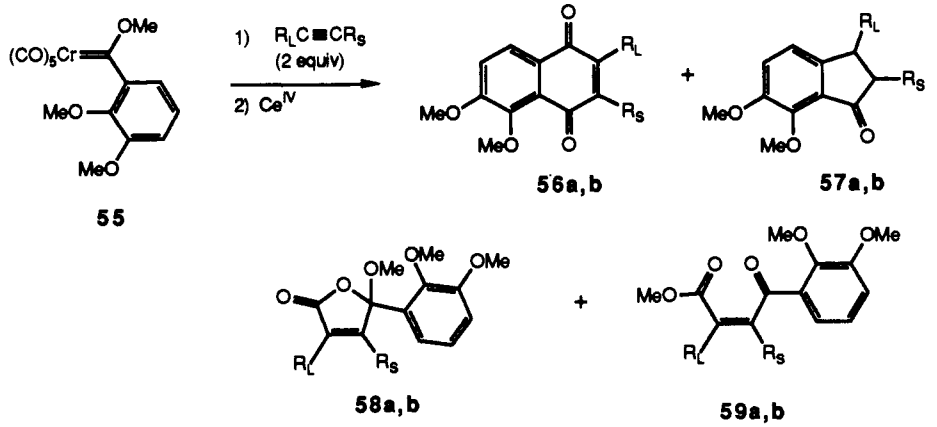


Table VIII. Reaction of Complex 55 with 3-Hexyne and 1-Pentyne[a]

product series	R_L	R_S	solvent	[55] (M)	temp (°C)	isolated yield (%)[b] 56	57	58	59	total mass recovery (%)
a	Et	Et	THF	0.5	45	45	D	14	D	59
				0.5	110	37	D	D	D	37
				0.005	110	<4	D	D	D	<4
b	nPr	H	THF	0.5	45	60	N	N	10	70[c]
				0.5	110	53	Tr	N	9	62
				0.005	110	39	10	N	10	59[c]

[a] Initial alkyne concentration is twice that of 2. Reaction times are 16–24 h at 45 °C and 0.5 M, 30–40 min at 110 °C and 0.5 M, and 1–2 h 110 °C and 0.005 M. [b] N indicates that the product was not detected in the 500 MHz ^{1}H NMR spectrum of the crude reaction mixture, D indicates that the reaction was not screened for this product and may have been present, and Tr indicates that a trace was observed but the amount was not determined. [c] Ratio of products from ^{1}H NMR.

concentrations. If the effects of the *o*- and *p*-methoxy groups were additive in the reaction of the 2,4-dimethoyphenyl complex **9a** with 1-pentyne, then the reaction profile to be expected would closely resemble that which is actually observed and presented in Table VII. Specifically, mixtures of phenol and indene products are produced in nonselective reactions under both low and high temperatures and at high concentrations, but under conditions of high temperatures and low concentrations the product distribution is observed to be in favor of indene formation (Scheme IX).

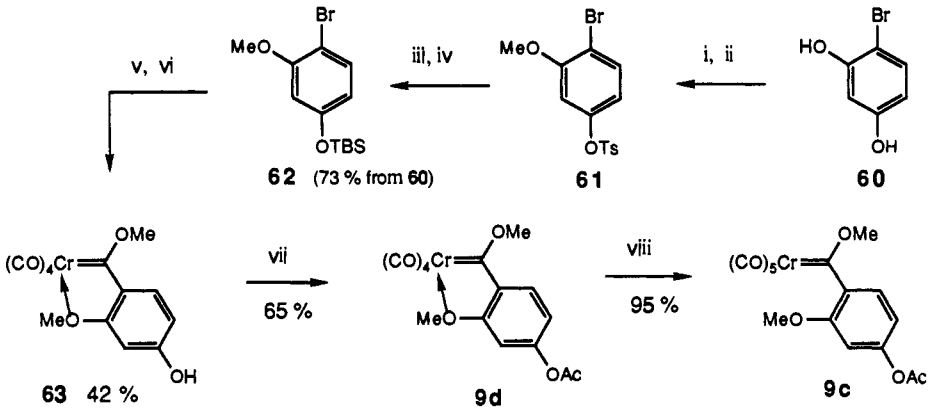
The benzannulation of the 2,4-dimethoxyphenyl complex **9a** with 1-pentyne is a model reaction for the proposed synthesis of olivin outlined in Scheme I, and it was disappointing to find that the best yield of phenol products over the entire reaction profile was in the range 43–46%. Further optimization of this reaction for phenol products by changing the solvent failed as essentially the same yield of the quinone **49** was seen in THF, benzene, and hexane. As was the case for the reactions of monooxygenated arylcarbene complexes with 1-pentyne, the reaction of **9a** with 1-pentyne in THF produced furans as minor products, which were isolated as the keto ester **53** subsequent to oxidative workup. Again the amount of furan products observed was not significantly dependent on either temperature or concentration. In benzene and hexane, the amount of furan products was diminished and, in addition, the cyclopentenedione **54b** was also formed as a minor product, but since these compounds are destroyed by Ce^{IV}, the yields of **54b** were determined in a separate experiment in which an oxidative workup was not employed.[11]

Reactions of the 2,3-Dimethoxyphenyl Complex 55 with 3-Hexyne and 1-Pentyne

The very unusual observation that the 2,5-dimethoxyphenyl complex **5a** gives both possible regioisomers of the indene products prompted us to examine the reactions of the 2,3-dimethoxyphenyl complex **55**. The reactions of **55** with 1-pentyne were fairly straightforward, and as expected, the product distribution profile is similar to that observed for the reaction of the *o*-methoxy complex **2b** (Table V) and the *m*-methoxy group is apparently having minimal effect on this reaction. The indene product **57b** that was obtained from the reaction at 110 °C and 0.005 M was found to be a single regioisomer with the "normal" regiochemistry (Scheme X).

The reactions of the complex **55** with 3-hexyne that are indicated in Table VIII were not screened for indene products. The quinone product **56a** was cleanly separated from the reaction mixtures, and the yields of the quinone **56a** under the various

Scheme XI



i, TsCl, K_2CO_3/acetone, reflux ii, MeI/acetone, reflux. iii, KOH, EtOH/H_2O. iv, TBSCl, NaH. v, (a) nBuLi, (b) $Cr(CO)_6$, (c) $MeSO_3F$. vi, $NaOCH_3$, CH_3OH. vii, Ac_2O, pyridine, DMAP. viii, 2 atm CO, benzene, 25 °C, 20 h.

Table IX. Reaction of Complexes **9c** and **9d** with 3-Hexyne and 1-Pentyne[a]

product series	R_L	R_S	solvent	[9] (M)	temp (°C)	isolated yield (%)[b] 64	65	66	67	68	69	total mass recovery (%)	six/five
					Nonchelated Complex **9c**								
a	Et	Et	THF	0.5	45	60	Tr	10	N	N	N	70	6.0
				0.5	110	35	8	42	N	N	N	85	0.7
				0.005	110	N	12	70	N	N	N	82	<0.01
b	nPr	H	THF	0.5	45	67	N	N	<2	<15	<2	<86	>3.4
				0.5	110	41	N	N	12	18	N	71	1.4
				0.005	110	25	N	N	24	12	N	61	0.7
			THF	0.5	110	52	N	N	9	13	N	74[c]	2.4
					Chelated Complex **9d**								
b	nPr	H	THF	0.5	45	68	N	N	<2	<15	<2	<85	>3.4
				0.5	110	41	N	N	14	14	N	69	1.4
				0.005	110	37	N	N	24	23	N	84	0.7
			PhH	0.5	45	51	N	N	10	26	N	87	1.4
				0.5	110	47	N	N	11	14	N	72	1.9

[a] All reactions with 2 equiv of alkyne. Reaction times are 16–24 h at 45 °C and 0.5 M, 30–40 min at 110 °C and 0.5 M, and 1–2 h at 110 °C and 0.005 M. [b] N indicates that the product was not detected in the 500 MHz ^1H NMR spectrum of the crude reaction mixture, and Tr indicates a trace was observed but the amount was not determined. [c] Reaction mixture was not deoxygenated by the freeze–thaw method but rather performed in a flask filled with argon.

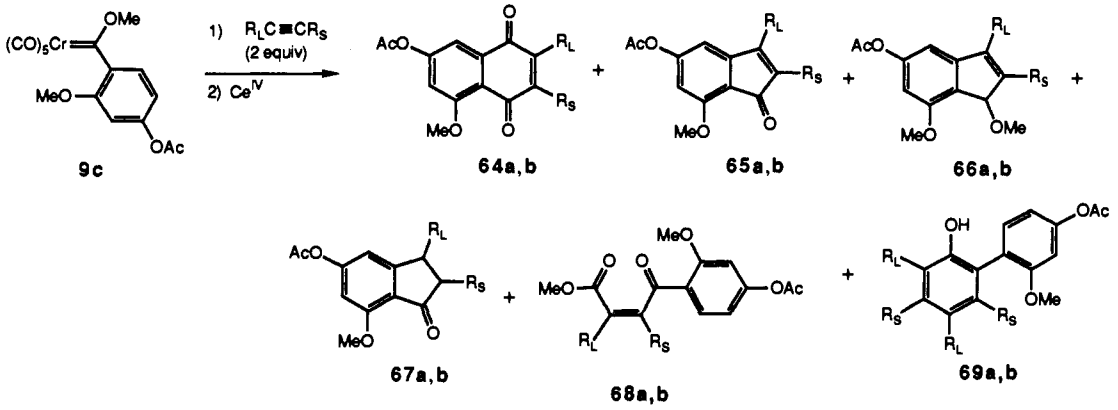
conditions have the same profile as those from the reaction of the *o*-methoxy complex **2b** with 3-hexyne (Table IV). The reaction mixtures from the reactions of **55** with 3-hexyne were quite complicated, with a disappointingly large number of minor products that coeluted from the silica gel column. It was not possible to separate any suspected indene components from this mixture, although the lactone **58a** was isolated from the reaction at 45 °C and 0.5 M.[2f] Many of these compounds may not be primary products of the reaction but instead could be the result of unwanted oxidative side reactions involving primary products. These reactions were not repeated employing an alternative workup to test for this possibility.

Electronic Influences on the Benzannulation of 2,4-Dioxygenated Arylcarbene Complexes

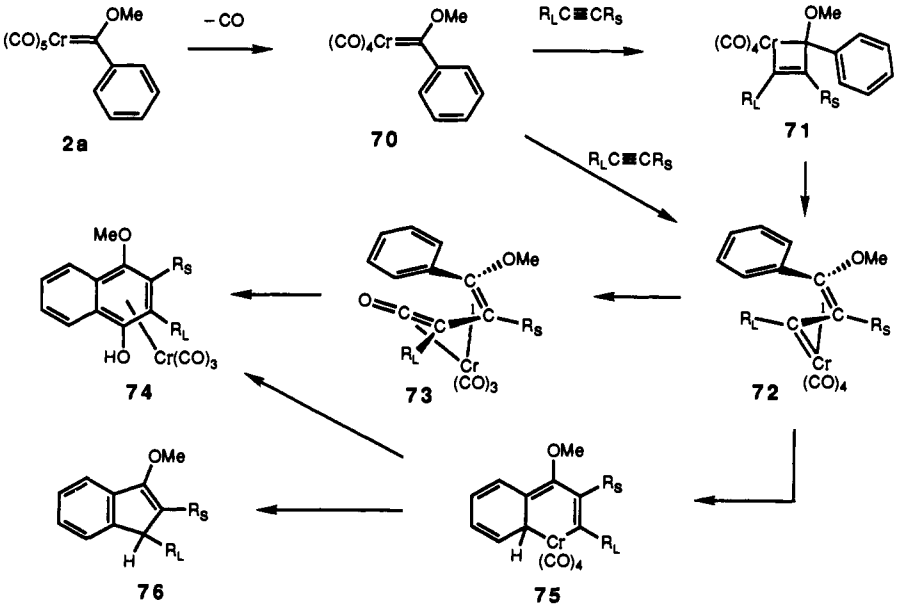
The benzannulation of the 2,4-dimethoxyphenylcarbene complex **9a** with 1-pentyne under the best conditions indicated in Table VII gave a maximum of 43–46% yield of the quinone product **49b**, and this was less than satisfactory for the synthesis of olivin and chromomycinone that is indicated in Scheme I. A consideration of the data in Table V reveals that it is the *p*-methoxy group rather than the *o*-methoxy group that is likely the source of the problem in this reaction. The benzannulation of the *p*-methoxyphenyl complex **2h** with 1-pentyne gives equal mixtures of phenol and indene products, and the partition cannot be influenced by temperature, concentration, or solvent. The source of this nonselectivity is the resonance-donating ability of the *p*-methoxy group. However, as revealed by the reaction of the *p*-acetoxyphenyl complex **2j** with 1-pentyne, it is possible to maintain an oxygen function in the para position and have the benzannulation be selective for phenol or quinone formation. Therefore, in a second-generation model reaction for the synthesis of olivin and chromomycinone, we chose to prepare the 2-methoxy-4-acetoxyphenylcarbene **9c** and evaluate its reactions with 1-pentyne and 3-hexyne. In the synthesis of chromomycinone, which is the aglycone of the antitumor agent mithramycin,[4] the substitution pattern in **9c** is ideal since the two oxygens of the A ring in chromomycinone need to be differentiated if the trisaccharide for mithramycin is to be selectively introduced at the 6-position (OR_2 in **8**, Scheme I).

Complex **9c** was prepared from the bromoresorcinol derivative **62** in a manner similar to that described for the *p*-acetoxy complex **2j** (Scheme VI). The procedure is presented in Scheme XI and the details are included in the Experimental Section. As can be seen from the data in Table IX the benzannulation of 2-methoxy-4-acetoxyphenyl complex **9c** is substantially more selective for quinone formation than the 2,4-dimethoxyphenyl complex **9a** with 1-pentyne (Table VII). Good yields of quinone **64** can be obtained from the reactions of **9c** with both 3-hexyne and 1-pentyne. The product distribution profile from the reaction of **9c** with 1-pentyne is very similar to that expected if the effects of an *o*-methoxy group and a *p*-acetoxy group were additive, i.e., the reaction of **9c** with 1-pentyne is as selective for quinone formation as the reaction of the *o*-methoxy complex **2b**. Again, small amounts of the furan-derived product **68** were observed from the reaction of **9c** with 1-pentyne but not 3-hexyne (Scheme XII). In this series we also investigated the effect of chelation of the *o*-methoxy group to the metal center prior to carrying out the reaction. As can be seen from the data in Table IX, the product distribution profile with 1-pentyne was independent of whether

Scheme XII



Scheme XIII



the reaction was initiated with the nonchelated complex **9c** or the chelated complex **9d**.

Mechanistic Considerations

All of the data that have been presented up to this point were gathered in an effort to establish the synthetic scope of the benzannulation reaction of oxygen-substituted arylcarbene complexes and to develop solutions to certain limitations encountered in specific planned synthetic applications of this reaction. From this data so collected, a number of observations and general phenomena were observed that were not anticipated from, nor can be explained by, previously published mechanistic considerations of the benzannulation reaction.[2,27,28] These include a host of factors that affect the distribution of products from this reaction, including temperature, solvent, concentration of the alkyne, chelating ability of an *o*-methoxy group,[29] and the resonance-delocalizing ability of a *p*-methoxy group.

A summary of the key features common to most proposed mechanisms for phenol and indene formation is presented in Scheme XIII.[2,27,28] A kinetic study of the reaction of complex **2a** with diphenylacetylene revealed that the first and rate-limiting step of the reaction is initial loss of carbon monoxide.[27c] It was found that the rate of this reaction was first-order in carbene complex and independent of the concentration of diphenylacetylene. It had been long proposed that the second step involved a [2 + 2] cycloaddition of the unsaturated complex **70** with the alkyne to give the metallacyclobutene intermediate **71**.[27] The origin of this proposal no doubt was the fact that metallacyclobutenes of this type are isolable from the reactions of alkylidene complexes and alkynes.[30] However, recent theoretical work suggests that this species would be significantly higher in energy than its tautomer **72** and it was concluded that the unsaturated species **70** reacts with the alkyne to give the η^1,η^3-vinylcarbene intermediate **72**.[28c] Whether or not **71** is a precursor to **72** will not bear on the present mechanistic discussions. The vinylcarbene complexed intermediate **72** has also been proposed as a branch point between phenol and indene formation as indicated in Scheme XIII.[27d] Migratory CO insertion in **72** leads to the vinyl ketene complexed intermediate **73**, which is a key intermediate in many mechanistic proposals and which was originally proposed by Dötz.[27a] Recently, the first example of an η^4-vinyl ketene complex has been isolated from the reaction of a chromium carbene complex and an alkyne.[28d] The formation of indene products was

(27) For early citations, see: (a) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449. (b) Casey, C. P. *React. Intermed.* **1981**, 2. (c) Fischer, H.; Mulheimer, J.: Markl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355. (d) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689.

(28) For recent citations to mechanistic aspects, see ref 2f,j, 11, 12, and 16c and (a) Sivavec, T. M.; Katz, T. J.; Chinag, M. Y.; Yang, G. S-Q. *Organometallics* **1989**, *8*, 1620. (b) Garrett, K. E.; Sheridan. J. B.; Pourreau, D. B.: Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383. (c) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908. (d) Anderson, B. A.; Wulff, W. D.; Rheingold. A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615.

(29) For a previous study concerning the chelating ability of an *o*-methoxy group and the distribution between phenol and cyclobutenone products, see ref 2f.

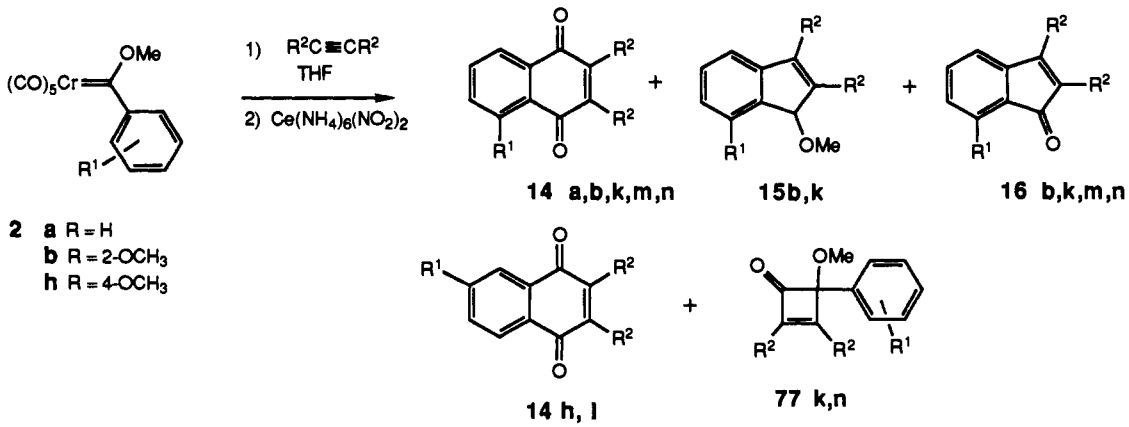
(30) (a) McKinny, R. J.; Tulip, T. H.: Thorn, D. L.; Coolbough, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876.

Table X. Reactions of Complexes **2a**, **2b**, and **2h** with Disubstituted Alkynes

product series	complex (R)	R^2	temp (°C)	time	[2] (M)	[alkyne]	isolated yield (%)[a] 14	15	16	77	total mass recovery (%)	six/five
b	2-OCH_3	Et	45	24 h	0.5	1.0	61	18	5	N	84	2.7
		Et	45	11 h	0.05	1.0	84	5	1	N	92	14
k		iPr	45	115 h	0.5	1.0	21	43	8	12	84	0.41
		iPr	45	70 h	0.05	1.0	29	36	9	11	85	0.64
h	4-OCH_3	Et	45	12 h	0.5	1.0	93	N	N	N	93	>10
l		iPr	45	44 h	0.5	1.0	83	N	D[b]	N	83	>10
a	H	Et	45	24 h	0.12	0.24	88	<0.3	<0.3	N	88[c]	>160
		Et	110	2 h	0.005	0.01	87	<1	<1	N	87	>45
m		iPr	45	24 h	0.5	1.0	78	N	<1	N	78	>78
		iPr	110	25 min	0.5	1.0	65	N	<1	N	65	>65
		iPr	110	2 h	0.005	0.01	45	N	21	N	66[d]	2.1
		iPr	45	20 h	0.5	1.0	71	N	<1	N	71[e]	>71
n		Ph	70	12 h	0.5	1.0	94	N	3	3	100	31
		Ph	70	15 h	0.005	0.001	89	N	8	3	100	11
		Ph	110	30 min	0.5	1.0	94	N	6	N	100	15.6
		Ph	110	4 h	0.005	0.01	64	N	24	7	95	2.6
		Ph	45	24 h	0.16	0.20	41[c]	N	38[c]	4[f]	83[e,g]	1.1

[a] N indicates that the product was not detected in the 500 MHz ^1H NMR of the crude reaction mixture. [b] Yield not determined, but **16l** could have been one of several minor products that were observed. [c] Reference 2f. [d] Ratio of products determined by ^1H NMR. [e] Reaction carried out in heptane. [f] See ref 34. [g] The amount of furan product from this reaction was not determined; see ref 33.

Scheme XIV



proposed to occur via an electrocyclic ring closure of **72** to give the chromacyclohexadiene complex **75** followed by reductive elimination, 1,5-hydrogen migration, and loss of the metal.[27d,b,31] The chromacyclohexadiene complex **75** has been proposed by Casey to be the branch point between phenol and indene products.[27b] The phenol product can thus be formed from either **73** or **75** and neither of these mechanisms has been rigorously ruled out.[2,27,28] However, there is more circumstantial evidence for the vinyl ketene mechanism,[2,27,28] and therefore, it will be assumed for the purposes of the discussion to follow that the branch point between phenol and indene products is the η^1,η^3-vinylcarbene complex **72**. At the end of the mechanistic discussion, the chromacyclohexadiene mechanism will be evaluated, and it will be shown that it cannot satisfactorily explain all of the data concerning the benzannulation reaction.

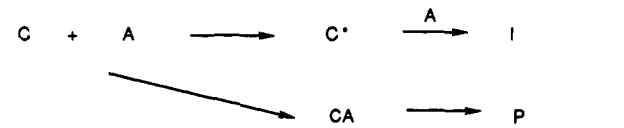
Of all of the various factors that can affect the distribution between phenol and indene products, the one that is the most fascinating and least understood is the concentration of the alkyne. The general observation from the present study is that the product distribution is more sensitive to the alkyne concentration for diethylacetylene than for 1-pentyne. In order to gain more information about the role of the alkyne in this phenomenon, the effects of other disubstituted alkynes were examined and the results are given in Table X. The reaction of the phenyl complex **1a** with diethylacetylene did not give any indene product in THF under any condition that was examined (Table III). On the other hand, both the reactions of diisopropyl- and diphenylacetylene with phenylcarbene complex **2a** can be induced to give indene products if the temperature is raised and/or if the concentration is lowered (Scheme XIV). The ratio of phenol to indene products drops to approximately a factor of 2 at 110 °C and 0.005 M in carbene complex and 0.01 M in alkyne. Likewise, it was observed that the more hindered diisopropylacetylene also gives more indene products with the *o*-methoxy complex **2b** than does diethylacetylene. The *p*-methoxy complex **2h** only produces phenol products with diisopropylacetylene, and here again, as was the case for the reaction with 3-hexyne (Table IV), we see quite different behavior for the *o*- and *p*-methoxy complexes. It is interesting to note that in going from diethyl- to diisopropylacetylene the rate is significantly slowed for the *o*-methoxy complex **2b** but not for the phenyl complex **2a**. This suggests that the reaction of **2b** proceeds through a second-order reaction involving the alkyne and the chelated complex **26** (Scheme VI), but we have no kinetic data to support this at this time. Finally, the reaction of the phenyl complex **2a** with diphenylacetylene is still the only example of a benzannulation that is less selective for phenol over indene products in heptane versus ether solvent and this has yet to be explained (entries 12 and 17).[33] However, this is apparently not related to the steric effects of the phenyl groups, since the reaction of **2a** with diisopropylacetylene produces only phenol products in both THF and heptane, with less than 1% indene being formed in the reaction in heptane (entries 9 and 12). The most

(31) For an alternate explanation, see ref 13b.
(32) The effect of alkyne concentration on product distribution has been found to be more general and more pronounced for molybdenum carbene complexes.[18]

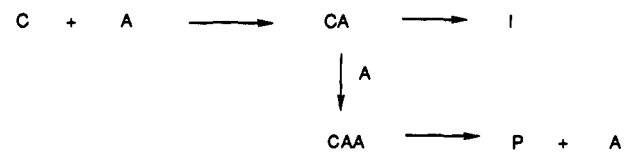
(33) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177.
(34) Anderson, B. A.; Wulff, W. D. Unpublished results.

Scheme XV

Preactivation Mechanism



Allochemical Mechanism



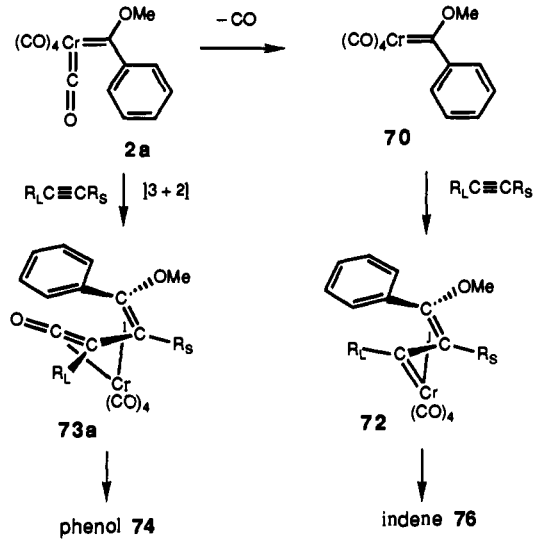
C = carbene complex; A = alkyne; I = indene; P = phenol

important observation to be made from the data in Table X is that more sterically hindered alkynes cause a shift in the distribution, favoring the indene products at the expense of the phenol products.

For purposes of analysis, the possible mechanisms can be divided into two general classes in which the origin of the effect of the concentration of the alkyne substrate on the distribution between phenol and indene products could occur either prior to or after the first alkyne has been covalently incorporated into the organic fragment. In Scheme XV, these two mechanistic regimes are indicated as either a preactivation mechanism or as an allochemical mechanism. In the former, the starting carbene complex can undergo a process that converts it to an intermediate that reacts differently with the alkyne than the starting complex. Alternatively, in the allochemical mechanism the carbene complex C and the alkyne A react to form the intermediate CA, which has the alkyne covalently incorporated into the organic fragment, and then this intermediate can either give an indene product or be intercepted by a second alkyne to give a new intermediate CAA, which gives rise to the phenol product rather than the indene. The effect of the alkyne in the latter process could, in principle, be catalytic since the second alkyne is not incorporated in the organic product. We shall consider both the preactivation and the allochemical mechanisms in turn in attempting to explain the effect of alkyne concentration on the distribution between phenol and indene products.

The second process in Scheme XV bears some relationship to that seen in allosteric enzymes in that a substrate is regulating product distribution. There are, however, distinct differences between the allosteric effect in enzymes and the allochemical effect indicated in Scheme XV. In the case where a substrate regulates distribution, an allosteric enzyme has both molecules bound at the same time but at different sites; allosteric is derived from the Greek words allo and steric, which in translation mean other place. We propose the term allochemical effect (other chemical species)[35] to define the second process in Scheme XV, and in the general sense it is intended to mean a nonenzymatic chemical reaction for which the product distribution is affected by a process that involves the interaction of a molecule of one of the substrates with a chemical intermediate of the reaction that already has a molecule of that substrate covalently incorporated, and further that this interaction lead to a change in the distribution of products, all of which have the first, but not the second, molecule of substrate covalently incorporated. It is quite common in organometallic chemistry to see product distributions that are dependent on the nature of added ligands; however, not so common are those reactions in which the product distribution is affected by a molecule that is also incorporated into the product. In addition to the reactions of carbene complexes with alkynes, the hydroformylation reactions display this phenomenon as it has been shown that the ratio of branched to nonbranched products is dependent on the pressure of carbon monoxide.[37]

Scheme XVI



Preactivation Mechanisms

One possible mechanistic scenario that would fall into the preactivation regime involves a competition between carbon monoxide dissociation from, and a [3 + 2] cycloaddition of an alkyne with, the starting pentacarbonylcarbene complex **2a** as indicated in Scheme XVI. A [3 + 2] cycloaddition of an alkyne with complex **2a** that simultaneously involved the carbene ligand and a carbon monoxide ligand has never been proposed in the literature before,[38] but it is attractive since it would directly generate the saturated η^4-vinyl ketene complex **73a**. Formation of the phenol product would thus be favored at higher concentrations of alkyne, since dissociation of CO from complex **2a** would be unimolecular. However, two lines of evidence can be advanced that are inconsistent with this mechanism. The first is that the kinetics of the reaction of the phenyl complex **2a** with diphenylacetylene reveal that the reaction is first-order in carbene complex and independent of the alkyne concentration under conditions in which the reaction gives phenol products. This is the only reaction of a carbene complex and an alkyne that has been studied kinetically, but at least for this particular reaction, the effect of the concentration of diphenylacetylene on the distribution of products that is revealed in Table X cannot be explained by the mechanism outlined in Scheme XVI. Secondly, this mechanism would have the amount of indene product formed suppressed by carbon monoxide. However, the data in entries 7, 10, 13, and 14 in Table II reveal that the product distribution from the reaction of the *o*-methoxy complex **2b** is not significantly changed under CO pressure at either 1.0 or 0.005 M in the initial concentration of 3-hexyne.

Several other possible scenarios for the preactivation mechanism specifically involving those complexes that have oxygen-chelating groups in the ortho position of the arene are presented in Scheme XVII. One possibility is that the complex **2b** dissociates CO to give the unsaturated intermediate **70b**, which reacts with alkyne to give the phenol **74** in competition with internal coordination

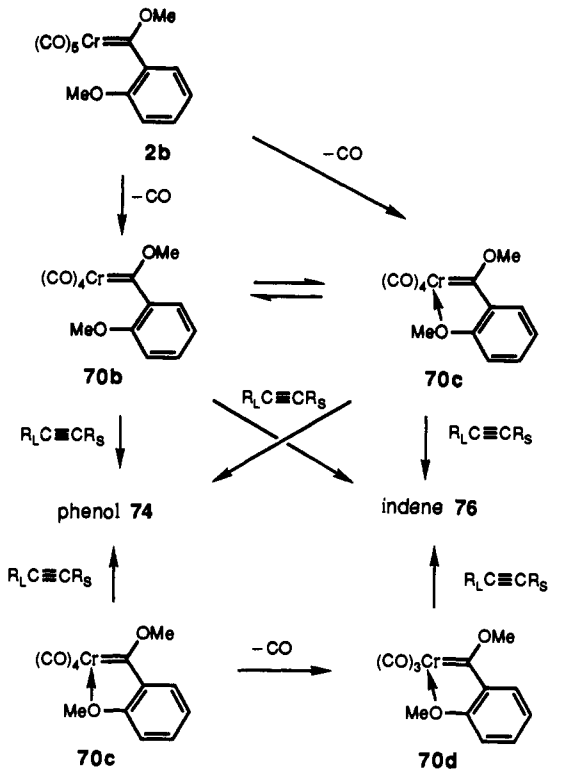
(35) The term allochemical has apparently not been used in chemistry or biochemistry, but the terms allochem and allochemical metamorphism are used in geochemistry.[36]

(36) *Dictionary of Geological Terms*; The American Geological Institute. Anchor Press: Garden City, NY, 1976.

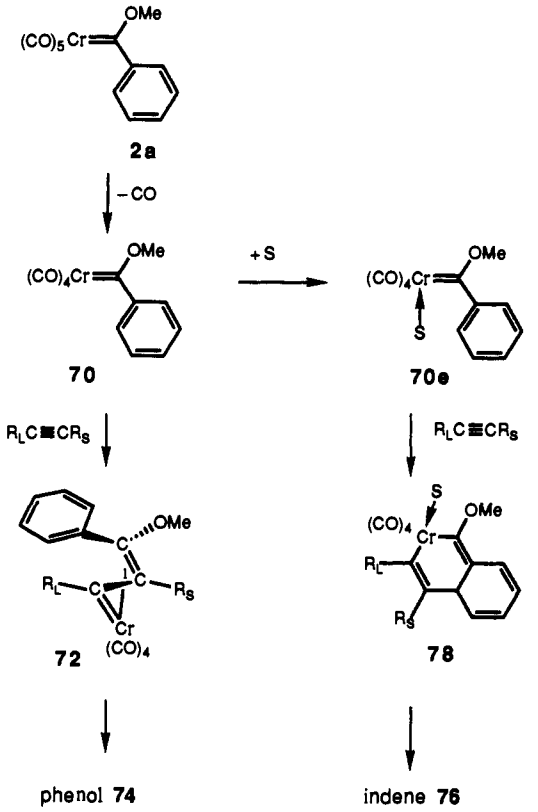
(37) (a) *Organic Synthesis via Metal Carbonyls*: Wender, I., Pino, P., Eds.; John Wiley: New York, 1977; Vol. II, pp 43–232. (b) *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer Verlag: New York, 1980. (c) Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259. (d) Davies, J. A. *The Chemistry of the Metal-Carbon Bond*: Hartley, F. R.; Patai, S., Eds.; Wiley: New York, 1985; Vol. 3, Chapter 8, pp 361–389.

(38) We would like to thank Professor E. J. Corey for suggesting this mechanistic possibility.

Scheme XVII



Scheme XVIII



by the methoxyl to give chelated complex **70c**, which reacts with alkyne to give indene **76**. This possibility can be ruled out on the basis of the experiments summarized in Table IX, where it was found that both the chelated complex **9d** and the nonchelated complex **9c** gave the same distribution of products with 1-pentyne over the entire product distribution profile. Another possibility is that the reaction of the chelated complex **70c** with alkyne to give phenol **74** is in competition with CO dissociation to give the unsaturated chelated species **70d**, which goes to indene. This scenario can be ruled out on the basis of the data in entries 7, 10, 13, and 14 in Table II, which reveal that there is no influence of the presence of CO on the ratio of phenol to indene products.

There are also possible explanations of the observed effects of alkyne concentration on the product distribution if there is an associative loss of CO from the pentacarbonyl complex **2b** to give the chelated complex **70c**, from which all products are derived. The situation where **70c** and **70b** are in rapid equilibrium can be ruled out since the ratio of products would then be independent of the concentration of alkyne. Also to be ruled out is the possibility that **70c** leads to indene and dechelation is irreversible with respect to reaction of **70b** with alkyne to give phenol, since this situation would require that higher concentrations of alkyne would favor indene products. The alternate situation where **70c** leads to phenol and dechelation is irreversible with respect to reaction of **70b** with alkyne to give indene is considered to be unlikely for two reasons: (1) ortho substituents that are most capable of chelation might be expected to give more phenol products, which is the reverse of what is seen, and (2) the unlikelihood of the premise that dechelation of **70c** be irreversible with respect to reaction of **70b** with alkyne. In support of the latter, it is known that the return of external CO in the reaction of **2a** (Scheme XII) can be competitive (under a CO atmosphere) with the reaction of the unsaturated intermediate **70** with diphenylacetylene,[27c] and therefore, certainly, internal return of the methoxyl group in **70b** should be competitive with the reaction of this intermediate with alkynes.

One final possibility for the preactivation mechanism is shown in Scheme XVIII and begins with the loss of CO to give the unsaturated complex **70**. The dependence of the product distribution on alkyne concentration could be accounted for by a situation where the reaction of **70** with alkyne to give phenol is in competition with formation of the solvated complex **70e**. This complex would have to give rise to indene by a mechanism that did not involve the η^1,η^3-vinylcarbene complex intermediate **72**, and a reasonable possibility would be a [4 + 2] cycloaddition with the alkyne to give the chromacyclohexadienyl intermediate **78**. This type of intermediate has been proposed in a heteroannulation of chromium carbene complexes.[39] Although this would explain the observation that more coordinating solvents lead to more indene products, it is not considered likely that alkyne coordination could compete with solvent coordination.[40] Furthermore, the mechanism in Scheme XVIII cannot account for the effect of alkyne concentration on product distribution for all of the complexes reported in this work. Specifically, it cannot apply to those complexes where chelation with an ortho substituent is possible for reasons outlined above. Although at this time we do not have evidence to definitively rule out this mechanism, we currently favor the allochemical mechanism, which is presented in more detail in Scheme XIX.

Allochemical Mechanism

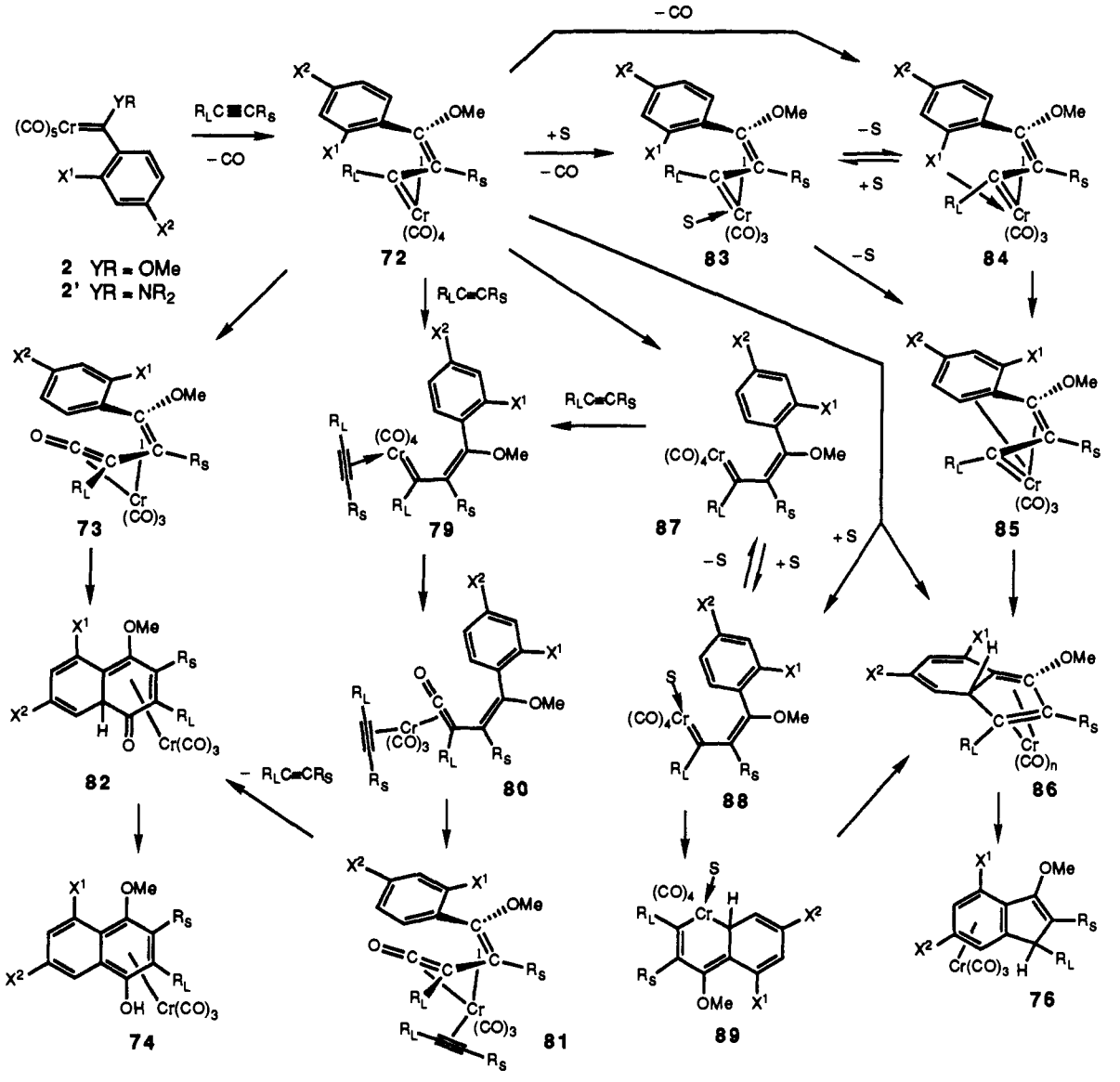
The basic premise of the proposed allochemical mechanism shown in Scheme XIX is that the product partition occurs at the η^1,η^3-vinylcarbene complexed intermediate **72** and that interaction of this species with a second molecule of alkyne results in the formation of greater proportions of phenol versus indene products. Specifically, we propose that a second molecule of alkyne reacts either with the η^1,η^3-vinylcarbene complexed intermediate **72**, or the η^2-vinylcarbene complexed intermediate **87** to give the alkyne complexed intermediate **79**. The alkyne complexed vinylcarbene intermediate **79** has been proposed as an intermediate in two-alkyne annulations[41] of carbene complexes and in the carbene

(39) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251.

(40) A stable 16 e⁻ carbene complex can be isolated if the proper substituents on the carbene carbon are present: Schubert, U.; Hepp, W.; Müller, J. *Organometallics* **1986**, *5*, 173.

(41) (a) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060. (b) For a related reaction, see: Sivavec, T. M.; Katz, T. J. *Tetrahedron Lett.* **1985**, *26*, 2159.

Scheme XIX



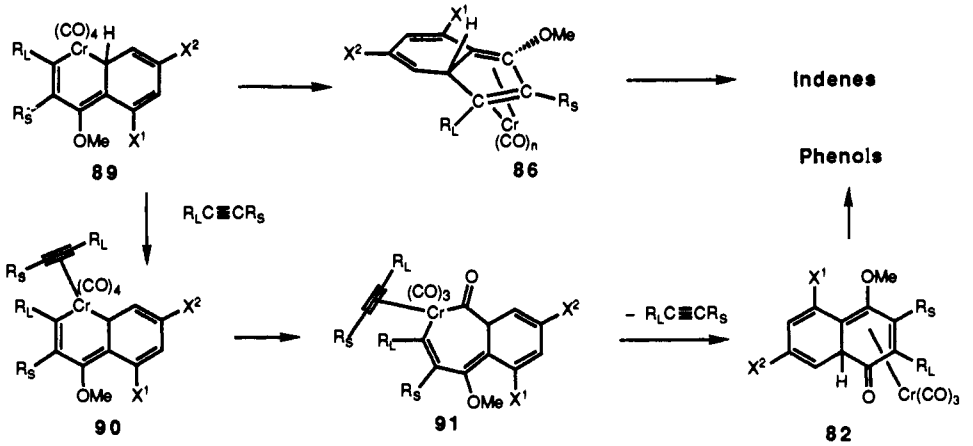
complex-induced polymerization of alkynes.[42] It is further proposed that the CO insertion step is accelerated by the coordination of the alkyne, thus leading to greater proportions of phenol product, possibly through intermediates **80** and **81**. The reason that alkyne coordination could accelerate CO insertion is thought to be related to the ability of an alkyne to be either a 2 or 4 e⁻ donor.[43] The traditional mechanism for phenol formation involves CO insertion in the η^1,η^3-vinylcarbene complex **72**, a process that results in the formation of the unsaturated 16 e⁻ η^4-vinyl ketene complex **73**. On the other hand, CO insertion in the alkyne complex **79** need not lead to an unsaturated vinyl ketene complex of the structure **80** if the alkyne switches from a 2 to a 4 e⁻ donor concomitant with the CO insertion step. Trigonal bipyramidal chromium complexes that have a single alkyne ligand that is a 4 e⁻ donor were unknown until the very recent report of Wink, who has isolated and structurally characterized a bis(phosphine)dicarbonylchromium alkyne complex, thereby supporting the contention that alkynes can have 4 e⁻ bonds in complexes with trigonal bipyramidal geometry.[44] It could be argued that the unsaturation encountered in the CO insertion in **72** to give **73** could be negated by an associative process involving solvent; however, this would lead to the wrong prediction that greater proportions of phenol products would be observed in more coordinating solvents, since it is well-known that polar coordinating solvents will accelerate CO insertions.[45] This could, however, be the explanation for the anomalous behavior of the reaction of the *o*-methoxy complex **2b** with 3-hexyne in acetonitrile (Table II). The ability of alkynes to switch from 2 to 4 e⁻ donors has not been previously invoked to account for the product distribution from the reactions of carbene complexes with alkynes, and to our knowledge, has not been previously invoked to account for changes in product distributions in any other organometallic reaction. We have examined the effect of the added 1,3-dienes isoprene and cyclopentadiene, which are also potential 4 e⁻ donors, on the reaction of **2b** with 3-hexyne and found no perturbations on the product distributions (details in the Experimental Section).[46] Certainly, the uniqueness of many of the aspects of this proposed mechanism in Scheme XIX will stimulate future investigations.

Discussion of Results

As is evidenced from the data presented in this work, there are a number of factors that influence the distribution from the reactions of carbene complexes and alkynes and all of these will be discussed in terms of the allochemical mechanism presented in Scheme XIX. First, with regard to the concentration of the alkyne,

(42) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.
(43) (a) Templeton, J. L. *Adv. Organomet. Chem.*, in press. (b) See also citations in ref 44.
(44) Wink. D. J.; Creagan, B. T. *J. Am. Chem. Soc.* **1990**, *112*. 8585.
(45) For leading references, see: Wax. M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.
(46) We thank Professor Donald Wink for suggesting this experiment.

Scheme XX



it is to be noted that consistent with this mechanism is the observation that, in all cases where an effect is seen, higher concentrations of alkyne lead to higher proportions of phenol over indene products. This mechanism is also consistent with the data in Table II, which reveal that the product partition is not dependent on the concentration of the carbene complex. The ability of the alkyne to intercept either **72** or **87** should be related to the steric bulk of the alkyne, with the outcome that more bulky alkynes give greater proportions of indene products since they cannot as readily intercept **72** or **87** as less hindered alkynes. This expectation is born out in all of the reactions described herein. In all cases where an effect is seen, a more bulky alkyne leads to a greater proportion of indene products. This is true for internal (3-hexyne) versus terminal (1-pentyne) alkynes (Tables III–IX) and also for a series of internal alkynes (Table X).

Key to the proposed allochemical mechanism in Scheme XIX is the special ability of alkynes to enhance the proportion of phenol products, i.e., they can function as 4 e^- donors. Normal 2 e^- donors would not be expected to enhance phenol formation according to the mechanism in Scheme XIX, and in fact there is a substantial body of literature that amply demonstrates that coordinating solvents and other two-electron donors will enhance indene (and cyclobutenone[2f]) products relative to phenol products.[2e,2f,13b] This is also observed in the present work for the reactions of **2a** and **2b** with 3-hexyne in heptane, benzene, THF, DMTHF, and acetonitrile (Tables II and III). The data reveal that more coordinating solvents lead to higher proportions of indene versus phenol products. The most convincing data suggesting this correlation with the coordinating ability of the solvent is that for DMTHF compared to THF and to heptane. It has also been previously reported that other 2 e^- donor ligands such as triphenylphosphine or dimethyl sulfide do not enhance phenol formation in the reaction of the complex **2b** with 3-hexyne but in fact shift the distribution toward indene products.[2f] Finally, as seen by entries 7, 10, 13, and 14 in Table II, the presence of the 2 e^- donor carbon monoxide does not influence the product ratio in a reaction where alkyne concentration is demonstrated to effect the product partition.

Two possible roles for the solvent in these reactions are indicated in Scheme XIX. It has been determined by ab initio calculations by Hoffmann[28c] that the η^2 complex **87**, which is unsaturated as a result of decomplexation of the double bond, is very close in energy to the η^1,η^3 complex **72**, and thus one role of the solvent may be to coordinate to **87**, thereby sequestering it from reaction with the alkyne. The interception of **87** by the solvent may be considered akin to a 2 e^- donor solvent playing the role of antagonist of the alkyne in the allochemical mechanism. Alternatively, the solvent may serve to facilitate an associative loss of CO from the saturated complex **72** resulting in the formation of **83**, which could lead to the indene products via the intermediates **85** and **86**. It is well-known that CO insertion reactions can be accelerated by polar coordinating solvents,[45] and thus it might have been anticipated that coordinating solvents would have accelerated the insertion of CO in **72** and thereby shifted the distribution toward phenol products. This effect may be the explanation for the anomalous result for the reaction of the *o*-methoxyphenyl complex **2b** with 3-hexyne in acetonitrile (Table II). Whereas the reaction of the parent phenyl complex **2a** with 3-hexyne (Table III) gives more indene products in acetonitrile than in THF, the reaction of complex **2b** gives more phenol products. Thus there appears to be a synergistic effect of the chelating ability of the *o*-methoxy group and the coordinating ability of acetonitrile, a phenomenon that has been observed in cyclobutenone formation.[2f] Nonetheless, the reaction of **2b** with 3-hexyne in acetonitrile displays the normal concentration dependence where increased proportions of phenol product are observed at higher alkyne concentrations.

The data also strongly suggest that chelation of groups in the ortho position of aryl substituents of the carbene carbon also plays a role in shifting the product distribution in favor of indene products. There are two reasonable explanations for this effect of chelating groups that are in line with the mechanism in Scheme XIX. The first is that there is an associative loss of CO from the intermediate **72** by the chelating heteroatom, leading to the chelated complex **84** in which there is now only three carbon monoxide ligands on the chromium and thus can no longer be a competent intermediate for CO insertion. The alternative explanation (not shown) is that the ortho chelating substituent X^1 in intermediate **87** coordinates to the metal center forming a seven-membered ring chelate, and again the chelating group is effectively functioning to block coordination of the alkyne. It is to be noted that in both of these explanations the coordinating group X^1 must decoordinate and rotation must occur about the arene sp^2 carbon bond to permit the five-membered ring annulation. This effect of chelating groups in the ortho position is most pronounced with an *o*-methoxy group for both 3-hexyne (Table IV) and 1-pentyne (Table V) and diminishes with either steric hindrance about the oxygen heteroatom (complexes **2d**, **2e**) or an increase in the ring size of the chelate (complexes **2c**, **2f**), both of which would be expected to lead to complexes for which the chelated intermediates would be less stable and/or less readily formed. The fact that higher temperatures swing the partition in favor of indenes may be due to more facile loss of CO from intermediate **72** to give either **83** or **84**, neither of which is capable of the CO insertion required for phenol formation.

The allochemical mechanism outlined in Scheme XIX is focused around the vinylcarbene complex intermediate **72** as the branch point between phenol and indene product. As indicated in Scheme XIII, it has also been previously suggested that the chromacyclohexadiene intermediate **75** (**89** in Scheme XIX) is also a possible branch point between these two products.[27b] Scheme XX outlines a possible scenario in which the allochemical mechanism could be applied to the situation where the branch point is the chromacyclohexadiene intermediate **89**. This mechanism could account for the observed effect of increased alkyne concentration giving increased proportions of phenol products, if it is viewed that alkynes are able to intercept **89** before reductive elimination to **86** occurs. In the absence of the alkyne, the CO insertion in **90**

occurs with an increase in unsaturation at the metal, which could be overcome if the alkyne can switch from a 2 to 4 e⁻ donor as the CO insertion occurs. This would also explain the fact that 2 e⁻ donors lead to an increase in indene products and not to an increase in phenol products. This mechanism could also account for the fact that polar coordinating solvents lead to more indene products by the argument that the solvent serves to coordinate to the intermediate **89** and block any reaction with an alkyne. However, this mechanism cannot satisfactorily account for the effect of chelating groups on the product distribution. Chelating groups in the ortho position of the aryl ring (X^1 in **89**) cannot be chelated to the metal in the chromacyclohexadiene intermediate **89**, and thus the chelating groups will be unable to modulate the effect of changes in the concentration of the alkyne on the product distribution, nor can the effects of chelating groups X^1 in **89** be exerted in an intermolecular manner since increased proportions of indene products are seen at lower concentrations. It is for this reason that we do not further consider the chromacyclohexadiene intermediate **89** as a branch point in the allochemical mechanism.

One of the very surprising and most difficult observations to explain by the allochemical mechanism, or any other mechanism, is that the product distributions from the reactions of the *p*-methoxy complex **2h** with both 3-hexyne and 1-pentyne are insensitive to either the temperature or the concentration of the alkyne. The source of this effect is the ability of the *p*-methoxy group to donate electrons by resonance, since this effect can be nullified by substitution of methoxyl with acetoxyl in complex **2j** (Tables IV and V) and in the complex **9c** (Table VIII). Presumably, the *o*-methoxy group does not display a resonance effect either because it is chelated to the metal (**84** or in **88**) or because the ortho substituent sterically prevents the arene ring in **72** from being in the plane of the three-coordinated carbons. Our interpretation of the effect of the *p*-methoxy group is that electron donation from the *p*-methoxyphenyl group in **72** (X^2 = OMe, X^1 = H) stabilizes the complex to the point where the double bond does not become free of the metal either on its own (intermediate **87**), under the influence of external alkyne (intermediate **79**), or does not lose CO under the influence of solvent (intermediate **83**). As a consequence, the product partition is determined only by the relative rates of CO insertion to give intermediate **73** (and hence phenols) and the rate of direct cyclization to the five-carbon annulated intermediate **86** (and then to indene). If this were indeed the case, then the annulations of the *p*-methoxy complex **2h** would represent the "real" benzannulation that would occur in the absence of the allochemical effect.

Although constant with temperature and alkyne concentration, the product partition from the annulations of the *p*-methoxy complex **2h** are different for 3-hexyne than they are with 1-pentyne. The disubstituted alkyne, 3-hexyne (Table IV), is highly selective for phenol products (as is diisopropylacetylene, Table V), whereas the less hindered 1-pentyne gives approximately equal mixtures of indene and phenol products. It is not clear at this time why CO insertion to give **73** would be more facile when R_L, R_S = Et than when R_L = nPr and R_S = H, or more specifically, how the partition **72** ⇒ **86** and **72** ⇒ **73** can be influenced by these particular substituents. Consistent with this interpretation is the observation that the *m*-methoxy complex **2i** gives only quinone products under all conditions with 1-pentyne and 3-hexyne (Tables IV and V), a pattern which is most similar to the unsubstituted phenyl complex.

From this model it would be anticipated that vinylcarbene complexed intermediates **72** derived from amino carbene complexes of the type **2'** (Scheme XIX) would also be resistant to the decoordination of the double bond. The explanation for the observations that the reactions of aryl amino complexes with alkynes give exclusively indene products[13,47] would thus be 2-fold: first, intermediate **72** would be inert to displacement of the double bond by an alkyne, and second, very electron-rich substituents on vinylcarbene complexed intermediates would disfavor migration of a CO ligand from the metal to generate the vinyl ketene complex **73**.

(47) A Nazarov type cyclization has also been proposed for the direct formation of **86** without the involvement of a metallacycle.[13b]

(48) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, 9, 165.

Conclusion

The distribution of phenol and indene products from the reactions of aryl chromium carbene complexes with alkynes was found to be dependent on a number of factors, including solvent, temperature, the concentration of the alkyne, the steric bulk of the alkyne substituents, and the nature and position of the substituents on the aryl group. The distributions of furan, cyclobutenone, and cyclopentenedione products were much less sensitive to these factors and were minor products under essentially all of the conditions reported in this study. It was found that the presence of ortho substituents on the aryl ring shifts the partition between phenol and indene products toward indenes, and this was most pronounced for ortho-oxygenated substituents. The evidence suggests that oxygen substituents in the ortho position exert their effect on the partition by chelation to the metal center. It was found that the product distribution from the reactions of para-substituted arylcarbene complexes was a function of the ability of the para substituent to donate electrons by resonance. Overall, with the knowledge of the effects of the various factors that affect this reaction, control can be exerted to effect chemoselective formation of phenol over indene products. This proved to be possible for the annulation of arylcarbene complexes with six of the nine possible substitution patterns for both mono- and dioxygenated aryl groups, thus greatly extending the synthetic utility of the benzannulation reaction.

The effect of alkyne concentration on the product distribution was greatest for complexes with chelating ortho substituents and least for complexes with resonance electron-donating para substituents. The degree to which the concentration of the alkyne affected the product partition was found to correlate with the steric bulk of the substituents of the alkyne. The dependence of the product distribution on the concentration of the alkyne substrate has been attributed to a process in which a second molecule of alkyne can coordinate to the metal center and determine the chemical outcome of an intermediate that has covalently incorporated the first alkyne. It is suggested that the special ability of an alkyne to display this effect is related to the ability of an alkyne to readily switch from a 2 to a 4 e⁻ donor. To our knowledge it has not been previously suggested that a product distribution from an organometallic reaction can be regulated by an alkyne ligand that switches from a 2 to a 4 e⁻ donor. This general phenomenon of substrate regulation of product distribution in organometallic chemistry, which we term the allochemical effect, is precedented for ligands other than alkynes, but it is a process that has not been widely pursued and one which may prove to be more prevalent than has been recognized. Given the uniqueness of these mechanistic issues and the synthetic importance of these reactions in the synthesis of polyoxygenated aromatics, the observations made here should serve to stimulate many future studies.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran (THF), ether, and benzene were distilled from benzophenone ketyl under nitrogen. Cerium(IV) oxidations employed a 0.5 M solution of ceric ammonium nitrate in 0.1 M aqueous nitric acid. Dichloromethane, acetic anhydride, and triethylamine were distilled from calcium hydride. 3-Hexyne was distilled from $NaBH_4$ before use. Chromatographic purifications were performed on silica gel (230–400 mesh) under gravity or by flash technique. Proton NMR data were obtained either on a University of Chicago built DS-1000 500-MHz instrument or a General QE-300 MHz instrument. Carbon-13 spectra were obtained on the QE-300 instrument at 75 MHz or on a Varian XL-400 instrument at 100 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 either by Microtech Laboratories in Skokie, IL (now Midwest Microlab, Indianapolis, IN)

or Galbraith Laboratories in Knoxville, TN. The following carbene complexes were prepared according to their literature procedures: **2a**,[19,49] **2b**,[2e,19] **2h**,[19] and **21**.[19] Complex **2d** was prepared with a procedure that is improved over that originally reported.[2f] Complexes **5a**, **9a**, and **9b** were also prepared according to the published procedures.[50]

Preparation of 2-Methoxymethyl Complex 2c. A. Preparation of 2-(Methoxymethyl)bromobenzene (24). Under an argon blanket, 2.4 g of NaH (60 wt % in mineral oil, 60 mmol) was washed twice with 10 mL of hexanes, slurried with 60 mL of THF, and cooled to 0 °C. A solution of 9.37 g of 2-bromobenzyl alcohol (**23**) (50 mmol) in 30 mL of THF was added slowly via cannula, washing in with an additional 10 mL of THF. After 30 min at 0 °C, 3.75 mL of iodomethane (60 mmol) was added all at once via syringe. The reaction was stirred at 0 °C for 30 min and then at room temperature for 40 min. After cooling to 0 °C, the reaction was quenched with water and then poured into ether. Washing with brine and drying ($MgSO_4$) followed by solvent removal in vacuo gave **24** as a slightly yellow oil, 10.05 g (99%), which was used without further purification. **24**: ^1H NMR ($CDCl_3$) δ 3.47 (s, 3 H, OCH_3), 4.52 (s, 2 H, CH_2OMe), 7.13 (t, 1 H, J = 7.7 Hz), 7.30 (t, 1 H, J = 7.5 Hz), 7.44 (d, 1 H, J = 7.6 Hz), 7.52 (d, 1 H, J = 8.0 Hz).

B. Conversion of 24 to Carbene Complex 2c. Complex **2c** was prepared by the general procedure developed by Fischer.[19] To 2.07 g of 2-(methoxymethyl)bromobenzene **24** (10.3 mmol) at −30 °C in 30 mL of ether was added 7.7 mL of 1.6 M nBuLi/hexanes (12.3 mmol) to give a bright yellow solution, which was stirred for 30 min and then warmed to 0 °C for 30 min. This was added to 2.72 g of $Cr(CO)_6$ (12.3 mmol) in 25 mL of ether at 0 °C via cannula to give a dark orange-brown solution, which was stirred at room temperature for 1 h. The solvent was removed under vacuum, and the residue was dissolved in water. After filtering the solution through Celite and washing with hexanes, the aqueous layer was treated with portionwise additions of trimethyloxonium tetrafluoroborate in the presence of a small amount of dichloromethane (~10 mL) until acidic by pH paper. After 30 min at room temperature, the reaction mixture was extracted with ether, washed with brine, and dried ($MgSO_4$). Chromatographic purification on silica gel with 10% ether in hexanes gave 3.05 g of complex **2c** (83.3%) as a red oil, which could be crystallized from hexanes at −78 °C to give a red solid (mp 26 °C). Spectral data for **2c**: ^1H NMR ($CDCl_3$) δ 3.39 (s, 3 H, CH_2OCH_3), 4.0–4.5 (br s, 3 H, OCH_3), 4.32 (s, 2 H, CH_2OCH_3), 6.85 (br s, 1 H, 6-H), 7.26–7.37 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 59.18, 66.81, 72.84, 120.72, 127.92, 128.30, 128.58, 129.35, 130.90, 216.45 ($C_{cis\text{-}CO}$), 224.68 ($C_{trans\text{-}CO}$), 357.07 ($C_{carbene}$); IR (neat) 2063 s, 1952 vs, 1270 s, 1147 s, 1109 s, 1097 s, 752 s cm^{-1}; mass spectrum, m/e (rel intensity) 356 M^+ (4), 300 (32), 272 (15), 244 (49), 216 (100), 186 (78), 171 (65), 156 (48), 133 (70); exact mass calcd for $C_{15}H_{12}CrO_7$ (m/e) 360.0005, found (m/e) 359.9992.

Preparation of 2-*tert*-Butoxy Complex 2d. This complex was prepared by an improved version of the published procedure.[2f] Metalation of *tert*-butyl phenyl ether **25** by the method of Shirley and Hendrix[51] was performed by treating a solution of 672.4 mg of *tert*-butyl phenyl ether (4.48 mmol) in 20 mL of cyclohexane with 3.42 mL of 1.7 M tBuLi/pentane (5.82 mmol) and refluxing the slightly yellow solution under positive argon pressure overnight. After cooling, the condenser was replaced with a septum and the red solution was transferred via cannula into a slurry of 1.28 g of $Cr(CO)_6$ (5.82 mmol) in 20 mL of THF at room temperature, washing in with 7 mL of THF. After the mixture was stirred for 2 h. the solvent was removed to give a yellow brown solid, which was taken up in 10 mL of dichloromethane at 0 °C under N_2. Addition of a small amount of water and then addition of trimethyloxonium tetrafluoroborate in portions until the water was acidic by pH paper gave a red solution, which was stirred for 30 min. This was poured into ether and extracted with saturated ammonium chloride, dried ($MgSO_4$). and chromatographed on silica gel with hexane to give 1.412 g of complex **2d** (82%), which had spectral data identical with that reported.[2f]

Preparation of Complex 2e. A. Preparation of 2-(*tert*-Butoxymethyl)bromobenzene (28). Under a nitrogen atmosphere, 800 mg of 60 wt % NaH (20.1 mmol) was washed twice with hexanes, mixed with 15 mL of THF, and cooled to 0 °C. *tert*-Butyl alcohol (1.75 mL, 18.5 mmol) in 5 mL of THF was added dropwise, followed after 30 min by 3.86 g of 2-(bromomethyl)bromobenzene (**27**) (15.43 mmol) in 10 mL of 1:1 DMF/THF over 15 min. The reaction was stirred at room temperature for 3 h. quenched at 0 °C by cautious addition of water, and poured into 200 mL of ether. After the solution was washed with brine and water, the dried ($MgSO_4$) organic layer was concentrated and chromatographed on silica gel, eluting first with hexanes and then with a 1:1:30 mixture of ether/methylene chloride/hexanes to ensure that **28** (R_f = 0.29 in hexane) was removed from the column. This gave 2.73 g of **28** (73%) as a clear oil that was crystalline at 0 °C. Spectral data for **28**: ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H, $C(CH_3)_3$), 4.49 (s, 2 H, CH_2OtBu). 7.09 (t, 1 H, J = 7.6 Hz), 7.28 (t, 1 H, J = 7.5 Hz), 7.48 (d, 1 H, J = 7.9 Hz), 7.53 (d, 1 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 27.23, 63.13, 73.32, 121.77, 126.88, 127.88, 128.43, 131.74, 138.72; IR (neat, as oil): 2974 s, 1465 m, 1373 m, 1194 s, 1086 s, 1025 m, 749 s cm^{-1}; mass spectrum, m/e (rel intensity) 244 M^{2+} (78, ^{81}Br), 242 M^+ (29, ^{79}Br), 229 (68), 227 (52), 187 (43), 185 (30), 171 (100), 169 (98); exact mass calcd for $C_{11}H_{15}BrO$ (m/e) 244.0286, found (m/e) 244.0277.

B. Conversion of 28 to Carbene Complex 2e. 2-(*tert*-Butoxymethyl)bromobenzene (**28**) (1.929 g, 7.93 mmol) was taken to the carbene complex **2e** by utilizing the procedure for the preparation of **2c** from **24**. The product was purified by chromatography on silica gel by first eluting with hexanes and then with a 1:1:20 mixture of ether/CH_2Cl_2/hexanes to give 2.50 g (79%) of **2e** (R_f = 0.43 in hexane), which was obtained as an orange solid, mp 72–74 °C. Spectral data for **2e**: ^1H NMR ($CDCl_3$) δ 1.27 (s, 9 H, $C(CH_3)_3$), 4.10–4.35 (br s, 5 H, CH_2OtBu and OCH_3), 6.76 (br s, 1 H, 5-H), 7.28 (t, 1 H, J = 7.1 Hz), 7.33 (t, 1 H, J = 7.4 Hz), 7.43 (d, 1 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 27.88, 61.92, 66.67, 74.30, 119.87, 127.91, 128.72, 128.92, 129.69, 164.54, 216.45, 224.78, 358.05; IR (neat) 2976 s, 2064 vs, 1950 vs, 1267 s, 1146 s, 655 s cm^{-1}; mass spectrum, m/e (rel intensity) 398 M^+ (14), 342 (−2 CO, 8), 314 (17), 286 (94), 258 (73), 200 (58), 174 (88), 170 (100). Anal. Calcd for $C_{18}H_{18}CrO_7$: C, 54.28; H, 4.55. Found: C, 54.25; H, 4.63.

Preparation of Complex 2f. A. Reduction of 2-Bromophenylacetic Acid (29). A solution of 2-bromophenylacetic acid (2.00 g, 9.30 mmol) in 20 mL of THF was cooled to 0 °C under nitrogen and treated with dropwise addition (0.35 mL/min) of 1.0 M BH_3–THF complex (10.2 mL, 10.2 mmol). After stirring for 1 h at 0 °C, the reaction was quenched with water and 0.5 N KOH. Extracting with ether, washing with brine, and drying ($MgSO_4$) gave, upon concentration, 1.57 g (84%) of 2-(2′-bromophenyl)ethanol (**30**) as a colorless oil. The purity of alcohol **30** as assessed by ^1H NMR was sufficient to carry on to the next step. Under a nitrogen blanket, 376 mg of NaH (60 wt % in mineral oil, 9.4 mmol) was washed twice with hexanes. Addition of THF (20 mL) was followed by addition at 0 °C of a solution of 1.57 g of alcohol **30** (7.8 mmol) in 20 mL of THF. After 1 h, 540 μL of iodomethane (8.6 mmol) in 10 mL of DMF was added all at once and stirring continued at room temperature overnight. The reaction was partitioned between ether and brine. The aqueous layer was extracted with 3 × 50 mL of ether, which was back-extracted with additional brine. Drying ($MgSO_4$) and concentrating gave 1.54 g of **31** (92%) as a colorless oil, sufficiently pure by crude ^1H NMR for direct use in the preparation of carbene complex **2f**. Spectral data for **31**: ^1H NMR ($CDCl_3$) δ 3.03 (t, 2 H, J = 7.1 Hz, CH_2CH_2OMe), 3.37 (s, 3 H, OCH_3), 3.61 (t, 2 H, J = 7.1 Hz, CH_2CH_2OMe), 7.06 (t, 1 H, J = 7.2 Hz), 7.20–7.26 (m, 2 H), 7.51 (d, 1 H, J = 8.0 Hz).

B. Conversion of 31 to Carbene Complex 2f. 1-Bromo-2-(2-methoxyethyl)benzene (**31**) (1.11 g, 5.14 mmol) was converted to carbene complex **2f** according to the procedure for the conversion of **24** to **2c**, except that *t*-BuLi (2 equiv) was used in the metal–halogen exchange step at −78 °C. The product was purified by chromatography on silica gel with a 1:1:20 mixture of ether/CH_2Cl_2/hexanes as eluent to give 1.494 g (78.6%) of **2f** (R_f = 0.22) as a red oil, which slowly crystallized at low temperature to give an orange solid (mp at or near ambient temperature). Spectral data for **2f**: ^1H NMR ($CDCl_3$) δ 2.69 (t, 2 H, J = 6.6 Hz, CH_2CH_2OMe), 3.33 (s, 3 H, OCH_3), 3.62 (t, 2 H, J = 6.5 Hz, CH_2CH_2OMe), 4.10–4.55 (br s, 3 H, carbene methoxy), 6.83 (br s, 1 H), 7.22–7.29 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 33.28 (CH_2CH_2OMe), 59.32, 66.96, 73.00, 121.18, 127.01, 128.89, 129.01, 130.10, 131.36, 216.62 ($C_{cis\text{-}CO}$), 225.03 ($C_{trans\text{-}CO}$), 359.68 ($C_{carbene}$); IR (neat) 2064 s, 1930 s cm^{-1}; mass spectrum, m/e (rel intensity) 370 M^+ (5), 314 (18), 286 (22), 258 (38), 230 (84), 215 (17), 200 (22), 187 (100), 168 (24), 129 (34); exact mass calcd for $C_{16}H_{14}CrO_7$ (m/e) 370.0144, found (m/e) 370.0138.

Preparation of *o*-Methyl Complex 2g. 2-Bromotoluene **32** (20 mmol) was converted to carbene complex **2g** according to the procedure for the conversion of **24** to **2c**, except that *t*-BuLi (2 equiv) was used in the metal–halogen exchange step at −78 °C. The product was purified by chromatography on silica gel with hexane to give 4.02 g (62%) of the tolyl complex **2g** (R_f = 0.32 in hexane) as a low-melting orange solid (mp 29–30 °C). Spectral data for **2g**: ^1H NMR ($CDCl_3$) δ 2.16 (s, 3 H, CH_3), 3.75–4.60 (br s, 3 H, OCH_3), 6.84 (br s, 1 H, 6-H), 7.17–7.36 (br m, 3 H); ^{13}C NMR ($CDCl_3$) δ 19.45 (CH_3), 66.37 (OCH_3), 121.11, 126.64, 126.78, 128.75, 128.90, 131.37, 216.65 ($C_{cis\text{-}CO}$), 225.12

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($C_{trans\text{-}CO}$). 360.14 ($C_{carbene}$); IR (neat) 2065 s, 1910–1886 vs (ν_{CO}), 1262 s, 1142 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 326 (M^+, 9), 298 (19), 270 (22), 242 (15), 214 (37), 186 (86), 156 (17), 143 (100), 118 (44); exact mass calcd for $C_{14}H_{10}CrO_6$ (*m/e*) 325.9897, found (*m/e*) 325.9871.

Preparation of Complex 35. 1-Bromo-4-[(*tert*-butyldimethylsilyl)-oxy]benzene (**33**) (3.399 g, 11.83 mmol) was converted to carbene complex **35** according to the procedure for the conversion of **24** to **2c**, except that *t*-BuLi (2 equiv) was used in the metal–halogen exchange step at −78 °C (90 min). The crude silylated carbene complex **34** was not purified but rather taken up in approximately 50 mL of ether at room temperature under argon and treated with 4 mL of a 25 wt % solution of $NaOCH_3/CH_3OH$. The reaction was stirred until TLC (20% EtOAc/hexanes) showed no more silylated compound, usually 30 min. The reaction was poured into brine/ether and separated. The organic layer was washed once with brine and set aside. The combined brine layers were acidified with 10% HCl and extracted with additional ether. Drying ($MgSO_4$), solvent removal, and chromatography on silica gel with 20% EtOAc/hexanes gave 1.77 g (43%) of **35** (R_f = 0.51) as a dark red solid (mp 95 °C dec). Spectral data for **35**: ^1H NMR ($CDCl_3$) δ 4.84 (s, 3 H, OCH_3), 6.03 (br s, 1 H, O*H*), 6.84 (d, 2 H, *J* = 7.8 Hz), 7.66 (d, 2 H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 67.14, 114.76, 129.63, 142.30, 159.44, 216.77, 233.72, 341.09; IR ($CHCl_3$) 3260 w, 2058 s, 1982 m, 1937 vs cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_4$: C, 47.58; H, 2.46. Found: C, 47.86; H, 2.62.

Preparation of Complex 2j. In 30 mL of dichloromethane at 0 °C under argon were combined 1.226 g (3.73 mmol) of the *p*-hydroxyphenylcarbene complex **35**, 422 μL of acetic anhydride (4.5 mmol), 392 μL of pyridine (4.9 mmol), and 9 mg of DMAP (0.75 mmol). The reaction was stirred for 30 min and then poured into ether and 10% aqueous HCl. The ether was washed twice with additional 10% HCl, dried ($MgSO_4$), and chromatographed on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexane to give 1.15 g (83%) of **2j** (R_f = 0.34) as a dark red solid (mp 77–79 °C). Spectral data for **2j**: ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H, $COCH_3$), 4.77 (s, 3 H, OCH_3), 7.15 (d, 2 H, *J* = 8.7 Hz), 7.43 (d, 2 H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 21.62, 67.79, 126.17, 128.65, 151.33, 153.02, 169.20, 216.58, 224.27, 348.31; IR ($CHCl_3$) 2062 m, 1946 vs cm^{-1}; mass spectrum, *m/e* (rel intensity) 370 M^+ (7), 342 (16), 314 (16), 286 (12), 258 (47), 230 (100), 215 (21), 187 (66), 158 (24), 145 (4). Anal. Calcd for $C_{15}H_{10}CrO_8$: C, 48.66; H, 2.72. Found: C, 48.94; H, 2.78.

Preparation of 2,3-Dimethoxyphenyl Complex 55. To 1.97 g (14.26 mmol) of freshly distilled veratrole in 60 mL of ether was added 14.3 mL (28.6 mmol) of 2.0 M *n*-butyllithium in hexanes at room temperature.[52] After the solution was stirred for 22 h, to the resulting white slurry was added 6.59 g (29.95 mmol) of chromium hexacarbonyl under an argon stream. After stirring for 3 h at room temperature, the resulting metal acylate was methylated according to the procedure for the preparation of **2c**. The product was purified by chromatography on silica gel, eluting first with hexanes and then with a 1:1:10 mixture of ether/CH_2Cl_2/hexane to give 2.41 g (6.48 mmol, 45%) of **55** as a red oil, which solidified on standing (mp 57–58 °C). Spectral data for **55**: ^1H NMR ($CDCl_3$) δ 3.89 (s, 3 H), 3.90 (s, 3 H), 4.0–4.3 (bs, 3 H), 6.49 (d, 1 H, *J* = 8.0 Hz), 6.84 (d, 1 H, *J* = 8.0 Hz), 7.08 (t, 1 H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 55.8, 60.7, 65.7, 102.6, 111.2, 112.3, 114.0, 124.0, 152.1, 216.0, 224.7, 348.3; IR (film) 2063 s, 1927 vs (br), 1469 w, 1256 w, 1211 w, 1150 w, 970 w, 639 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 372 M^+ (5), 344 (6), 316 (15), 288 (12), 260 (30), 232 (100), 217 (20), 189 (55); exact mass calcd for $C_{15}H_{12}O_8Cr$ (*m/e*) 371.9937, found (*m/e*) 317.9908.

Preparation of Complex 63. A. Etherification of 4-Bromoresorcinol (60). To 2.12 g (11.2 mmol) of 4-bromoresorcinol (**60**) and 10.0 g (72.0 mmol) of potassium carbonate in 150 mL of acetone was added 2.14 g (11.2 mmol) of tosyl chloride and the mixture heated to reflux for 14 h. At this time 1.87 mL (30.0 mmol) of methyl iodide was added, and the mixture was heated for another 16 h. The solution was cooled, about 100 mL of ether added, and the mixture filtered through a pad of Celite and concentrated. Chromatography on silica gel using 20–30% ethyl acetate in hexanes as eluent gave an unknown dimeric compound as the front-running, colorless, UV-inactive band, followed by a colorless, strongly UV active band containing 3.51 g (9.83 mmol, 88%) of **61** as a white solid. Spectral data for **61**: ^1H NMR ($CDCl_3$) δ 2.46 (s, 3 H), 3.78 (s, 3 H), 6.39 (dd, 1 H, *J* = 9, 2 Hz), 6.58 (s, 1 H), 7.30 (d, 2 H, *J* = 8 Hz), 7.37 (d, 1 H, *J* = 9 Hz), 7.69 (d, 2 H, *J* = 8 Hz); IR ($CHCl_3$) 1731 m, 1597 s, 1374 s, 1138 s, 1093 m, 951 s cm^{-1}.

B. Hydrolysis of 61 To Give 4-Bromo-3-methoxyphenol (61b).[54] The ether **61** prepared as described above (6.12 g, 17.13 mmol) was combined with a solution of KOH in EtOH/H_2O (21 g, 350 mL, 350 mL) and heated to 90 °C for 2 h, cooled, concentrated to about half-volume on a rotary evaporator, and neutralized with acetic acid. The mixture was extracted several times with ether; the combined ether layers were washed twice with sodium bicarbonate and extracted four times with 3% KOH. After acidification with 6 N HCl the aqueous portion was extracted several times with ether; the combined extracts were washed with brine, dried with magnesium sulfate, filtered, and concentrated, yielding 3.00 g (14.79 mmol, 86%) of 4-bromo-3-methoxyphenol (**61b**) as a white solid. Spectral data for **61b**: ^1H NMR ($CDCl_3$) δ 3.58 (s, 3 H), 6.31 (dd, 1 H, *J* = 8.5, 2.5 Hz), 6.44 (d, 1 H, *J* = 2.5 Hz), 7.31 (d, 1 H, *J* = 8.5 Hz), (O*H* not seen); ^{13}C NMR ($CDCl_3$) δ 56.1, 100.5, 102.1, 108.7, 133.0, 155.8, 156.3.

C. Silylation of 61b and the Preparation of 62. To 0.798 g (3.93 mmol) of the phenol **61b** in 20 mL of THF at −60 °C was added 0.24 g (5.9 mmol, 1.5 equiv) of a 60% dispersion of NaH and 0.770 g of (5.1 mmol, 1.3 equiv) *tert*-butyldimethylsilyl chloride, and then the cooling bath was removed and the mixture stirred for 3 h. At this time the mixture was poured into brine along with excess ether, and the layers were separated. The organic layer was washed twice with water and once with brine, dried with magnesium sulfate, filtered, and concentrated. Chromatography on silica gel using 3% ethyl acetate in hexanes as eluent gave 1.205 g (3.80 mmol, 97%) of **62** as a colorless oil. Spectral data for **62**: ^1H NMR ($CDCl_3$) δ 0.23 (s, 6 H), 1.01 (s, 9 H), 3.85 (s, 3 H), 6.35 (dd, 1 H, *J* = 9, 2 Hz), 6.40 (d, 1 H, *J* = 2 Hz), 7.32 (d, 1 H, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$) δ −4.5, 18.1, 25.6, 56.0, 103.0, 105.0, 113.1, 133.0, 156.2, 156.4; IR (neat) 2956 s, 2859 s, 1588 s, 1448 s, 1404 s, 1302 s, 1257 s, 1206 s, 1170 s, 1053 s, 979 s, 842 s, 782 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 318 M^+ (39), 316 (37), 261 (100), 259 (98), 180 (90), 165 (19), 139 (12), 73 (19), 63 (10); exact mass calcd for $C_{13}H_{21}BrO_2Si$ (*m/e*) 316.0494, found (*m/e*) 316.0492.

D. Preparation of Carbene Complex 63. To 0.96 g (2.86 mmol) of the aryl bromide **62** in 30 mL of ether at −15 °C was added 2.32 mL (3.71 mmol, 1.3 equiv) of a solution of nBuLi in hexanes. After 15 min, 0.82 g (3.71 mmol, 1.3 equiv) of $Cr(CO)_6$ was added and stirred for 20 h. To this was added 0.34 mL (4.3 mmol, 1.5 equiv) of $MeSO_3F$, and after stirring for 20 min, the mixture was poured into a mixture of saturated aqueous $NaHCO_3$ and hexanes. The organic layer was washed with water and brine, dried over magnesium sulfate, filtered, and concentrated. Chromatographic purification of the product on silica gel was performed with 5% ethyl acetate in hexanes, and this gave 0.693 g (1.47 mmol, 51% yield) of the nonchelated product, which underwent complete conversion to the silylated chelated complex **63b** after storage in the freezer overnight, giving a red-brown solid. Spectral data for complex **63b**: ^1H NMR ($CDCl_3$) δ 0.24 (s, 6 H), 1.00 (s, 9 H), 3.77 (s, 3 H), 4.17 (br s, 3 H), 6.36 (s, 1 H), 6.48 (d, 1 H, *J* = 8 Hz), 6.67 (d, 1 H, *J* = 8 Hz). Desilylation of **63b** to the 4-hydroxy-2-methoxyphenyl complex **63** was accomplished by treating 0.693 g of complex **63b** in argon-purged methanol with 0.48 g (8.8 mmol, 6 equiv) of sodium methoxide, and the mixture was stirred for 1 h before it was poured into ether and a pH 4 buffer. The aqueous layer was extracted with ether until colorless, and then the combined organic extracts were washed with water and brine, dried over magnesium sulfate, filtered, and concentrated. Chromatographic purification on silica gel with 40–50% ethyl acetate in hexanes gave 0.381 g (1.20 mmol, 82%) of **63** as a brown solid. Spectral data for **63**: ^1H NMR ($CDCl_3$) δ 4.18 (s, 3 H), 4.80 (s, 3 H), 6.42 (d, 1 H, *J* = 1 Hz), 6.45 (dd, 1 H, *J* = 9, 1 Hz), 7.45 (d, 1 H, *J* = 9 Hz), (O*H* not seen).

Preparation of Complexes 9d and 9c. To 0.381 g (1.2 mmol) of carbene complex **63** in 50 mL of dichloromethane were added 0.17 mL (1.8 mmol, 1.5 equiv) of acetic anhydride, 0.146 mL (1.8 mmol, 1.5 eq) of pyridine, and several crystals of 4-(dimethylamino)pyridine, and the mixture was stirred for 10 min. The mixture was poured into ether and brine and separated, and the organic layer was washed with water and brine, dried over magnesium sulfate, filtered through Celite, and concentrated on a rotary evaporator. Purification of the product was achieved by chromatography on silica gel upon elution with a 1:1:4 mixture of ether/CH_2Cl_2/hexanes to give 0.280 g (0.778 mmol, 65%) of the chelated complex **9d** as a brown oil, which solidified in the refrigerator overnight (mp 142–5 °C dec). Spectral data for **9d**: ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 4.22 (s, 3 H), 4.87 (s, 3 H), 6.80–6.82 (m, 2 H), 7.57 (d, 1 H, *J* = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 21.2, 65.0, 68.0, 104.9, 115.3, 118.5, 130.4, 155.1, 165.7, 168.6, 213.6, 231.0, 232.0, 332.3; IR ($CHCl_3$) 2064 w, 2020 s, 1936 s, 1852 s, 1767 w, 1604 w, 1458 w, 1142 w, 1115 w, 996 w cm^{-1}; mass spectrum, *m/e* (rel intensity) 372 M^+ (50),

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Table XI. Reactions of Complex **2b** with 3-Hexyne in the Presence of 1,3-Dienes

solvent	temp (°C)	[2b] (M)	[alkyne]	additive (equiv, conc)	isolated yield (%)[a] 14b	15b	16b	total mass recovery (%)	six/five
THF	110	0.005	0.01	none	Tr	65	10	75	≤0.01
		0.005	0.01	C_5H_6 (200, 1.0 M)	N	73	12	85	≤0.01
		0.005	0.01	isoprene (200, 1.0 M)	N	55	16	71	≤0.01
THF	45	0.5	1.0	none	61	18	5	84	2.7
benzene		0.5	1.0	none	77	2	5	84	11.0
heptane		0.5	1.0	none	81	<2	<4	~87	>14
isoprene		0.5	1.0	none	80	N	4	84[b]	>20

[a] N indicates product not detected by 500 MHz ^{1}H NMR of the crude reaction mixture, and Tr indicates that a trace amount was observed but the amount was not determined. Reaction times are 16–24 h at 45 °C and 2–4 h at 110 °C. [b] Yields based on a 10% recovery of the starting carbene complex as methyl *o*-methoxybenzoate.

344 (30), 316 (20), 288 (100), 260 (70), 255 (20), 151 (100); exact mass calcd for $C_{15}H_{12}CrO_8$ (*m/e*) 371.9936, found 371.9924.

The chelated complex **9d** could be converted to the nonchelated complex by stirring a benzene solution of **9d** under a balloon of carbon monoxide at room temperature for 20 h to cleanly give (after removal of solvent) **9c** in 95% yield as a red solid (mp 76–78 °C). Spectral data for **9c**: ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 3.80 (s, 3 H), 4.19 (br s, 3 H), 6.69 (s. 1 H). 6.76 (d. 1 H, *J* = 9 Hz), 6.78 (d, 1 H, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1, 55.6, 65.5, 105.2, 113.7, 121.9, 149.3, 151.5, 169.0, 186.8, 215.8, 225.0, 353.4; IR (film) 2063 m (sharp), 1927 vs (broad), 1770 m, 1203 m, 1146 m cm^{-1}.

General Procedure for the Product Studies from the Benzannulation Reactions of Carbene Complexes with Alkynes. The carbene complex (typically 0.5–1.0 mmol) and a small stirring bar were introduced into small single-necked pear flask that had been modified by replacement of the 14/20 joint with a 10-mm threaded high-vacuum stopcock (Kontes No. 826610). Alternatively, and particularly for small-scale reactions and/or reactions at high concentration, the hydrolysis tubes commercially available from Kontes (No. 896860) may be employed as the reaction vessel. A sufficient amount of the proper solvent was introduced to produce the desired concentration. After the proper number of equivalents was added, the reaction vessel was sealed with the threaded stopcock and the contents of the vessel were deoxygenated by the freeze–pump–thaw method (−196 °C to 25 °C, 3 cycles). The sealed reaction vessel was placed in an oil bath that had previously been equilibrated to the proper temperature, and the reaction mixture was stirred at this temperature until TLC indicated that the reaction was complete. (Generally, reactions run at 45 °C/0.5 M required at least stirring overnight for completion; those run at 110 °C/0.5 M required less than 1 h, 110 °C/0.005 M required from 1 to 3 h, and those carried out at 180 °C/0.5 M required between 5 and 15 min. See tables for specific reactions.) Upon completion of the reaction, the reaction mixture was transferred to a single-necked flask and stripped of solvent with a rotary evaporator. The residue was dissolved in approximately 20 mL of ether, and the crude reaction mixture was then treated with an oxidant. Unless otherwise specified, oxidation was effected by the addition of excess (>7 equiv) 0.5 M ceric ammonium nitrate solution in 0.1 N aqueous nitric acid, and the combined organic and aqueous layers were stirred for 20–30 min at room temperature (or where specified at 0 °C). After separation of the layers and extraction of the aqueous phase with additional ether, the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The ^{1}H NMR spectrum of the crude reaction mixture was obtained to facilitate identification and isolation of components. (Typically, if the crude ^{1}H NMR spectrum showed the presence of minor products, all solvent eluting from the column before or after the main bands came off was collected, concentrated, weighed, and examined by NMR in order to obtain a maximum limit for yield for these components.) Unless otherwise specified, the products of each reaction were separated by flash chromatography on silica gel with the eluent solvent mixture that is specified for each reaction.

It is important to note that from the point of view of quinone synthesis it is not necessary to take the precaution of rigorously deoxygenating the reaction mixture by the freeze–thaw method. This was done to ensure that the product distributions were reproducible even for the very minor products. All of the reactions in all of the tables were carried out by the above general procedure unless specified in the table. For preparative purposes, these reactions give quinone products in many cases in yields that are the same whether or not the system is carefully deoxygenated. This is demonstrated in entries 7 and 8 in Table V and in entry 7 in Table VIII. For these reactions, the carbene complex was introduced into the reaction flask, which was then evacuated and filled with argon. The solvent was then added, which in the case of THF was from a sodium benzophenone still and in the case of heptane was directly from a bottle as supplied by the Aldrich Chemical Co. The alkyne was added, the threaded stopcock sealed, and the flask heated to the proper temperature. As can be seen from the data in Table V, the yield of quinone **11b** did not seem to be affected by the level of oxygen introduced by this procedure.

Reaction of *o*-Methoxyphenylcarbene Complex 2b with 3-Hexyne. The products obtained from these reactions are the indene **15b**, the indenone **16b**, the quinone **14b**, and the cyclobutenone **72b**, which were found to have spectral data identical with that reported previously for these compounds.[2f] The reactions under carbon monoxide atmosphere were performed by filling the evacuated reaction vessel in the last freeze–thaw cycle with carbon monoxide. A slightly positive pressure of CO was introduced at room temperature, and then the threaded stopcock was closed and the flask heated to 100 °C for the time indicated in Table II. Only for the reaction of complex **2b** with 3-hexyne was the quinone product observed to be sensitive to oxidation. In some reactions (180 °C and 0.5 M) the quinone **14b** was obtained contaminated with an unknown oxidation product, **14b′**. This product also formed upon chromatography on silica gel if elution was slow (**14b** and **14b′** coelute and cannot be separated). Oxidation of **14b** also occurs slowly standing in $CDCl_3$. Spectral data for **14b′**: ^{1}H NMR ($CDCl_3$) δ 1.10 (t, 3 H, *J* = 7.5 Hz), 2.23–2.29 (m, 1 H), 2.37 (q, 2 H, *J* = 7.5 Hz), 2.57–2.61 (m, 1 H), 2.93–2.98 (m, 1 H), 2.98 (br s, 1 H, D_2O exchangeable), 3.58–3.62 (m, 1 H), 3.91 (s, 3 H), 7.01 (d, 1 H, *J* = 8.1 Hz), 7.34 (t, 1 H, *J* = 8.0 Hz), 7.67 (d, 1 H, *J* = 7.8 Hz); IR (neat) 3457 sharp m, 2917 s, 2849 s, 1639 m, 1580 m, 1463 m, 1280 m, 1261 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 260 M$^+$ (10), 244 (100), 226 (59), 215 (65), 203 (92). The reaction in acetonitrile also produced the cyclobutenone **77b** in amounts that varied with the conditions as indicated in Table II. Cyclobutenone **77b** had spectral data identical with those previously reported for this compound.[2f]

This reaction was also carried out in the presence of varying amounts of isoprene and cyclopentadiene to examine the effects of these reagents on the distribution between phenol and indene products.[46] As can be seen from the data in Table XI, these reagents did not appear to have any influence on the distribution.

Reaction of Complex 2b with 6-Dodecyne.[22] This reaction was carried out in THF as described in the general procedure, with 2 equiv of alkyne and a concentration of **2b** of 0.005 M, and was complete within 20 min. After oxidative workup and chromatography with a 1:1:20 mixture of ether/CH_2Cl_2/hexanes as eluent, this reaction gave the indene **36b** (86%) as a colorless oil and indenone **37b** (10%) as a yellow oil. Spectral data for **36b**: R_f = 0.26 (1:1:10); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 6 H, *J* = 6.8 Hz), 1.2–1.6 (m, 12 H), 2.21–2.27 (m, 1 H), 2.36–2.40 (m, 1 H), 2.44 (t, 2 H, *J* = 7.7 Hz), 2.99 (s, 3 H), 3.90 (s, 3 H), 5.10 (s, 1 H), 6.70 (d, 1 H, *J* = 8.3 Hz), 6.81 (d, 1 H, *J* = 7.4 Hz), 7.24 (t, 1 H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ (missing three aliphatic peaks due to overlap) 14.5, 23.0, 25.8, 26.1, 28.9, 29.6, 32.4, 52.0, 55.9, 81.7, 108.7, 112.3, 127.3, 130.5, 139.3, 143.4, 147.8, 156.5; IR (neat) 2955 s, 2929 s, 2858 m, 1605 m, 1588 m, 1478 m, 1260 s, 1084 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 316 M$^+$ (62), 259 (81), 245 (100), 189 (36), 171 (24). Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.69; H, 10.19. Found: C, 79.45; H, 10.19. Spectral data for **37b**: R_f = 0.14 (1:1:20); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.8 Hz), 0.92 (t, 3 H, *J* = 6.8 Hz), 1.26–1.61 (m, 12 H), 2.22 (t, 2 H, *J* = 7.6 Hz), 2.48 (t, 2 H, *J* = 7.8 Hz), 3.92 (s, 3 H), 6.66 (d, 1 H, *J* = 7.1 Hz), 6.74 (d, 1 H, *J* = 8.6 Hz), 7.26 (dd, 1 H, *J* = 7.4 Hz, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ (missing two aliphatic peaks due to overlap) 14.4, 22.9, 23.2, 26.6, 28.5, 29.4, 32.2, 32.5, 56.3, 112.8, 113.8, 116.2, 135.5, 135.6, 148.7, 155.3, 156.2, 197.1; IR (neat) 2956 s, 2931 s, 2859 m, 1701 s, 1597 s, 1475 s, 1278 m, 1149 m, 1066 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 300 M$^+$ (15), 258 (4), 243 (47), 229 (10), 187 (35), 178 (34), 137 (30), 124 (100); exact mass calcd for $C_{20}H_{28}O_2$ (*m/e*) 300.2089, found (*m/e*) 300.2099.

Reactions of *o*-Methylphenyl Complex 2g with 3-Hexyne. At high concentrations (Table III) this reaction gives only the quinone **14g**, which

is obtained as a yellow crystalline solid (mp 81.5 °C). Spectral data for **14g**: ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 1.16 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 2.63 (q, 2 H, J = 7.5 Hz, CH_2CH_3), 2.64 (q, 2 H, J = 7.4 Hz, CH_2CH_3), 2.75 (s, 3 H, CH_3), 7.45 (d, 1 H, J = 7.4 Hz, H-6), 7.51 (t, 1 H, J = 7.6 Hz, H-7), 7.99 (d, 1 H, J = 7.7 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 13.77, 13.94, 19.85, 20.20, 22.75, 124.86, 129.81, 132.91, 133.52, 137.08, 140.50, 146.19, 149.12, 185.16, 186.81; IR ($CHCl_3$) 1653 s, 1590 w, 1326 m, 1279 m cm^{-1}; mass spectrum, m/e (rel intensity) 228 M^+ (100), 213 (36), 199 (10), 185 (48), 171 (15), 141 (12), 128 (15). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.91; H, 7.06. Found: C, 78.61; H, 7.03.

At lower concentrations this reaction similarly gives the quinone **14g**, but it also gives the indene **15g** as a minor product that can be separated by flash chromatography on silica gel with a 1:1:30 mixture of ether/CH_2Cl_2/hexanes as eluent. The indene **15g** was obtained as a yellow oil, and the following spectral data were collected: ^{1}H NMR ($CDCl_3$) δ 1.11 (t, 3 H, J = 7.6 Hz, CH_2CH_3), 1.12 (t, 3 H, J = 7.6 Hz, CH_2CH_3), 2.19–2.28 (m, 1 H, $CHHCH_3$), 2.37 (s, 3 H, CH_3), 2.40–2.46 (m, 3 H, $CHHCH_3$, CH_2CH_3), 2.82 (s, 3 H, OCH_3), 5.07 (s, 1 H, $CHOCH_3$), 6.89 (d, 1 H, J = 7.6 Hz), 6.98 (d, 1 H, J = 7.3 Hz), 7.16 (t, 1 H, J = 7.5 Hz); IR (neat) 2966 vs, 2931 s, 2871 m, 1460 m, 1084 s cm^{-1}; mass spectrum, m/e (rel intensity) 216 M^+ (65), 201 (18), 187 (100), 172 (27), 155 (19), 141 (16), 128 (17), 115 (13). Also isolated in a trace amount from these reactions was the indenone **16g** (yellow oil), which precedes the quinone on TLC. Spectral data for **16g**: ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 1.22 (t, 3 H, J = 7.6 Hz, CH_2CH_3), 2.27 (q, 2 H, J = 7.5 Hz, CH_2CH_3), 2.51 (s, 3 H, CH_3), 2.54 (q, 2 H, J = 7.6 Hz, CH_2CH_3), 6.86 (d, 1 H, J = 7.2 Hz), 6.90 (d, 1 H, J = 8.2 Hz), 7.15 (t, 1 H, J = 7.4 Hz); IR (neat) 2969 s, 2933 s, 1700 vs, 1594 s, 1467 s, 1378 m, 1259 m, 1157 m, 912 m, 785 m, 731 m cm^{-1}. The reaction at 0.005 M and 110 °C produced both quinone and indene as indicated in Table III, and while the isolated ratio of quinone to indene was 3.6:1, by crude ^{1}H NMR spectra the ratio was approximately 2:1.

Reactions of o-(Methoxymethyl)phenyl Complex 2c with 3-Hexyne. The reaction at 47 °C and 0.5 M was complete in 38 h, and separation of the products on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes gave a fast-moving yellow compound, which by ^{1}H NMR was revealed to have not incorporated the carbene ligand and was probably an alkyne oligomer, but it was not further characterized. Further elution gave the quinone **14c** in 74% yield as a yellow solid (mp 94–5 °C). Spectral data for **14c**: R_f = 0.27 (1:1:20); ^{1}H NMR ($CDCl_3$) δ 1.14 (t, 6 H, J = 7.5 Hz, CH_2CH_3), 2.61 (q, 4 H, J = 7.3 Hz, CH_2CH_3), 3.53 (s, 3 H, CH_2OCH_3), 4.96 (s, 2 H, CH_2OCH_3), 7.66 (t, 1 H, J = 7.7 Hz, H-7), 7.99 (d, 1 H, J = 7.9 Hz, H-6), 8.01 (d, 1 H, J = 7.7 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 13.86, 13.99, 19.99, 20.25, 58.90, 72.91, 125.48, 128.52, 131.46, 132.92, 133.36, 141.82, 146.69, 148.88, 185.19, 187.08; IR ($CHCl_3$) 1653 vs, 1284 m, 1107 m cm^{-1}; mass spectrum, m/e (rel intensity) 258 M^+ (17), 243 (27), 230 (49), 215 (100). Anal. Calcd for $C_{16}H_{18}O_3$: C. 74.40; H, 7.02. Found: C, 74.13; H, 7.12.

The reaction at 110 °C and 0.5 M was complete in 13.5 h and gave several products, which were separated on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes. The products were identified as the indene **15g**, which resulted from reduction of the o-methoxymethyl group and was obtained from the column contaminated with an alkyne oligomer (9% maximum yield of **15g**), the quinone **14c** in 59% yield, and finally the (methoxymethyl)indene **15c** (R_f = 0.31, 1:1:10), which was obtained in 8% yield as a colorless oil. Spectral data for **15c**: ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 1.16 (t, 3 H, J = 7.4 Hz, CH_2CH_3), 2.21–2.29 (m, 1 H, $CHHCH_3$), 2.46–2.52 (m, 3 H, CH_2CH_3, $CHHCH_3$), 2.86 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 4.56 (d, 1 H, J = 12.1 Hz, $CHHOCH_3$), 4.72 (d, 1 H, J = 12.2 Hz, $CHHOCH_3$), 5.15 s, 1 H, $CHOCH_3$), 7.09 (d, 1 H, J = 7.4 Hz), 7.18 (d, 1 H, J = 7.6 Hz), 7.28 (t, 1 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.60, 14.27, 18.41, 18.80, 50.32, 58.58, 71.08, 81.48. 117.70, 123.91, 128.67, 134.83, 138.30, 140.80, 142.68, 144.89; IR ($CHCl_3$) 2967 vs, 2932 vs, 2875 m, 1456 m, 1197 m, 1102 vs, 1083 s cm^{-1}; mass spectrum, m/e (rel intensity) 246 M^+ (60), 231 (9), 217 (100), 199 (11), 185 (23), 171 (10), 157 (19); exact mass calcd for $C_{16}H_{22}O_2$ (m/e) 246.1620, found (m/e) 246.1622.

In the same manner, the reaction at 110 °C and 0.005 M in 14 h gave the reduced indene **15g** (3.2–4.7%), an inseparable mixture containing the quinone **14c** (6% yield), the indenone **16c** (16% yield), and the enol ether **20c** (9% yield), and finally, a fraction containing the indene **15c** (24% maximum yield) that was contaminated with an unknown compound. Spectral data for **16c** (yellow oil): ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 7.6 Hz, CH_2CH_3), 1.17 (t, 3 H, J = 7.6 Hz, CH_2CH_3), 2.22 (q, 2 H, J = 7.6 Hz, CH_2CH_3), 2.59 (q, 2 H, J = 7.6 Hz, CH_2CH_3), 3.41 (s, 3 H, CH_2OCH_3), 4.79 (s, 2 H, CH_2OCH_3), 6.92 (dd, 1 H, J = 1.3 Hz, 3.4 Hz), 7.26 (d, 2 H, J = 3.3 Hz). Spectral data for **20c**: partial ^{1}H NMR data (derived from mixture, missing data for vinylic ethyl group due to overlap with resonances from indenone **16c**) ^{1}H NMR ($CDCl_3$) δ 0.54 (t, 3 H, $CHHCH_3$), 1.76–1.87 (m, 1 H, $CHHCH_3$), 1.98–2.08 (m, 1 H, $CHHCH_3$), 3.32 (t, 1 H, $CHCH_2CH_3$), 3.43 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.71 (s, 2 H, CH_2OCH_3), 7.11 (t. 1 H), 7.24–7.26 (m, 2 H).

Reactions of 2-*tert*-Butoxy Complex 2d with 3-Hexyne. This reaction was run under the three conditions indicated in Table IV and gave a distribution of the products **14d**, **15d**, and **16d** in the ratios that are indicated in Table IV. The quinone **14d** could be separated by chromatography on silica gel with a 1:1:20 mixture of ether/CH_2Cl_2/hexanes as eluent, but the indene **15d** and the indenone **16d** could not be separated under these conditions and thus the yields in Table IV are determined on this mixture. The spectral data of **14d** and **15d** were found to be the same as those reported for these products from this reaction.[2f] The indenone **16d** was not previously reported from this reaction but was observed in the present reactions at higher temperatures and was isolated as a yellow oil. Spectral data for **16d**: ^{1}H NMR ($CDCl_3$) δ 1.06 (t, 3 H, J = 7.6 Hz), 1.22 (t, 3 H, J = 7.6 Hz), 1.44 (s, 9 H), 2.25 (q, 2 H, J = 7.5 Hz), 2.52 (q, 2 H, J = 7.6 Hz), 6.73 (d, 1 H, J = 7.1 Hz), 6.79 (d, 1 H, J = 8.5 Hz), 7.17 (t, 1 H, J = 7.6 Hz); IR (neat) 2973 s, 2934 m, 1703 s, 1592 s, 1462 s, 1165 s, 867 m cm^{-1}; mass spectrum, m/e (rel intensity) 258 M^+ (6), 243 (12), 202 (100), 187 (95), 173 (100), 159 (21), 145 (22), 141 (17), 128 (20), 115 (45).

Reactions of o-*tert*-Butoxymethyl Complex 2e with 3-Hexyne. At high concentration (0.5 M) this reaction produces the quinone **14e** as the only detectable product in the yields indicated in Table IV. The quinone **14e** was isolated as a yellow solid (mp 74–5 °C) and the following spectral data were obtained: ^{1}H NMR ($CDCl_3$) δ 1.12 (t, 3 H, J = 7.5 Hz. CH_2CH_3), 1.13 (t, 3 H, J = 7.5 Hz, CH_2CH_3), 1.31 (s, 9 H, $C(CH_3)_3$), 2.64 (q, 4 H, J = 7.5 Hz, CH_2CH_3), 4.96 (s, 2 H, CH_2OtBu), 7.65 (t, 1 H, J = 7.8 Hz, H-7), 8.02 (d, 1 H, J = 7.6 Hz, H-6), 8.16 (d, 1 H, J = 7.9 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 14.29, 14.46, 20.41, 20.66, 28.10, 62.78, 74.01, 125.53, 128.70, 132.32, 133.22, 133.55, 144.16, 146.94, 149.21, 185.69, 187.60; IR ($CHCl_3$) 1651 vs, 1284 m, 1100 m cm^{-1}; mass spectrum, m/e (rel intensity) no parent was observed with either EI or CI, showed loss of C_4H_8 to give 244 (M^+ – 56, 100), 226 (26), 211 (17), 177 (21), 149 (25). Anal. Calcd for $C_{19}H_{24}O_3$: C, 76.0; H, 8.10. Found: C, 75.85; H, 8.25.

At low concentration (0.005 M) and 110 °C, this reaction was complete in 1 h and produced several minor products. Chromatography on silica gel with a 1:1:20 mixture of ether/CH_2Cl_2/hexanes gave an 8% yield of the indene **15g** (from reduction of the *tert*-butoxy group) and an inseparable mixture of the quinone **14e** (44% yield) and the indene **15e** (13% yield). The ratio and yields of **14e** and **15e** were determined by integration of the benzylic protons. Also observed on occasion in varying but small amounts from this reaction was indenyl ether **20e**. Spectral data for **15e** (R_f = 0.73 in 1:1:20, coelutes with quinone **14e**): ^{1}H NMR ($CDCl_3$, derived from mixture) δ ~1.16 (m, 6 H), 1.32 (s, 9 H), 2.42–2.55 (m, 1 H), ~2.64 (m, 3 H), 2.86 (s, 3 H), 4.56 (d, 1 H, J = 11.7 Hz), 4.67 (d, 1 H, J = 11.6 Hz), 4.82 (s, 1 H), 6.90 (d, 1 H, J = 7.0 Hz), 7.26 (t, 1 H, J = 7.5 Hz), 7.37 (d, 1 H, J = 8.2 Hz). Spectral data for **20e** (light yellow oil, R_f = 0.40, 1:1:30): ^{1}H NMR ($CDCl_3$) δ 0.55 (t, 3 H, J = 7.4 Hz), 1.16 (t, 3 H, J = 7.5 Hz), 1.33 (s, 9 H), 1.76–1.81 (m, 1 H), 2.00–2.05 (m, 1 H), 2.14–2.18 (m, 1 H), 2.68–2.72 (m, 1 H), 3.33 (t, 1 H, J = 4.8 Hz), 3.81 (s, 3 H), 4.78 (s, 2 H), 7.13 (t, 1 H, J = 7.5 Hz), 7.20 (d, 1 H, J = 7.3 Hz), 7.35 (d, 1 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 8.28, 14.15, 18.03, 22.30, 27.75, 45.66, 59.89, 60.93, 73.14, 121.57, 124.55, 126.63, 131.17, 133.53, 137.49, 145.09, 154.21; IR (neat) 2969 s, 2932 m, 2873 m, 1628 m, 1352 m, 1275 m, 1196 m, 1059 m, 766 m cm^{-1}.

Reaction of o-(Methoxyethyl) Complex 2f with 3-Hexyne. As indicated, this reaction at high concentrations gives the quinone **14f** as the only isolable product. In the crude mixture from the reaction at 0.5 M and 110 °C, a trace amount of indene **15f** was observed in the crude ^{1}H NMR spectrum but could not be isolated. The reaction at 0.005 M and 110 °C gave three compounds that could not be separated upon chromatography on silica gel with a 1:1:20 mixture of ether/CH_2Cl_2/hexanes as eluent; they eluted as a single band. The yields in Table IV were determined by integration of the methoxyl groups of **14f**, **15f**, and **16f** from this mixture. Also observed on occasion in varying but small amounts from this reaction was the indenyl ether **20f**. Analytical samples of **15f** and **16f** could be obtained by preparative TLC. Spectral data for **14f**: R_f = 0.17 (1:1:20), yellow solid; mp 33–35 °C; ^{1}H NMR ($CDCl_3$) δ 1.14 (t, 6 H, J = 7.5 Hz), 2.59–2.65 (m, 4 H), 3.35 (s, 3 H), 3.42 (t, 2 H, J = 6.4 Hz), 3.65 (t, 2 H, J = 6.5 Hz), 7.49–7.55 (m, 2 H), 8.00 (d, 1 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.78, 13.94, 19.87, 20.29, 35.23, 58.52, 72.46, 125.54, 129.93, 132.30, 133.86, 137.48, 141.17, 146.25, 149.35, 185.16. 186.92; IR (neat) 2972 m, 2935 m, 1656 vs, 1623 m, 1589 m, 1464 m, 1325 m, 1285 s, 1256 m, 1114 s cm^{-1}; mass spectrum, m/e (rel intensity) 272 M^+ (3), 240 (100), 225 (74), 197 (17). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.44; H, 7.59.

Spectral data for **15f**: R_f = 0.17 (1:1:20), light yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 3 H, J = 7.2 Hz), 1.17 (t, 3 H, J = 7.2 Hz), 2.24–2.29 (m, 1 H), 2.46–2.51 (m, 3 H), 2.88 (s, 3 H), 2.96–3.00 (m, 1 H), 3.15–3.19 (m, 1 H), 3.38 (s, 3 H), 3.68 (t, 2 H, J = 7.1 Hz), 5.14 (s, 1 H), 6.99 (d, 1 H, J = 7.6 Hz), 7.03 (d, 1 H, J = 7.4 Hz), 7.21 (t, 1 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.62, 14.28, 18.38, 18.80, 31.84, 50.24, 58.57, 72.56, 81.62, 116.59, 125.92, 128.55, 135.61, 138.99, 140.78, 142.56, 145.04; IR (neat) 2967 s, 2931 s, 2873 s, 2822 m, 1460 m, 1116 s, 1083 s cm^{-1}; decomposed upon attempted mass spectrum. Spectral data for **16f**: R_f = 0.17 (1:1:20), yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3 H, J = 7.6 Hz), 1.22 (t, 3 H, J = 7.6 Hz), 2.26 (q, 2 H, J = 7.6 Hz), 2.53 (q, 2 H, J = 7.6 Hz), 3.21 (t, 2 H, J = 6.8 Hz), 3.35 (s, 3 H), 3.62 (t, 2 H, J = 6.7 Hz), 6.89 (d, 1 H, J = 7.1 Hz), 6.99 (d, 1 H, J = 7.8 Hz), 7.19 (t, 1 H, J = 7.5 Hz); IR (neat) 2968 m, 2928 s, 2874 m, 1701 vs, 1592 m, 1466 m, 1116 m cm^{-1}; mass spectrum, m/e (rel intensity) 244 M^+ (38), 212 (100), 197 (68), 183 (99), 169 (19), 155 (19), 141 (20), 128 (17), 115 (17). Spectral data for **20f**: R_f = 0.38 (1:1:20), yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.55 (t, 3 H, J = 7.4 Hz), 1.17 (t, 3 H, J = 7.6 Hz), 1.76–1.82 (m, 1 H), 2.00–2.05 (m, 1 H), 2.14–2.21 (m, 1 H), 2.68–2.76 (m, 1 H), 3.12–3.25 (m, 2 H), 3.33 (t, 1 H, J = 4.8 Hz), 3.38 (s, 3 H), 3.61–3.63 (m, 2 H), 3.82 (s, 3 H), 7.04–7.08 (m, 2 H), 7.18 (d, 1 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 8.22, 14.18, 18.14, 22.34, 32.07, 45.58, 58.53, 60.85, 74.11, 121.02, 124.37, 128.44, 129.99, 132.67, 138.47, 145.53, 154.23; mass spectrum, m/e (rel intensity) 260 M^+ (60), 231 (100), 228 (13), 213 (35), 199 (17), 169 (15); exact mass calcd for $C_{17}H_{24}O_2$ (m/e) 260.1776, found (m/e) 260.1780.

Reactions of 4-Methoxy Complex 2h with 3-Hexyne. The only product that could be isolated and characterized from this reaction is the quinone **14h** for all of the reaction conditions indicated in Table IV. The spectral data obtained for **14h** were identical with those that have been previously reported for the product of this reaction.[2f] No five-membered ring products were observed in the crude ^{1}H NMR spectra for the reactions under any of the conditions indicated in Table IV, except for perhaps that at 45 °C and 0.5 M. In the workup of this reaction, a small amount of yellow material followed the quinone off the column with a 1:1:20 mixture of ether/CH_2Cl_2/hexane as solvent, and despite the fact that this fraction was a mixture of many components, absorptions that would have been anticipated for the indenone **16h** were present, but based on the weight of this fraction the maximum yield would be 5%.

Reactions of 3-Methoxy Complex 2i with 3-Hexyne. The benzannulation reaction with meta-substituted arylcarbene complexes can give two possible regioisomers. This aspect of the regiochemistry of the reaction has been briefly examined previously, and it was found that the selectivity was dependent on the electronic nature of the meta substituent.[17a] The reaction of the *m*-methoxyphenyl complex **2i** with 3-hexyne has been previously reported[17a] to give a 2.1:1.0 mixture of the quinones **14h** and **14b**, and we find here that this regioselectivity is only slightly affected by temperature or concentration, as indicated by the data in Table IV. These reactions were unusually clean and no evidence for five-membered rings or other minor products could be gleaned from the crude ^{1}H NMR spectra or the TLCs of these reactions.

Reactions of 4-Acetoxy Complex 2j with 3-Hexyne. At 45 °C and 0.5 M, this reaction produced a 94.4% yield of quinone **14j** along with a small amount of another colored annulated product (presumably indenone), which was observed but not isolated. Spectral data for **14j** (yellow solid, mp 68–70 °C): ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 6 H, J = 7.5 Hz, CH_2CH_3), 2.34 (s, 3 H, $COCH_3$), 2.636 (q, 2 H, J = 7.5 Hz, CH_2CH_3), 2.640 (q, 2 H, J = 7.5 Hz, CH_2CH_3), 7.36 (dd, 1 H, J = 2.3, 8.6 Hz, H-6), 7.74 (d, 1 H, J = 2.3 Hz, H-5), 8.08 (d, 1 H, J = 8.3 Hz, H-8); ^{13}C NMR ($CDCl_3$) δ 13.90, 13.93, 20.10, 20.15, 21.04, 119.20, 126.52, 128.22, 129.81, 133.79, 148.22, 148.16, 154.55, 168.64, 184.06, 183.96; IR ($CHCl_3$) 2877 m, 1760 vs, 1667 vs, 1614 s, 1594 s, 1462 m, 1369 m, 1345 m, 1320 m, 1136 m, 987 m, 948 m, 867 m cm^{-1}; mass spectrum, m/e (rel intensity) 272 M^+ (38), 230 (100), 215 (27), 83 (64). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.42; H, 6.00. The crude mixture from the reaction at 110 °C and 0.5 M was subjected to oxidation and gradient elution chromatography, first with a 1:1:8 mixture of ether/CH_2Cl_2/hexanes and then a 1:1:4 mixture. After a colored band containing alkyne oligomers eluted, a fraction containing an 80.4% yield of quinone **14j** was obtained. Three other minor products were collected each in an impure state, two of which are probably aldehydes (based on ^{1}H NMR shifts at 9.6 and 9.7 ppm); however, no compounds with spectra expected for the indenyl or indenone products were observed.

Reaction of Complex 2g with 1-Pentyne. As indicated in Table V, this reaction at high concentrations (0.5 M) gave exclusively the quinone **11g** as a yellow solid (mp 63–65 °C), for which the following spectral data were obtained: ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.3 Hz, $CH_2CH_2CH_3$), 1.62 (q, 2 H, J = 7.4 Hz, $CH_2CH_2CH_3$), 2.52 (t, 2 H, J = 7.6 Hz, $CH_2CH_2CH_3$), 2.75 (s. 3 H, CH_3), 6.69 (s, 1 H, 3-H), 7.48 (d, 1 H, J = 7.4 Hz, 6-H), 7.55 (t, 1 H, J = 7.6 Hz, 7-H), 8.00 (d, 1 H, J = 7.5 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 13.83, 21.10, 22.55, 31.01, 125.42, 129.56, 132.60, 133.74, 136.49, 137.48, 140.85, 149.66, 185.59, 187.26; IR ($CHCl_3$) 1656 vs cm^{-1}; mass spectrum, m/e (rel intensity) 214 M^+ (100), 199 (52), 186 (34), 171 (55), 158 (22), 143 (20), 128 (49), 115 (27). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.49; H, 6.70%. The crude ^{1}H NMR from the reaction at 110 °C and 0.5 M showed one additional product besides quinone. Separation of the two products by chromatography on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes gave a 77% yield of quinone **11g** (R_f = 0.69) and a 7% yield of butenoate **40g** (R_f = 0.28), which was obtained as a pale yellow oil. Spectral data for **40g**: ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.4 Hz, $CH_2CH_2CH_3$), 1.59 (q, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 2.41 (t, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 2.54 (s, 3 H, CH_3), 3.61 (s, 3 H, CO_2CH_3), 6.55 (s, 1 H, C=CH), 7.22 (t, 1 H, J = 8.5 Hz), 7.35 (t, 1 H, J = 7.5 Hz), 7.56 (d, 1 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 13.6, 20.7, 20.9, 36.1, 52.0, 125.5, 129.5, 130.5, 131.6, 131.7, 137.1, 138.7, 145.8, 169.0, 194.3; IR (neat) 2961 s, 2932 m, 1733 vs, 1700 m, 1671 s, 1616 m, 1457 m, 1435 m, 1258 s, 1210 s cm^{-1}.

Reaction of the *o*-Methoxy Complex 2b with 1-Pentyne. This reaction produces two products at high concentrations (0.5 M, Table V) with THF solvent as judged by the ^{1}H NMR spectrum of the crude reaction mixtures, subsequent to the standard oxidative workup procedure. These two products were separated on a silica gel column with first a 1:1:4 mixture of ether/CH_2Cl_2/hexane as eluent and then with a 1:1:2 mixture to give the keto ester **40b** and the quinone **11b** in the yields indicated in Table V. The spectral data obtained for quinone **11b** were identical with those that have been reported for this compound.[2f] Spectral data for **40b** (yellow oil): ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.4 Hz, $CH_2CH_2CH_3$), 1.58 (sextet, 2 H, J = 7.4 Hz, $CH_2CH_2CH_3$), 2.39 (t, 2 H, J = 7.3 Hz, $CH_2CH_2CH_3$), 3.73 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.74 (s, 1 H, C=CH), 6.93 (d, 1 H, J = 8.3 Hz), 6.99 (t, 1 H, J = 7.6 Hz), 7.45 (dt, 1 H, J = 1.6 Hz, J = 8.5 Hz), 7.69 (dd, 1 H, J = 1.6 Hz, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.43, 20.60, 36.17, 45.62, 52.04, 111.63, 120.75, 127.80, 130.42, 130.99, 133.88, 144.67, 158.75, 169.98, 191.05; IR (neat) 1732 vs, 1661 m, 1614 m, 1598 m, 1485 m, 1465 m, 1437 m, 1293 s, 1254 s, 1242 s, 1203 s cm^{-1}; mass spectrum, m/e (rel intensity) 262 M^+ (13), 231 (18), 201 (20), 187 (13), 173 (12), 155 (8), 135 (100), 121 (8), 110 (8), 92 (15), 77 (32); exact mass calcd for $C_{15}H_{18}O_4$ (m/e) 262.1205, found (m/e) 262.1205. As indicated in Table V, the reactions at high concentrations with benzene as solvent produce the quinone **11b** but not the keto ester **40b**. In the benzene reactions it is anticipated that cyclopentenedione products are likely formed as minor products but are not detected since these products are destroyed by Ce^{IV}.[11]

The reaction at 110 °C and 0.005 M was done in 35 min and gave four products. These could be separated by chromatography on silica gel with gradient elution, beginning with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes, then with a 1:1:8 mixture, and finally with a 1:1:4 mixture to give a 13% yield of the indene **12b**, a 6% yield of slightly impure keto ester **40b**, a 23% yield of the quinone **11b**, and a 28% yield of the indanone **38b**. Spectral data for indene **12b** (colorless oil, R_f = 0.54 in 1:1:4): ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.3 Hz, $CH_2CH_2CH_3$), 1.59–1.69 (m, 2 H, $CH_2CH_2CH_3$), 2.34 (t, 2 H, J = 7.4 Hz, $CH_2CH_2CH_3$), 3.04 (s, 3 H, $CHOCH_3$), 3.90 (s, 3 H, OCH_3), 5.06 (s, 1 H, $CHOCH_3$), 6.37 (s, 1 H, C(*H*)=CnPr), 6.68 (d, 1 H, J = 8.3 Hz), 6.78 (d, 1 H, J = 7.3 Hz), 7.20 (t, 1 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 14.04, 21.40, 30.29, 51.80, 55.39, 82.43, 108.25, 113.47, 126.84, 126.87, 130.27, 145.85, 150.79, 156.17; IR (neat) 2959 m, 2930 m, 1480 m, 1261 m, 1089 m, 909 s, 734 s cm^{-1}; mass spectrum, m/e (rel intensity) 218 M^+ (38), 189 (100), 175 (33), 115 (23); exact mass calcd for $C_{14}H_{18}O_2$ (m/e) 218.1307, found (m/e) 218.1291. Spectral data for indanone **38b** (yellow oil, R_f = 0.24 in 1:1:4): ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7.1 Hz, $CH_2CH_2CH_3$), 1.36–1.48 (m, 3 H, $CHHCH_2CH_3$), 1.83–1.88 (m, 1 H, $CHHCH_2CH_3$), 2.34 (dd, 1 H, J = 3.3 Hz, J = 18.8 Hz, $COCHHCH$(nPr)), 2.81 (dd, 1 H, J = 7.7 Hz, J = 18.8 Hz, $COCHHCH$(nPr)), 3.25–3.29 (m, 1 H, $COCH_2CH$(nPr)), 3.93 (s, 3 H, OCH_3), 6.75 (d, 1 H, J = 8.2 Hz, C=CH), 7.01 (d, 1 H, J = 7.5 Hz), 7.50 (t, 1 H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ 14.10, 20.61, 37.58, 38.33, 43.58, 55.73, 108.87, 117.32, 124.79, 136.29, 157.82, 161.81, 204.20; IR (neat) 2958 m, 2930 m, 1708 vs, 1593 s, 1480 s, 1280 m, 1229 m, 1027 m cm^{-1}; mass spectrum, m/e (rel intensity) 204 M^+ (100), 175 (61), 162 (65), 144 (20), 115 (19), 103 (23); exact mass calcd for $C_{13}H_{16}O_2$ (m/e) 204.1150, found (m/e) 204.1142.

Reactions of *o*-(Methoxymethyl) Complex 2c with 1-Pentyne. Under conditions of low temperature (45 °C) and high concentration (0.5 M) this reaction goes to completion in 14 h and produces only the quinone **11c** in 56% yield, as indicated in Table V. Spectral data for quinone **11c** (yellow solid, mp 71–72 °C): ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 7.4 Hz, $CH_2CH_2CH_3$), 1.62 (q, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 2.53 (t, 2 H, J = 7.3 Hz, $CH_2CH_2CH_3$), 3.55 (s, 3 H, CH_2OCH_3), 4.99 (s, 2 H,

Table XII. Effect of Lewis Acids on the Reaction of Complex **2h** with 1-Pentyne[a]

solvent	temp (°C)	[**2h**] (M)	[alkyne]	additive (equiv)	isolated yield (%)[b] **11h**	**38h**	**40h**	total mass recovery (%)	six/five
THF	110	0.5	1.0	none	41	39	13	93	1.1
		0.5	1.0	$tBuMe_2SiCl$ (1.5)	46	28	N	74	1.6
heptane	110	0.5	1.0	none	50	23	2	75	2.0
		0.5	1.0	$tBuMe_2SiCl$ (1.5)	55	26	2	83	2.0
		0.5	1.0	Me_3SiCl (1.5)	52	22	N	74[c]	2.4
		0.5	1.0	Ac_2O (1.5)	26	12	9	47[d]	1.2
		0.5	1.0	$BF_3{\cdot}OEt_2$ (1.5)	56	20	N	76	2.8

[a] Reaction time is 25 min in each case. [b] N indicates product not detected by 500 MHz ^1H NMR of the crude reaction mixture. [c] This reaction also produced a 20% yield of *p*-anisaldehyde. [d] This reaction also produced a 19% yield of *p*-anisaldehyde.

CH_2OCH_3), 6.69 (s, 1 H, 3-H), 7.70 (t, 1 H, J = 7.8 Hz, 7-H), 8.03 (d, 1 H, J = 8.01 Hz, 6-H), 8.06 (d, 1 H, J = 7.7 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 13.81, 21.10, 31.06, 58.88, 72.57, 125.88, 128.08, 131.74, 133.15, 133.36, 136.00, 141.94, 149.98, 185.29, 187.18; IR ($CHCl_3$) 1656 vs, 1274 w, 1120 w, 1107 w cm^{-1}; mass spectrum, *m/e* (rel intensity) 244 M^+ (86), 229 (100), 201 (23), 187 (16), 183 (21), 128 (12), 115 (19). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.91; H, 6.64.

Both of the reactions at 110 °C (0.5 and 0.005 M, see Table V) produced a mixture, after oxidative workup, that contained three products as revealed by ^1H NMR. These could be separated chromatographically on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes to give the quinone **11c** (R_f = 0.38), followed by an impure band containing the indanone **38c** (R_f = 0.29, this can be further purified by chromatography on silica gel with 10% ethyl acetate in hexanes), and finally a clean band of the keto ester **40c** (R_f = 0.15). Spectral data for indanone **38c** (yellow oil): ^1H NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 7.2 Hz, $CH_2CH_2CH_3$), 1.41–1.51 (m, 3 H, $CHHCH_2CH_3$), 1.87–1.90 (m, 1 H, $CHHCH_2CH_3$), 2.34 (dd, 1 H, J = 3.3 Hz, J = 18.9 Hz, $COCHHCH$(nPr)), 2.82 (dd, 1 H, J = 7.6 Hz, J = 18.9 Hz, $COCHHCH$(nPr)), 3.32–3.48 (m, 1 H, $COCH_2CH$(nPr)), 3.50 (s, 3 H, CH_2OCH_3), 4.94 (s, 2 H, CH_2OCH_3), 7.37 (d, 1 H, J = 7.5 Hz), 7.48 (d, 1 H, J = 7.4 Hz), 7.55 (t, 1 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 14.12, 20.76, 37.88, 38.46, 43.44, 58.85, 70.38, 124.15, 125.06, 132.83, 134.35, 139.05, 159.70, 207.09; IR (neat) 2958 m, 2929 m, 2873 m, 1704 s, 1593 m, 1115 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 218 M^+ (28), 203 (100), 115 (10), 101 (10), 91 (10), 83 (20); exact mass calcd for $C_{14}H_{18}O_2$ (*m/e*) 218.1307, found (*m/e*) 218.1314. Spectral data for keto ester **40c** (pale yellow oil): ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.3 Hz, $CH_2CH_2CH_3$), 1.60 (q, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 2.42 (t, 2 H, J = 7.6 Hz, $CH_2CH_2CH_3$), 3.46 (s, 3 H, CH_2OCH_3), 3.62 (s, 3 H, CO_2CH_3), 4.76 (s, 2 H, CH_2OCH_3), 6.59 (s, 1 H, C=CH), 7.32 (t, 1 H, J = 7.5 Hz), 7.49 (t, 1 H, J = 7.5 Hz), 7.63 (d, 1 H, J = 7.8 Hz), 7.65 (d, 1 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.57, 20.76, 36.13, 52.09, 58.70, 72.20. 126.75, 127.59, 129.55. 130.09, 132.12, 135.56, 139.96, 145.95, 168.94, 193.78; IR (neat) 2961 s, 2932 s, 1733 s, 1668 s, 1259 s, 1213 s, 1201 s, 1105 s cm^{-1}; mass spectrum, *m/e* (rel intensity) no parent was observed, decomposed with loss of CH_3OH to give 244 (M^+ – 32, 100), 215 (38), 185 (47), 171 (62), 155 (24), 133 (30), 91 (43).

Reactions of *p*-Methoxy Complex 2h with 1-Pentyne. The reaction of complex **2h** with 1-pentyne in THF produced a mixture of three products under all of the conditions specified in Table V. Separation was accomplished on silica gel by elution, first with a 1:1:10 mixture of ether/CH_2Cl_2/hexane and then with a 1:1:8 mixture, to give the quinone **11h**, the indanone **38h**, and the keto ester **40h**. Spectral data for quinone **11h** (yellow solid, mp 85 °C):[11] ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.3 Hz), 1.60 (m, 2 H), 2.53 (t, 2 H, J = 7.5 Hz), 3.94 (s, 3 H), 6.72 (s, 1 H), 7.18 (dd, 1 H, J = 2.6 Hz, J = 8.6 Hz), 7.52 (d, 1 H, J = 2.6 Hz), 8.00 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 13.7, 21.1, 31.3, 55.7, 109.8, 120.0, 125.6, 128.3, 134.2, 134.9, 151.0, 163.8, 184.25, 185.26; IR ($CHCl_3$) 3010 m, 2970 w, 2930 w, 2870 w, 2840 w, 1655 s, 1610 w, 1590 s, 1575 m, 1490 w, 1460 w, 1305 s, 1200 s, 1025 w, 720 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 230 M^+ (100), 215 (32), 202 (40), 188 (60), 160 (37), 145 (20), 135 (37), 115 (24), 116 (27), 102 (29), 63 (62). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.93; H, 6.19. Spectral data for indanone **38h** (yellow oil):[55] ^1H NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 7.1 Hz, $CH_2CH_2CH_3$), 1.39–1.52 (m, 3 H, $CHHCH_2CH_3$), 1.86–1.90 (m, 1 H, $CHHCH_2CH_3$), 2.35 (dd, 1 H, J = 3.2 Hz, J = 18.8 Hz, $COCHHCH$(nPr)), 2.82 (dd, 1 H, J = 7.5 Hz, J = 18.7 Hz, $COCHHCH$(nPr)), 3.28–3.31 (m, 1 H, $COCH_2CH$(nPr)), 3.89 (s, 3 H, OCH_3), 6.87–6.89 (m, 2 H), 7.64 (d, 1 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 14.00, 20.59, 37.84, 38.10, 43.09, 55.47, 108.73, 115.02, 124.97, 129.89, 161.83, 165.11, 204.47. Spectral data for keto ester **40h** (pale yellow oil): ^1H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 7.3 Hz, $CH_2CH_2CH_3$), 1.62 (q, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 2.44 (t, 2 H, J = 7.2 Hz, $CH_2CH_2CH_3$), 3.67 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.70 (s, 1 H), 6.92 (d, 2 H, J = 8.9 Hz), 7.88 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.60, 20.83, 36.11, 52.07, 55.46, 113.82, 128.04, 126.88, 130.84, 145.66, 163.62, 169.14, 189.70; IR (neat) 2961 m, 1731 s, 1662 s, 1598 vs, 1259 vs, 1214 s, 1170 s cm^{-1}.

As indicated in Table V, the reactions in benzene were similar, except that all of the five-membered-ring products were obtained in the form of the indanone **38h**. In addition, as indicated in Table XII, the product distribution could not be affected by carrying out this reaction in the presence of a variety of electrophiles and Lewis acids.[10,24,56]

Reactions of *m*-Methoxy Complex 2i with 1-Pentyne. The reaction at 45 °C and 0.5 M took 13 h, and after separation on a silica gel column with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes, the three products were identified as the keto ester **40i** and the pair of isomeric quinones **11k** and **11l**.[17a] Spectral data for 6-methoxy-2-propylnaphthoquinone (**11k**) (yellow solid, mp 77–78 °C from MeOH/H_2O): ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.3 Hz), 1.61 (sextet, 2 H, J = 7.6 Hz), 2.52 (t, 2 H, J = 7.4 Hz), 3.93 (s, 3 H), 6.72 (s, 1 H), 7.15 (dd, 1 H, J = 8.6, 2.3 Hz), 7.45 (d, 1 H, J = 2.3 Hz), 8.00 (d, 1 H, J = 8.6 Hz); mass spectrum, *m/e* (rel intensity) 230 M^+ (20), 215 (22), 202 (20), 187 (33), 174 (18), 159 (27), 135 (31), 115 (25), 106 (26), 102 (22), 77 (23), 75 (27), 63 (100). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.96; H, 6.30. Spectral data for 5-methoxy-3-propylnaphthoquinone (**11l**) (yellow solid, mp 51–53 °C from ether/hexane): ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.2 Hz), 1.61 (sextet, 2 H, J = 7.4 Hz), 2.52 (t, 2 H, J = 7.8 Hz), 4.01 (s, 3 H), 6.71 (s, 1 H), 7.29 (d, 1 H, J = 8.0 Hz), 7.62–7.73 (m, 2 H); IR ($CHCl_3$) 3005 w, 2960 m, 2930 m, 2865 w, 1658 s, 1588 s, 1470 m, 1304 m, 1272 m, 1210 m, 1048 m cm^{-1}; exact mass calcd for $C_{14}H_{14}O_3$ (*m/e*) 230.0942, found (*m/e*) 230.0947. Spectral data for keto ester **40i** (pale yellow oil): ^1H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 7.4 Hz, $CH_2CH_2CH_3$), 1.58–1.64 (m, 2 H, $CH_2CH_2CH_3$), 2.44 (dt, 2 H, J = 1.0 Hz, J = 7.3 Hz, $CH_2CH_2CH_3$), 3.67 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 6.70 (t, 1 H, J = 1.1 Hz, C=CH), 7.09 (dd, 1 H, J = 2.1 Hz, J = 8.1 Hz), 7.34 (t, 1 H, J = 7.9 Hz), 7.44–7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.59, 20.81, 36.11, 52.12, 55.42, 112.34, 119.97, 121.26, 127.96, 129.59, 138.21, 146.46, 159.85, 168.98, 190.92; IR (neat) 2961 m, 1731 s, 1669 s, 1596 m, 1434 m, 1275 s, 1237 s, 1201 s, 1029 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 262 M^+ (59), 203 (6), 155 (19), 135 (100); exact mass calcd for $C_{15}H_{18}O_4$ (*m/e*) 262.1205, found (*m/e*) 262.1221.

The benzannulation reaction with meta-substituted arylcarbene complexes can give two possible regioisomers. The reaction of the *m*-methoxyphenyl complex **2i** with 1-pentyne has been previously reported to give a 10.5:1.0 mixture of the quinones **11k** and **11l** at 45 °C and 0.1 M.[17a] We find here that this regioselectivity is affected by temperature, as indicated by the data in Table V; and this is in contrast to the reaction of complex **2i** with 3-hexyne (Table IV) where there is no significant change in regiochemistry with temperature. The ratios of quinones **11k**:**11l** are 11.3:1.0 at 45 °C and 0.5 M, 5.6:1.0 at 110 °C and 0.5 M, and 5.0:1.0 at 110 °C and 0.005 M.

Reactions of *p*-Acetoxy Complex 2j with 1-Pentyne. This reaction was carried out under the two conditions indicated in Table V and the general procedure described above to give the quinone **11j** as the only observable product of the reaction. Spectral data for **11j** (yellow solid, mp 68 °C from $CHCl_3$/hexane): ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.3 Hz, $CH_2CH_2CH_3$), 1.61 (m, 2 H, $CH_2CH_2CH_3$), 2.35 (s, 3 H, $COCH_3$), 2.54 (t, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 6.75 (s, 1 H), 7.41 (dd, 1 H, J =

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2.3 Hz, J = 8.3 Hz), 7.77 (d, 1 H, J = 2.3 Hz), 8.06 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.79, 21.03, 22.06, 31.49, 119.67, 126.84, 128.03, 129.66, 133.89, 134.87, 151.76, 154.78, 168.55, 184.12, 184.35; IR ($CHCl_3$) 1769 m, 1665 m, 1600 m, 1299 m, 1185 m cm^{-1}; mass spectrum, m/e (rel intensity) 258 M$^+$ (27), 216 (100), 201 (22), 188 (26), 173 (23), 121 (40), 83 (74). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.61; H, 5.47.

Reactions of 2,5-Dimethoxyphenyl Complex 5a with 3-Hexyne. The reactions were carried out under the reaction conditions specified in Table VI and with the general procedure described above, except that for entries 1 and 4 in Table VI an oxidative workup was not employed. The crude reaction was simply opened and stirred in air at room temperature for a few minutes, filtered through Celite, stripped of solvent, and then loaded onto a silica gel column. The reason for not employing an oxidative workup is that the quinone derived from **41a** has significant water solubility, which leads to substantial losses during aqueous extractions. An oxidative workup was employed for the reactions in entries 2 and 3 in Table VI that involved stirring the crude reaction mixture in ether with a ferric chloride–DMF complex for 10 min at room temperature, which interestingly did not oxidize the phenol product **41a**.[55] This reaction was carried out under the four sets of conditions indicated in Table VI, and the four products of this reaction could be separated by elution with a 1:1:6 mixture of ether/CH_2Cl_2/hexane. Spectral data for phenol **41a**: ^{1}H NMR ($CDCl_3$) δ 1.24 (q, 6 H, J = 7.5 Hz), 2.82 (m, 4 H), 3.75 (s, 3 H), 3.93 (s, 3 H), 4.00 (s, 3 H), 6.64 (s, 2 H), 9.18 (s, 1 H); IR ($CHCl_3$) 3377 w (broad), 2967 s, 1614 s, 1446 s, 1337 s, 1252 s, 1088 s, 996 s, 853 s cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 15.0, 16.5, 20.4, 20.6, 57.3, 57.4, 63.4, 104.3, 105.3, 116.2, 121.1, 126.8, 136.5, 146.7, 148.6, 150.8, 151.3. Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.06; H, 7.67. Spectral data for indenone **42a**: ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 3 H, J = 7.5 Hz), 1.18 (t, 3 H, J = 7 Hz), 2.21 (q, 2 H, J = 7.5 Hz), 2.63 (q, 2 H, J = 7 Hz), 3.82 (s, 3 H), 3.88 (s, 3 H), 6.72 (d, 1 H, J = 9 Hz), 6.90 (d, 1 H, J = 9 Hz); IR ($CHCl_3$) 2950 w, 1953 m, 1874 w, 1694 s, 1490 w, 955 w cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 13.0, 14.3, 15.6, 21.5, 56.1, 56.2, 120.7, 132.0, 134.65, 134.67, 147.6, 150.6, 158.0, 196.6. Spectral data for indene **45a**: ^{1}H NMR ($CDCl_3$) δ 0.40 (t, 3 H, J = 7 Hz), 1.14 (t, 3 H, J = 7.5 Hz), 1.85 (m, 1 H), 2.10 (m, 1 H), 2.35 (m, 1 H), 2.65 (m, 1 H), 3.51 (t, 1 H, J = 4 Hz), 3.78 (s, 3 H), 3.83 (s, 3 H), 3.86 (s, 3 H), 6.62 (d, 1 H, J = 9 Hz), 6.75 (s, 1 H, J = 9 Hz); IR ($CHCl_3$) 2962 s, 1635 m, 1494 s, 1291 s, 1252 s, 1087 s, 1044 s cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 8.1, 15.0, 18.2, 20.6, 45.1, 55.3, 57.2, 61.7, 108.4, 111.5, 131.3, 133.7, 134.1, 147.6, 151.0, 152.7; mass spectrum, m/e (rel intensity) 262 M$^+$ (23), 247 (6), 233 (100), 218 (10), 203 (20), 189 (7), 175 (9), 115 (15); exact mass calcd for $C_{16}H_{22}O_3$ (m/e) 262.1569, found 262.1532. Spectral data for indene **44a**: ^{1}H NMR ($CDCl_3$) δ 1.10 (m, 6 H), 2.20 (m, 1 H), 2.40 (m, 1 H), 2.58 (q, 2 H, J = 7 Hz), 2.97 (s, 3 H), 3.79 (s, 3 H), 3.84 (s, 3 H), 5.10 (s, 1 H), 6.62 (d, 1 H, J = 9 Hz), 6.76 (d, 1 H, J = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 14.4, 14.6, 18.4, 20.3, 51.3, 55.89, 55.91, 80.9, 108.8, 113.0, 129.2, 133.7, 140.5, 142.2, 148.2, 150.7; IR (film) 2963 m, 2933 m, 2832 w, 1495 s, 1463 m, 1314 w, 1254 s, 1136 w, 1095 m, 1068 s, 977 w, 789 w cm^{-1}; mass spectrum, m/e (rel intensity) 262 M$^+$ (25). 247 (8), 233 (100), 218 (10), 203 (15), 187 (12), 149 (18), 115 (20); exact mass calcd for $C_{16}H_{22}O_3$ (m/e) 262.1569, found (m/e) 262.1583.

Reactions of 2,5-Dimethoxyphenyl Complex 5a with 1-Pentyne. The reactions were carried out under the reaction conditions specified in Table VI and with the general procedure described above, except that an oxidative workup was not employed. The crude reaction was simply opened and stirred in air at room temperature for a few minutes, filtered through Celite, stripped of solvent, and then loaded onto a silica gel column. The products were then separated by elution of the column with a 1:1:4 mixture of ether/CH_2Cl_2/hexane. In the case of entry 6 in Table VI, the products **46b** and **48b** coeluted and were separated by preparative TLC on silica gel with a 1:1:10 solvent mixture. For entries 5 and 8 in Table VI, a modified workup (indicated as acid workup in footnote) procedure was employed to simplify the analysis of the regioisomeric enol ethers. Only the phenol **41b** was taken from the fractions resulting from the initial chromatography on silica gel with the 1:1:4 solvent mixture. All of the fractions that came before and after the phenol were combined, and after removal of the solvent at reduced pressure, the residue was taken into methanol and stirred with a few drops of 1 N HCl until by TLC no enol ethers remained. The methanolic solution was shaken with saturated aqueous $NaHCO_3$ and ether, and then the ethereal layer was washed with water and brine. Following drying with $MgSO_4$, filtration, and solvent removal, the organic products were separated by preparative TLC on silica gel with a 1:1:4 solvent mixture. The indanones were collected as intensely UV-active, fluorescent bands, which in entry 8 of Table VI were not separated, and the ratio of **43b** to **46b** was determined on the ^{1}H NMR of the mixture. Spectral data for phenol **41b** (white solid, mp 91.0–93.5 °C): ^{1}H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7 Hz), 1.68 (pentet, 2 H, J = 8 Hz), 2.69 (t, 2 H, J = 8 Hz), 3.86 (s, 3 H), 3.88 (s, 3 H), 6.65 (m, 2 H), 6.78 (s, 1 H), 9.65 (s, 1 H); IR ($CHCl_3$) 3378 w (broad), 2958 m, 2933 m, 2840 m, 1616 s, 1454 m, 1381 s, 1073 s cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 14.1, 22.9, 32.3, 56.6, 57.2, 58.5, 104.8, 105.4, 114.0, 117.2, 118.8, 124.3, 145.7, 148.8, 150.0, 151.7; mass spectrum, m/e (rel intensity) 276 M$^+$ (100), 261 (70), 207 (65), 196 (100), 181 (30), 165 (85), 137 (10), 83 (75), 77 (15). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.29. Found: C, 69.06; H, 7.36. Spectral data for quinone **41c** (from oxidation of **41b**): ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 7 Hz), 1.57 (pentet, 2 H, J = 7 Hz), 2.46 (t, 2 H, J = 7 Hz), 3.93 (s, 6 H), 6.58 (s, 1 H), 7.25 (s, 2 H); IR ($CHCl_3$) 2975 m, 2874 m, 1655 s, 1110 s, 908 m cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 13.9, 21.1, 31.1, 56.8, 119.9, 134.7, 150.7, 153.3, 153.7, 185.0, 185.2; mass spectrum, m/e (rel intensity) 260 M$^+$ (100), 245 (65), 231 (15), 217 (20), 203 (10), 189 (10), 115 (10), 76 (12). Spectral data for indanone **43b**: ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7.0 Hz), 1.28–1.36 (m, 3 H), 2.04 (m, 1 H), 2.39 (dd, 1 H, J = 18.7, 1.6 Hz), 2.78 (dd, 1 H, J = 18.7, 7.6 Hz), 3.38 (m, 1 H), 3.84 (s, 3 H), 3.89 (s, 3 H), 6.70 (d, 1 H, J = 8.7 Hz), 6.97 (d, 1 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.6, 35.6, 36.3, 43.5, 55.7, 55.9, 109.5, 117.1, 125.8, 149.1, 150.5, 151.4, 204.7; IR (film) 2956 m, 2867 w, 1711 s, 1593 m, 1497 s, 1464 m, 1268 s, 1066 m, 1032 m cm^{-1}; mass spectrum, m/e (rel intensity) 234 M$^+$ (50). 219 (5), 205 (35), 191 (100), 176 (10), 161 (20), 133 (14), 118 (8), 105 (12); exact mass calcd for $C_{14}H_{18}O_3$ (m/e) 234.1256, found 234.1327. Spectral data for indene **45b**: ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, J = 7 Hz), 1.27–1.40 (m, 3 H), 2.18 (m, 1 H), 3.46–3.48 (m, 1 H), 3.82 (s, 3 H), 3.84 (s, 3 H), 3.86 (s, 3 H), 5.26 (s, 1 H), 6.66 (d, 1 H, J = 8.8 Hz), 6.73 (d, 1 H, J = 8.9 Hz); ^{13}C NMR δ 14.4, 20.6, 32.6, 44.1, 55.6, 55.9, 56.4, 82.9, 103.0, 108.8, 109.5, 110.2, 112.6, 117.2, 123.0. Spectral data for indanone **46b**: ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7.2 Hz), 1.41–1.47 (m, 3 H), 1.88–1.95 (m, 1 H), 2.60–2.62 (m, 1 H), 2.65 (dd, 1 H, J = 17.5, 2.5 Hz), 3.16 (dd, 1 H, J = 17.4, 7.3 Hz), 3.84 (s, 3 H), 3.89 (s, 3 H), 6.70 (d, 1 H, J = 8.7 Hz), 6.95 (d, 1 H, J = 8.7 Hz); ^{13}C NMR δ 14.1, 20.6, 29.2, 34.0, 47.4, 55.8, 55.9, 109.3, 116.4, 125.9, 144.5, 150.2, 151.7, 207.1; IR (film) 2956 m, 2929 m, 2871 w, 2836 w, 1710 s, 1597 m, 1496 s, 1464 m, 1437 m, 1256 s, 1069 m, 1015 w cm^{-1}; mass spectrum, m/e (rel intensity) 234 M$^+$ (15), 205 (12), 192 (100), 177 (25), 160 (32); exact mass calcd for $C_{14}H_{18}O_3$ (m/e) 234.1256, found 234.1260. Spectral data for indene **47b**: ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7.3 Hz), 1.56 (m, 2 H), 2.43 (t, 2 H, J = 7.4 Hz), 3.13 (s, 2 H), 3.79 (s, 3 H), 3.84 (s, 3 H), 3.86 (s, 3 H), 6.62 (d, 1 H, J = 8.7 Hz), 6.75 (d, 1 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.2, 33.4, 55.6, 56.6, 60.8, 107.2, 109.3, 110.7, 116.4, 128.5, 130.2, 146.9, 149.7; IR (film) 2957 m, 2929 m, 1705 w, 1631 w, 1497 m, 1464 w, 1265 m, 1251 m, 1078 m, 1059 m cm^{-1}; mass spectrum, m/e (rel intensity) 248 M$^+$ (30), 219 (100), 205 (40), 189 (8), 175 (15), 161 (7); exact mass calcd for $C_{15}H_{20}O_3$ (m/e) 248.1412, found 248.1487. Spectral data for keto ester **48b**; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7 Hz), 1.56 (pentet, 2 H, J = 7 Hz), 2.37 (t, 2 H, J = 7 Hz), 3.74 (s, 3 H), 3.77 (s, 3 H), 3.82 (s, 3 H), 6.77 (s, 1 H), 6.87 (d, 1 H, J = 9 Hz), 7.01 (dd, 1 H, J = 9, 3 H), 7.23 (d, 1 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.3, 37.0, 52.9, 56.5, 57.1, 114.2, 114.8, 121.7, 128.7, 130.8, 145.8, 154.1, 154.3, 172.0, 191.3; IR (film) 2957 m, 2928 m, 2867 m, 1767 m, 1733 m, 1700 m, 1660 m, 1492 s, 1464 m, 1419 m, 1284 m, 1223 m, 1167 m, 1037 m cm^{-1}; mass spectrum, m/e (rel intensity) 292 M$^+$ (20), 261 (10), 231 (15), 203 (20), 189 (10), 175 (5), 165 (100), 150 (15); exact mass calcd for $C_{16}H_{20}O_5$ (m/e) 292.1311, found 292.1302.

Reactions of 2,4-Dimethoxyphenyl Complex 9a with 3-Hexyne. These reactions were carried out under the conditions indicated in Table VII with the general procedure described above, including an oxidative workup with ceric ammonium nitrate. The products were separated on a column of silica gel, eluting first with 20% ethyl acetate in hexane and then with a 50% mixture. Spectral data for quinone **49a** (yellow solid, mp 154–6 °C): ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 6 H, J = 7 Hz), 2.60 (sextet, 4 H, J = 7 Hz), 3.48 (s, 3 H), 3.49 (s, 3 H), 6.68 (s, 1 H), 7.23 (s, 1 H); IR ($CHCl_3$) 1654 m, 1597 s, 1464 w, 1323 m cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 13.8, 14.0, 19.9, 20.2, 55.7, 56.3, 102.5, 103.7, 114.6, 136.1, 145.0, 149.9, 161.4, 164.1, 183.2, 185.1; mass spectrum, m/e (rel intensity) 274 M$^+$ (100), 259 (80), 231 (20), 217 (5), 165 (5), 122 (5), 106 (8), 69 (5); exact mass calcd for $C_{16}H_{18}O_4$ (m/e) 274.1205, found (m/e) 274.1208. Spectral data for indenone **50a** (yellow solid): ^{1}H NMR ($CDCl_3$) δ 1.06 (t, 3 H, J = 8 Hz), 1.20 (t, 3 H, J = 8 Hz), 2.26 (q, 2 H, J = 8 Hz), 2.48 (q, 2 H, J = 8 Hz), 3.85 (s, 3 H), 3.92 (s, 2 H), 6.14 (d, 1 H, J = 1.5 Hz), 6.29 (d, 1 H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.3, 14.1, 16.1, 18.9, 55.7, 55.9, 95.7, 101.5, 109.0, 137.3, 153.4, 166.2, 195.2; IR ($CHCl_3$) 2843 m, 1700 s (broad), 1618 s, 1460 w, 1362 m, 1116 m, 984 m, 901 m cm^{-1}; mass spectrum, m/e (rel intensity) 246 M$^+$ (58), 232 (15), 231 (100), 203 (6), 189 (7), 165 (11), 128 (5), 115 (8), 87 (8), 71 (11); exact mass calcd for $C_{15}H_{18}O_3$ (m/e) 246.1256, found (m/e) 246.1265. Spectral data for indene **51a** (yellow oil): ^{1}H NMR

($CDCl_3$) δ 1.13 (t, 6 H, J = 7.5 Hz), 2.24 (m, 1 H), 2.42 (m, 3 H), 2.98 (s, 3 H). 3.82 (s, 3 H), 3.87 (s, 3 H), 5.08 (s, 1 H), 6.25 (d, 1 H, J = 2 Hz), 6.38 (d, 1 H, J = 2 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.2, 18.3, 18.8. 51.3. 55.5 (2 carbons overlap), 80.5, 95.0, 97.5, 118.9, 139.5, 144.7, 147.8. 156.6, 162.2: IR ($CHCl_3$) 2968 w, 2936 w, 1597 s, 1465 m, 1143 m, 1080 w cm^{-1}; mass spectrum, *m/e* (rel intensity) 262 M^+ (38), 247 (25), 234 (16), 233 (100), 231 (7), 218 (7), 202 (12), 201 (6), 128 (4), 115 (5), 71 (3), 57 (5); exact mass calcd for $C_{16}H_{22}O_3$ (*m/e*) 262.1569, found (*m/e*) 262.1571.

Reactions of 2,4-Dimethoxyphenyl Complex 9a with 1-Pentyne. These reactions were carried out under the conditions indicated in Table VII with the general procedure described above, including an oxidative workup with ceric ammonium nitrate. The products were separated on a column of silica gel, eluting first with 20% ethyl acetate in hexane and then with a 50% mixture. It was found that the cyclopentenedione products **54b** were destroyed by the oxidative workup, and the yields indicated for these compounds in Table VII were determined in a separate experiment where the oxidation step was omitted. Spectral data for quinone **49b** (yellow solid, mp 126–8 °C): ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7 Hz), 1.60 (m, 2 H), 2.48 (t, 2 H, J = 7 Hz), 3.94 (s, 3 H), 3.96 (s, 3 H). 6.61 (s, 1 H), 6.70 (s, 1 H), 7.25 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 30.8, 43.7, 55.3, 55.8, 103.4, 103.9, 114.3, 136.2, 137.2, 148.1, 161.5. 164.4, 183.5, 185.3: IR ($CHCl_3$) 2950 w, 1652 s, 1596 s, 1317 m, 1160 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 260 M^+ (20), 219 (12), 192 (100), 177 (15), 161 (10), 139 (40), 69 (15). 57 (20). Spectral data for indanone **52b** (off-white solid, mp 102–4 °C): ^1H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 7 Hz), 1.35–1.50 (m, 3 H), 1.8–1.9 (m, 1 H), 2.33 (dd, 1 H, J = 18.5, 3 Hz), 2.79 (dd, 1 H, J = 18.5, 8 Hz), 3.2–3.3 (m, 1 H), 3.88 (s, 3 H), 3.90 (s, 3 H), 6.29 (s, 1 H), 6.48 (s, 1 H): ^{13}C NMR ($CDCl_3$) δ 14.1, 20.6, 37.9, 38.2, 43.7, 55.7, 55.8, 97.3, 100.7, 102.6, 159.1, 164.3, 166.9, 202.5: IR ($CDCl_3$) 2931 w, 1690 s, 1600 s, 1469 w, 1326 m, 1157 w cm^{-1}; mass spectrum, *m/e* (rel intensity) 234 M^+ (100), 205 (40), 192 (65), 174 (25), 163 (10), 148 (5), 103 (5), 91 (5). 77 (10). Spectral data for keto ester **53b**: ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7 Hz). 1.58 (sextet, 2 H, J = 7 Hz), 2.38 (t, 2 H, J = 7 Hz), 3.74 (s, 3 H), 3.85 (s, 3 H), 3.89 (s, 3 H), 6.42 (d, 1 H, J = 2 Hz), 6.52 (dd, 1 H, J = 9, 2 Hz), 6.77 (s, 1 H), 7.76 (d, 1 H, J = 9 Hz): ^{13}C NMR ($CDCl_3$) δ 15.5, 20.7, 36.1, 52.1, 55.5, 55.6, 98.4, 105.3, 120.8, 131.0. 133.3. 143.9. 160.8, 164.8, 170.2, 189.3; IR ($CHCl_3$) 1721 m, 1652 m, 1610 s. 1598 s, 1463 w, 1280 w, 1130 w cm^{-1}. Spectral data for cyclopentenedione **54b**: ^1H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7 Hz), 1.05 (t, 3 H, J = 7 Hz), 1.1–1.2 (m, 2 H), 1.5–1.8 (m, 4 H), 3.50 (d, 1 H, J = 20 Hz), 3.59 (d, 1 H, J = 20 Hz), 3.83 (s, 3 H), 3.90 (s, 3 H), 6.40 (d, 1 H. J = 2 Hz), 6.43 (dd, 1 H, J = 9, 2 Hz), 6.94 (s, 1 H), 7.68 (d. 1 H, J = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.0, 14.4, 18.1, 20.4, 27.6, 37.8, 48.6, 52.7, 55.48, 55.52, 98.2, 105.2, 119.0, 133.0, 142.3, 161.4, 164.1, 165.0, 195.6, 206.4, 207.2; IR ($CHCl_3$) 2931 w, 2859 w, 1697 s, 1601 s, 1111 s. 908 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 358 M^+ (11), 344 (2), 302 (2), 181 (11), 165 (100), 151 (5), 122 (2), 77 (11); exact mass calcd for $C_{21}H_{26}O_5$ (*m/e*) 358.1780, found (*m/e*) 358.1767.

Reaction of Complex 55 with 3-Hexyne. The reactions were carried out as described in the general procedure with the temperatures, concentrations, and yields indicated in Table VIII. The high-temperature reactions led to reaction mixtures from which the separation of the quinone **56a** was more difficult but could be effected by careful chromatography on silica gel, first eluting with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes and then with a 1:1:6 mixture. In all three reactions indicated in Table VIII, no attempt was made to isolate and determine the amount of indene products since the reaction mixtures were too complex to permit isolation. Spectral data for quinone **56a** (yellow solid, mp 64.0–66.0 °C): ^1H NMR ($CDCl_3$) δ 1.14 (t, 3 H, J = 7.6 Hz), 1.15 (t, 3 H, J = 7.6 Hz). 2.60 (q, 2 H, J = 7.6 Hz), 2.61 (q, 2 H, J = 7.6 Hz), 3.91 (s, 3 H), 3.94 (s, 3 H), 7.12 (d, 1 H, J = 8.6 Hz), 7.87 (d, 1 H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8, 13.9. 19.9, 20.2, 56.1, 61.0, 115.1, 124.0, 125.5. 126.1, 146.4, 148.6, 149.3, 158.3, 184.0, 184.5; IR (film) 2971 m, 2939 m, 1732 w, 1658 s, 1576 m, 1487 m, 1330 m, 1273 s, 1240 m, 1073 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 274 M^+ (100), 259 (73), 245 (12), 244 (15), 241 (15), 231 (32), 217 (14), 205 (20); exact mass calcd for $C_{16}H_{18}O_4$ (*m/e*) 274.1205, found 274.1246. Spectral data for lactone **58a**: ^1H NMR ($CDCl_3$) δ 0.83 (t, 3 H, J = 7.6 Hz), 1.20 (t, 3 H, J = 7.6 Hz), 2.11 (q, 2 H, J = 7.6 Hz), 2.37 (q, 2 H, J = 7.6 Hz), 3.31 (s, 3 H), 3.76 (s, 3 H), 3.84 (s, 3 H), 6.93 (d, 1 H, J = 8.1 Hz), 7.05 (t, 1 H, J = 8.1 Hz), 7.33 (d, 1 H, J = 8.0 Hz); IR (film) 2974 m, 2939 m, 1765 s, 1688 w, 1600 w, 1479 m, 1265 m, 1075 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 306 M^+ (85), 290 (5), 275 (31), 261 (7). 247 (40), 233 (27), 217 (16), 203 (15). 196 (100), 169 (83), 165 (97); exact mass calcd for $C_{17}H_{22}O_5$ (*m/e*) 306.1467, found 306.1455.

Reaction of Complex 55 with 1-Pentyne. The reactions were carried out as in the general procedure with the temperatures, concentrations, and yields indicated in Table VIII. Purification was accomplished by chromatography on silica gel with a 1:1:4 mixture of ether/CH_2Cl/hexanes as eluent. In entries 4 and 6 in Table VIII, this was not sufficient to completely separate the products, and therefore fractions containing all products were combined and the yields determined by ^1H NMR on this mixture. Spectral data for quinone **56b** (mp 114.0–115.0 °C, thin yellow needles from ether): ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.4 Hz), 1.59 (sext, 2 H, J = 7.4 Hz), 2.48 (t, 2 H, J = 7.6 Hz), 3.90 (s, 3 H), 3.95 (s, 3 H), 6.63 (s, 1 H), 7.14 (d, 1 H, J = 8.6 Hz), 7.89 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8, 21.0, 31.0, 56.2, 61.1, 115.3, 124.6, 125.1, 126.1, 136.4, 148.7, 149.9, 158.6, 184.2, 184.5; IR (film) 2938 m, 2846 w, 1656 s, 1575 m, 1484 m, 1271 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 260 M^+ (83), 245 (100), 231 (60), 217 (45), 203 (40), 191 (32), 165 (43), 115 (48). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.02; H, 6.32. Spectral data for indanone **57b**: ^1H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 7.1 Hz), 1.37–1.47 (m, 3 H), 1.82–1.88 (m, 1 H), 2.36 (dd, 1 H, J = 18.6, 3.6 Hz), 2.84 (dd, 1 H, J = 18.7, 7.6 Hz), 3.21–3.28 (m, 1 H), 3.89 (s, 3 H), 3.99 (s, 3 H), 7.10 (d, 1 H, J = 8.3 Hz), 7.16 (d, 1 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.7, 36.9, 38.7, 44.5, 56.9, 61.9, 120.0, 120.1, 129.2, 146.8, 151.2, 152.1, 204.0; IR (film) 2960 m, 2873 w, 1710 s, 1579 w, 1491 s, 1264 s, 1050 m, 1027 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 234 M^+ (40), 219 (22), 205 (35), 191 (100), 173 (10), 161 (11), 146 (10), 133 (11); exact mass calcd for $C_{14}H_{18}O_3$ (*m/e*) 234.1256, found 234.1329. Spectral data for keto ester **59b**: ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.3 Hz), 1.58 (sext, 2 H, J = 7.5 Hz), 2.39 (t, 2 H, J = 7.1 Hz), 3.75 (s, 3 H), 3.83 (s, 3 H), 3.89 (s, 3 H), 6.76 (t, 1 H, J = 1.1 Hz), 7.04 (dd, 1 H, J = 8.0, 1.7 Hz), 7.08 (t, 1 H, J = 7.9 Hz), 7.24 (dd, 1 H, J = 7.4, 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.5, 20.6, 36.2, 52.2, 56.0, 61.9. 116.1, 121.7, 124.3, 130.3, 133.0, 145.2, 149.0, 152.9, 169.9, 191.4; IR (film) 2958 m, 2930 m, 2873 w, 1731 s, 1660 m, 1615 w, 1579 w, 1477 m, 1265 s, 1216 s, 1028 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 292 M^+ (15), 261 (11), 260 (12), 245 (5), 231 (18), 203 (20), 189 (7), 165 (100), 151 (15), 122 (25); exact mass calcd for $C_{16}H_{20}O_5$ (*m/e*) 292.1311, found 292.1311.

Reactions of Complex 9c with 3-Hexyne. The reactions were carried out as described in the general procedure with the temperatures, concentrations, and yields indicated in Table IX. The products were separated by chromatography on silica gel with a 1:1:2 mixture of ether/CH_2Cl_2/hexanes as eluent. Spectral data for quinone **64a**: ^1H NMR ($CDCl_3$) δ 1.10–1.15 (m, 6 H), 2.33 (s, 3 H), 2.57–2.62 (m, 4 H), 3.95 (m, 3 H), 6.96 (d, 1 H, J = 2.1 Hz), 7.42 (d, 1 H, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.7, 14.0, 19.9, 20.2, 21.0, 56.6, 110.5, 112.1, 118.0, 135.7, 145.6, 149.9, 154.9, 160.8, 168.5, 183.4, 184.2; IR (film) 2972 m, 2938 m, 1773 s, 1657 s, 1622 m, 1594 s, 1464 s, 1423 m, 1370 m, 1354 m, 1319 s, 1295 s, 1195 s, 1140 s, 1057 m, 1022 m, 976 m cm^{-1}; mass spectrum *m/e* (rel intensity) 302 M^+ (35), 260 (100), 245 (88), 217 (28), 203 (13), 115 (20); exact mass calcd for $C_{17}H_{18}O_5$ (*m/e*) 302.1154, found 302.1176. Spectral data for indenone **65a**: ^1H NMR ($CDCl_3$) δ 1.06 (t, 3 H, J = 7.4 Hz), 1.20 (t, 3 H, J = 7.8 Hz), 2.26 (q, 2 H, J = 7.4 Hz), 2.32 (s, 3 H), 2.49 (q, 2 H, J = 7.7 Hz), 3.90 (s, 3 H), 6.45 (s, 1 H), 6.49 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.0, 14.1, 16.0, 19.1, 21.2, 56.1, 106.1, 107.0, 113.2, 136.9, 149.5, 154.4, 156.3, 156.4, 168.9, 195.3; IR (film) 2960 m, 2935 m, 2874 m, 1772 s, 1700 s, 1595 s, 1457 m, 1370 m, 1305 m, 1198 s, 1141 m, 1131 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 274 M^+ (30), 232 (100), 217 (98), 203 (59), 189 (18), 175 (20), 151 (15), 115 (18); exact mass calcd for $C_{16}H_{18}O_4$ (*m/e*) 274.1205, found 274.1223. Spectral data for indene **66a**: ^1H NMR ($CDCl_3$) δ 1.11–1.16 (m, 6 H), 2.31 (s, 3 H), 2.42–2.45 (m, 4 H), 3.01 (s, 3 H), 3.87 (s, 3 H), 5.09 (s, 1 H), 6.43 (d, 1 H, J = 1.2 Hz), 6.55 (d, 1 H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.6, 14.2, 18.3, 18.8, 21.1, 51.8, 55.6, 80.7, 102.0, 105.3, 124.1, 139.2, 145.0, 147.7, 152.6, 156.1, 169.6; IR (film) 2987 m, 2935 m, 2875 w, 1767 s, 1608 s, 1465 m, 1427 w, 1369 m, 1310 m, 1207 s, 1127 s, 1083 m, 1066 m, 1015 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 290 M^+ (28), 275 (4), 261 (23), 248 (20), 233 (38), 219 (100), 201 (10), 188 (18), 173 (6). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.56; H, 7.56.

Reactions of Complexes 9c and 9d with 1-Pentyne. The reactions were carried out as described in the general procedure with the temperatures, concentrations, and yields indicated in Table IX. The products were separated by chromatography on silica gel with a 1:1:2 mixture of ether/CH_2Cl_2/hexanes as eluent. Spectral data for quinone **64b** (yellow solid, mp 102.5–104.5 °C): ^1H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7 Hz), 1.58 (m, 2 H), 2.35 (s, 3 H), 2.48 (t, 2 H, J = 7 Hz), 3.97 (s, 3 H), 6.65 (s, 1 H), 7.0 (d, 1 H, J = 2 Hz), 7.45 (d, 1 H, J = 2 Hz); IR ($CHCl_3$) 1773 m, 1695 m, 1659 s, 1370 w, 1310 m, 1140 m, 964 w cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 13.8, 21.0, 21.1, 30.9, 56.7, 110.9, 112.7, 117.8, 135.8, 137.1, 148.8, 155.2, 160.9, 168.5, 183.6, 184.5; mass spectrum, *m/e* (rel intensity) 288 M^+ (46), 247 (18), 246 (100), 231 (22), 229 (15), 228 (20), 218 (11), 217 (23), 203 (10), 200 (6), 199 (6), 189 (17), 175 (6),

137 (7), 95 (7), 81 (21), 69 (40), 57 (13), 55 (11); exact mass calcd for $C_{16}H_{16}O_5$ (*m/e*) 288.0998, found (*m/e*) 288.0999. Spectral data for indanone **67b**: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H, J = 7.1 Hz), 1.39 (sext, 2 H, J = 7.3 Hz). 1.46 (m, 1 H), 1.82 (m, 1 H), 2.33 (s, 3 H). 2.35 (dd, 1 H, J = 18.9, 3.2 Hz), 2.82 (dd, 1 H, J = 18.6, 7.6 Hz), 3.27 (m, 1 H), 3.91 (s, 3 H), 6.51 (s, 1 H), 6.78 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.6, 21.2, 37.8, 38.1, 43.8, 56.0, 103.5, 110.5, 122.6, 157.1, 158.5, 163.0, 168.7, 203.0: IR (film) 2958 m, 2930 m, 1770 s, 1711 s, 1591 s, 1458 w, 1312 m, 1199 s, 1139 s, 1012 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 262 M$^+$ (20), 220 (100), 203 (10), 191 (46), 178 (88), 160 (20), 149 (13); exact mass calcd for $C_{15}H_{18}O_4$ (*m/e*) 262.1205, found 262.1147. Spectral data for phenol **69b**: ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 7 Hz), 1.65–1.75 (m, 4 H), 2.35 (s, 3 H), 2.55 (t, 2 H, J = 7 Hz), 2.67 (t, 2 H, J = 7 Hz), 3.88 (s, 3 H), 5.78 (s, 1 H, exchangeable with D_2O), 6.79 (d, 1 H, J = 1 Hz), 6.84 (dd, 1 H, J = 9, 2 Hz), 6.88 (d, 1 H, J = 1 Hz), 6.97 (d, 1 H, J = 1 Hz), 7.40 (d, 1 H, J = 9 Hz); IR ($CHCl_3$) 3300 w (broad), 2957 w, 2933 w, 2873 w, 1765 s, 1699 m, 1607 m, 1465 m, 1151 m, 1124 w, 960 w cm^{-1}. Spectral data for keto ester **68b**: ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7 Hz), 1.60 (sext, 2 H, J = 7 Hz), 2.35 (s. 3 H), 2.39 (t, 2 H, J = 7 Hz), 3.75 (s, 3 H), 3.86 (s, 3 H), 6.70–6.75 (m, 3 H), 7.73 (d, 1 H, J = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.4, 20.5, 21.1, 36.1, 52.1, 55.8, 105.5, 113.2, 114.0, 125.2, 130.1, 132.2, 145.1, 155.0, 159.7, 168.8, 189.7; IR ($CHCl_3$) 2951 w, 1766 s, 1726 s, 1661 m, 1613 s. 1465 w, 1371 m, 1153 m, 1116 w, 936 w cm^{-1}; mass spectrum, *m/e* (rel intensity) 320 M$^+$ (3), 278 (10), 262 (20), 217 (15), 151 (100): exact mass calcd for $C_{17}H_{20}O_6$ (*m/e*) 320.1260, found 320.1269.

Reaction of Complex 2a with Diisopropylacetylene. The reactions were carried out as described in the general procedure with the temperatures, concentrations, and yields indicated in Table X. Diisopropylacetylene was prepared according to the method of Nicholas.[53] The products were separated from impurities by chromatography on silica gel with a 1:1:4 mixture of ether/CH_2Cl_2/hexanes as eluent, giving the quinone **14m** and indenone **16m** as a single yellow band; the ^{1}H NMR resonances of the methine protons were sufficiently different to allow for the determination of yield from their integration. The products were eventually separated by preparative TLC on silica gel with a 1:1:50 solvent mixture. The indenone moved slightly faster, and near-complete separation was achieved giving **16m** slightly contaminated by the quinone. Spectral data for quinone **14m** (yellow solid, mp 71.5–72.5 °C): ^{1}H NMR ($CDCl_3$) δ 1.37 (d, 12 H, J = 7.0 Hz), 3.40 (sept, 2 H, J = 7.0 Hz), 7.63 (dd, 2 H, J = 5.6, 3.3 Hz), 7.98 (dd, 2 H, J = 5.6, 3.4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.0, 28.3, 125.9, 132.4, 133.1, 151.3, 185.5; IR (film) 2952 m, 2877 m, 1656 s, 1593 m, 1457 m, 1287 s, 1102 m, 717 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 242 M$^+$ (100), 227 (83), 213 (25), 199 (15), 185 (30), 157 (18), 133 (22), 105 (20). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.70; H, 7.61. Spectral data for indenone **16m**: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 6 H, J = 7.1 Hz), 1.36 (d, 6 H, J = 7.1 Hz), 2.91 (sept, 1 H, J = 7.0 Hz), 3.23 (sept, 1 H, J = 7.0 Hz), 7.12 (t, 1 H, J = 7.3 Hz), 7.18 (d, 1 H, J = 7.2 Hz), 7.26 (t, 1 H, J = 7.1 Hz), 7.33 (d, 1 H, J = 6.9 Hz): ^{13}C NMR ($CDCl_3$) δ 20.2, 21.3, 24.9, 27.4, 121.0, 121.7, 127.6, 131.7, 132.9, 137.7. 143.8, 161.4, 198.5; IR (film) 2965 m, 1697 s, 1598 w, 1471 w, 1456 w, 1055 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 214 M$^+$ (50), 199 (75), 184 (20), 171 (100), 157 (18), 143 (17), 129 (16). 115 (15); exact mass calcd for $C_{15}H_{18}O$ (*m/e*) 214.1358, found 214.1349.

Reaction of Complex 2b with Diisopropylacetylene. The reactions were carried out as described in the general procedure with the temperatures, concentrations. and yields indicated in Table X. Diisopropylacetylene was prepared according to the method of Nicholas.[53] The products were separated by chromatography on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes as eluent, which gave indene **15k**, cyclobutenone **77k**, indenone **16k**, and quinone **14k**. Spectral data for quinone **14k** (yellow solid): ^{1}H NMR ($CDCl_3$) δ 1.34 (d, 6 H, J = 7.1 Hz), 1.36 (d, 6 H, J = 7.1 Hz), 3.31 (septet, 2 H, J = 7.0 Hz), 3.97 (s, 3 H), 7.18 (d, 1 H, J = 8.3 Hz), 7.55 (t, 1 H, J = 8.0 Hz), 7.62 (d, 1 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 20.52, 20.74, 27.69, 28.22, 55.96, 116.39, 118.11, 120.26, 133.53, 134.46, 148.34, 152.75, 158.43, 184.95, 185.29; IR (neat) 2962 s, 1658 vs, 1586 s, 1471 s, 1455 m, 1271 vs, 1253 s, 934 m, 914 m, 759 s, 733 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 272 M$^+$ (100), 257 (53), 243 (23), 229 (16), 215 (16), 76 (23); exact mass calcd for $C_{17}H_{20}O_3$ (*m/e*) 272.1412, found (*m/e*) 272.1414. Spectral data for indene **15k** (white solid): ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 3 H, J = 7.1 Hz), 1.27 (d, 3 H, J = 7.0 Hz), 1.29 (d, 3 H, J = 7.1 Hz), 1.36 (d, 3 H, J = 7.1 Hz), 2.95–3.01 (m, 1 H), 3.01 (s, 3 H), 3.12–3.15 (m, 1 H), 3.89 (s, 3 H), 5.21 (s, 1 H), 6.68 (d, 1 H, J = 8.2 Hz), 6.99 (d, 1 H, J = 7.4 Hz), 7.21 (t, 1 H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ 20.67, 21.24, 21.68, 22.08, 26.62, 27.16, 51.48, 55.33, 81.15, 107.90, 113.96, 127.55, 129.64, 143.38, 145.16, 145.60, 155.86; IR (neat) 2961 vs, 2934 vs, 2906 m, 2873 m, 1606 s, 1585 s, 1478 s, 1467 s, 1260 s, 1099 s, 1072 s, 777 m, 735 m cm^{-1}; mass spectrum *m/e* (rel intensity) 260 M$^+$ (23), 245 (4), 217 (100), 202 (18), 187 (9); exact mass calcd for $C_{17}H_{24}O_2$ (*m/e*) 260.1776, found (*m/e*) 260.1787. Spectral data for indenone **16k** (yellow oil): ^{1}H NMR ($CDCl_3$ δ 1.24 (d, 6 H, J = 7.0 Hz), 1.34 (d, 6 H, J = 7.2 Hz), 2.88 (septet, 1 H, J = 7.0 Hz), 3.17 (septet, 1 H, J = 7.1 Hz), 3.91 (s, 3 H), 6.73 (d, 1 H, J = 8.6 Hz), 6.83 (d, 1 H, J = 7.1 Hz), 7.22–7.25 (m, 1 H); IR (neat) 2962 m, 1966 vs, 1599 s, 1589 s, 1476 s, 1279 s, 1255 m, 1064 m, 805 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 244 M$^+$ (69), 229 (100), 215 (36), 201 (77). Spectral data for cyclobutenone **77k** (white solid): ^{1}H NMR ($CDCl_3$) δ 0.99 (d, 3 H, J = 7.0 Hz), 1.07 (d, 3 H, J = 7.0 Hz), 1.26 (d, 3 H, J = 6.9 Hz), 1.30 (d, 3 H, J = 7.0 Hz), 2.72 (septet, 1 H, J = 6.9 Hz), 2.82 (septet, 1 H, J = 6.9 Hz), 3.43 (s, 3 H), 3.72 (s, 3 H), 6.83 (d, 1 H, J = 8.1 Hz), 6.97 (d, 1 H, J = 8.1 Hz), 7.22–7.26 (m, 1 H), 7.61 (dd, 1 H, J = 1.6 Hz, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.07, 20.34, 20.62, 20.70, 25.84, 28.59, 53.01, 55.23, 97.65, 111.40, 120.73, 125.60, 128.47, 128.98, 156.91, 158.18, 178.98, 192.95; IR (neat) 2967 m, 1757 vs, 1490 m, 1464 m, 1251 m, 1098 m, 1025 m, 756 m cm^{-1}; mass spectrum, *m/e* (rel intensity) 288 M$^+$ (99), 273 (43), 229 (48), 135 (100), 121 (26), 77 (28); exact mass calcd for $C_{18}H_{24}O_3$ (*m/e*) 288.1725, found (*m/e*) 288.1728.

Reaction of Complex 2h with Diisopropylacetylene. The reactions were carried out as described in the general procedure with the temperatures, concentrations, and yields indicated in Table X. Diisopropylacetylene was prepared according to the method of Nicholas.[53] The product was purified by chromatography on silica gel with a 1:1:10 mixture of ether/CH_2Cl_2/hexanes as eluent, giving the quinone **14l** in 83% yield. Spectral data for quinone **14l** (bright yellow solid, mp 95–6 °C): ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 12 H, J = 7.1 Hz), 3.34–3.43 (m, 2 H), 3.91 (s, 3 H), 7.10 (dd, 1 H, J = 8.6, 2.7 Hz), 7.41 (d, 1 H, J = 2.4 Hz), 7.91 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) 21.01, 21.08, 28.14, 28.28, 55.74, 108.69, 120.05, 126.06, 128.31, 134.37, 150.82, 151.37, 163.51, 184.58, 185.59. Anal. Calcd for $C_{17}H_{20}O_3$: C, 75.0; H, 7.40. Found: C, 74.95; H, 7.43.

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